Analysis of Thermal Behavior of Crystalline Minerals in Bituminous Coal Samples under Air and Argon Atmospheres

Tadanori Hashimoto,* Kentaro Takai, Hung Viet Quang Nguyen, Masakatsu Nomura, and Atsushi Ishihara*

ABSTRACT: The thermal behavior of ash components in two bituminous coal samples [Upper Freeport (the “UF”) and Illinois #6 (the “IL”)] was investigated under air and argon atmospheres in the temperature range of 800–1200 °C using thermal gravimetric–differential thermal analysis, X-ray diffraction transmission electron microscopy (TEM), and TEM–energy dispersive X-ray spectrometry measurements. The UF treated under air formed the needle-like crystals which were assumed to be mullite-related substances formed by transformation of andalusite, because the crystals are mainly composed of SiO2 and Al2O3. In contrast to the UF, the IL did not generate such crystals; however, when the IL was treated under air after carbonization under Ar, crystals appeared. The composition of the UF with an Al/Si ratio higher than that of the IL favored the formation of mullite-related substances, while the presence of lime in the IL inhibited the formation of mullite-related substances. Oldhamite was formed by the reaction of lime with sulfur at the carbonization of the IL under Ar and remained even at the successive air treatment. As lime was consumed, the formation of mullite-related substances was ceased to be inhibited under air after Ar treatment.

1. INTRODUCTION

Coal is mainly used for coal-fired power generation fuel and iron-making coke, while the coal utilization brings about the generation of a large amount of ash. The coal fly ash can be used for (1) recovery of Na2O and Al2O3, (2) absorbents of SO2 and urea, (3) structural materials, (4) dielectric materials, and so on. On the other hand, ash components in coal have problems of affecting the high-temperature corrosion of gas turbine blades in thermal power generation,8–10 use of coal combustion byproducts,11 and the production and property of coke used in iron making.12–14 Coal samples of various mines in America,12,13–15 China,8,9,19–21 South Africa,22,23 Indonesia,24–26 and others27,28 have been investigated to overcome the problems above.

The current major interest in the ash problems is the formation of fine ash particles during the coal conversions such as pyrolysis, liquefaction, gasification, and combustion. The presence of organosilicatious aluminosilicates may contribute to the formation of such fine ash particles, because such aluminosilicates are very reactive with alkali and alkali-earth metals to be fusible during the gasification and combustion, causing the slagging problems.24 Control over the reaction atmosphere is very important, because several gases such as N2,20 and He,25 in pyrolysis processes of coal, H2O/He,25 and N2/CO2,29 in gasification processes and N2/O2,8 N2/air,12 air/O2,23 air/CO, CO2,20 and air12,20,29 in combustion processes were used, respectively. The coal sintering temperate under reducing conditions was lower than that under air20 in combustion processes.

As the coal ash-based products are still subject to the actual research theme, it is very important to understand the thermal behavior of ash components, because the microscopic structures of such components and their quantification have not yet been clarified completely and would have affected the processes.

There are some relevant studies on coal samples used such methods as the X-ray diffraction (XRD) method,12,17,30 transmission electron microscopy (TEM),15,17,18,28,31 thermal gravimetric analysis (TGA),11,28,32–34 differential thermal analysis (DTA),11,15,34 solid-state nuclear magnetic resonance (NMR),16,17,26,35 and emission.23,27,36 In refs,11,15,17,18 the structures of coal were investigated using TEM, but information on ash was not given. In refs,28,31 details of the thermal behavior of ash components were not given.

Received: September 3, 2020
Accepted: December 24, 2020
Published: January 5, 2021
Thus, it has not yet been clarified satisfactorily what chemicals are formed and how ash components change with varying atmosphere and treating temperature. In addition, the crystallization behavior of ash components and the morphology of ash-based products have not attracted such attention as to the problems of high-temperature corrosion of gas turbine blades. Therefore, in this reported study, changes in the behavior of ash components were investigated for the two bituminous coal samples [Upper Freeport (UF) and Illinois #6 (IL) differing each other in carbon content and ash component] of the Argonne Premium Coal Sample series with varying atmospheres (air, argon, and argon to air) and treating temperatures (800–1200 °C) using XRD, TEM, TEM–energy-dispersive X-ray spectrometry (EDS), and TG–DTA.

