Introduction

Trace elements are of environmental concerns with respect to their emissions during coal combustion. Numerous studies have reported the physical and chemical fates of trace elements during coal combustion. However, there are some important questions. For example, in what forms the trace elements exist in coal and how they are transformed with the thermal conditions are still not well known. The staged leaching method is widely used to determine the modes of occurrence of trace elements in coal. We have recently proposed a determination method by leaching not only raw coal but also ashes. In this paper, we examine the leaching behaviors of coal ash and char. This provides the further information on the modes of trace elements in coal as well as on the transformations of trace elements during coal combustion and pyrolysis.

Experimental

Coal combustion and pyrolysis were carried out in a horizontal tubular reactor. In combustion, some 1.5 g of coal sample loaded was heated in an air flow of 1 L/min at 10 °C/min, and held at the final temperature for 1 h. In pyrolysis, a nitrogen gas was used in place of air. The maximum temperature used in this experiment was 1150 °C. Quantification of the major and trace metallic elements in raw coal, char and ash was conducted on an inductively coupled plasma atomic emission spectroscope (Optima 3300XL ICP-AES instrument, Perkin-Elmer). Coal or its resultant ash (or char) was leached in a sealed polyethylene container with 30 mL of 6% hydrochloric acid. After leaching, the solution was filtered and then used for ICP-AES analysis. Taiheyo (THY) sub-bituminous, Ermelo (EL) and Datong bituminous coals were used in this study.

Results and Discussion

Leaching of Major Metallic Elements. Figure 1 shows the leaching percentage of the major metallic elements in hydrochloric acid from ash and char, where the left figure represents the data for EL ashes and the right figure represents those for EL coal chars. For comparison, leaching results of the raw coal are also illustrated. The leaching percentage is referred to as the amount of an element leached from coal, ash, or char divided by the amount contained in the original coal. Analysis of the ashes and chars showed that the major elements were not lost by volatilization during the combustion and pyrolysis under the used experimental conditions. XRD showed that the crystalline mineral phases in EL coal were kaolinite, quartz, calcite, dolomite, pyrite, and gypsum. Ca and Mg were highly leached out from the raw coals, 550-950 °C ashes, and 550-950 °C chars; this is because the major Ca- or Mg-containing carbonates in coal and their decomposed species are soluble in hydrochloric acid. Mg in the 1150 °C ashes and chars was relatively stable. Fe in the 550-750 °C ashes was greatly soluble as compared with that in the raw coal, while the leaching percentage of Fe significantly decreased from the 950-1150 °C ashes. Pyrite turned to hematite upon the ashing. Hematite in the 550 °C ash was readily soluble in hydrochloric acid; however, hematite was well crystallized with increasing temperature, resulting in a low solubility. Fe in all chars was greatly soluble. This is due to the transformation of pyrite to pyrrhotite. Al in the raw coal was hardly dissolved, whereas it was fairly leached out from the 550-750 ashes and chars. This is due to the breakage of the structure of clay by the dehydration. The formed species such as meta-kainilinite become partly extracted by hydrochloric acid. However, with increasing the ashing temperature to 1150 °C, the leaching percentage of Al is significantly reduced; this is because of the formation of some stable species such as mullite, examined by XRD. The leaching features of K were similar to those of Al.

Leaching of Non-vaporized Trace Elements. In a previous study, we found that Zn and Pb was vaporized, whereas the trace elements as shown in Figure 2 entirely remained in the ashes or chars under the used combustion and pyrolysis conditions. Figure 2 shows the leaching results of the non-vaporized elements in EL coal. The leaching percentage of Mn in the raw coal, ashes and chars was relatively high; this is because Mn exists mainly as carbonate. Mn turned to a stable phase at 1150 °C in both the combustion and pyrolysis. Be, V, Cr, and Ni in the raw coal and chars were hardly soluble, whereas these elements in the 550-750 ashes were significantly soluble. These elements are postulated partly as the organic associations. When the organic matter burns out, the liberated species become soluble in hydrochloric acid. In pyrolysis, these elements are not liberated. With the exception of V, the elements including Be, Co, Cr and Ni in the ashes were hardly soluble as the temperature increased to 1150 °C. The leachability of As in the ashes was higher than that in the raw coal. Arsenic easily forms oxyanion in an oxidizing atmosphere that may be soluble in acid. In pyrolysis, Arsenic appeared to form a less-soluble species.

Leaching of Volatile Trace Elements. Figure 3 show the results of Zn and Pb in EL coal. For clarify, the volatilization loss is denoted in the figure; it is referred to as the difference in the amount of an element between the coal and the residual ash or char, divided by the amount of the element containing in the original coal. Zn and Pb significantly volatilized during the pyrolysis above 950 °C, whereas in the combustion, only Pb volatilized slightly at 1150 °C. Zn and Pb exists mainly as sulfide in coal. In pyrolysis, their oxide and sulfides are reduced by carbon; these reduction reactions lead to the vaporization of the two elements as metals. However, such reduction reactions can not occur in the slow-heating combustion because of the burn-out of carbon ahead of 550 °C. Leaching results showed that both Zn and Pb in the ashes became less soluble with increasing temperature. This probably implies the interaction of these trace elements with other mineral matter to form less soluble species.
Figure 1. Leaching of major metallic elements from EL raw coal, its ashes (the left figure), and its chars (the right figure). The ashes and chars were obtained from the slow-heating combustion and pyrolysis at different temperatures.

Figure 2. Leaching of non-vaporized trace elements from EL raw coal, its ashes (the left figures), and its chars (the right figures). The preparation of the ashes and chars is noted in Figure 1.

Figure 3. Leaching of volatile trace elements from EL coal ashes (the left figures) and chars (the right figures). The preparation of the ashes and chars is noted in Figure 1.

Conclusions
Leaching behaviors of the major metallic elements in the raw, coal, ashes and chars are well explained by their existing form in coal and their transformations during the combustion and pyrolysis. Leaching results of trace elements showed that Mn is easily dissolved from the raw coal, ashes and chars, implying its existing form of carbonate. Be, Co, V, Cr, Ni in 550-750 ashes were more soluble than those in the raw coal and chars, suggesting their organic association. The liberated species of Be, Co, Cr and Ni in the ashes became less soluble at higher temperatures. Arsenic in the ashes is more soluble than that in the chars, implying a different transformation of As between the combustion and pyrolysis. Zn and Pb significantly volatilized during pyrolysis but little volatilized in the combustion.

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References