2. RESULTS AND DISCUSSION

2.1. Thermal Behavior of the UF and IL under Air. Figure 1 shows TG–DTA curves of the UF and IL (Tables S2 and S3) up to 1200 °C under air or argon atmosphere and TG–DTA curves of the UF and IL up to 800 °C under air again after heat-treated at 800 °C under argon atmosphere. TG–DTA curves of the UF and IL under argon atmosphere did not show such significant weight loss as observed under air atmosphere, and it was found that the weight gradually decreased from the beginning to the end of measurement: 30% and 65% weight losses were observed up to 1200 °C for the UF and IL measured under argon atmosphere, respectively. On the other hand, the weak peak of the DTA profile of the IL was observed around 400 °C. When TG–DTA of the UF and IL heat-treated under argon atmosphere was performed under air atmosphere again, the peaks of the DTA profile were observed at the temperatures higher than those of the coal samples heat-treated only under air atmosphere. In this analysis, large weight losses were also observed at 600–700 °C. Similar results were obtained for the UF and IL heat-treated down to the lower temperatures.

Figure 2 gives XRD patterns of the UF and IL heat-treated under air atmosphere at each temperature. The raw UF mainly consists of quartz (SiO$_2$), kaolinite [$\text{Al}_4\text{Si}_4\text{O}_{10}\text{(OH)}_8$], calcite (CaCO$_3$), and pyrite (FeS$_2$). The quartz and andalusite (Al$_2$SiO$_5$) existed under all heat-treatment conditions. The calcite was present in the UF heat-treated at 800 °C and disappeared at 1000 °C. The kaolinite and pyrite were transformed to the andalusite, anhydrite (CaSO$_4$), and hematite (Fe$_2$O$_3$), respectively, with increasing heat-treatment temperature. In the present case, mullite (Al$_6$Si$_2$O$_13$) was not observed. Table S1 was used for the assignment of XRD data.
hematite, respectively, with increasing heat-treatment temperature. The calcite was transformed to anhydrite and lime (CaO). The difference between UF and IL is considered to be because of the difference in the amount of calcium contained in the ash, as seen from Table S3.

Figure 3 shows TEM images of the UF and IL heat-treated at various temperatures under air atmosphere. From the TEM observation, needle-like crystals, which were not seen in the untreated coal samples, were observed after heat treatment of the UF under air atmosphere. From the TEM observation of the IL, needle-like crystals, which were observed above for the UF heat-treated under air atmosphere, were not observed.

2.2. Thermal Behavior of the UF and IL under Argon. Figure 4 gives XRD patterns of the UF and IL heat-treated under argon atmosphere at each temperature. The quartz and andalusite existed under all heat-treatment conditions, and the kaolinite was transformed to the andalusite with increasing heat-treatment temperature, similar to the case under air atmosphere. Pyrite (FeS₂) was transformed to troilite (FeS), and calcite disappeared unlike the case under air atmosphere.

In the case of the IL, the quartz and andalusite existed under all heat-treatment conditions, and the kaolinite and pyrite were transformed to the andalusite and troilite with increasing heat-treatment temperature, similar to the case of the UF. The calcite was transformed to oldhamite (CaS) as a point segregating the IL from the UF. The difference between UF and IL is considered to be because of the difference in the amount of calcium and sulfur contained in the untreated coal samples as seen from Tables S2 and S3. It can also be seen that the diffraction line of oldhamite becomes strong as the temperature rises, indicating that calcium oxide (lime) would react with the hydrogen sulfide formed from the reduction of pyrite to eventually produce calcium sulfide (oldhamite) under the reduction conditions.

Figure 5 shows TEM images of the UF and IL heat-treated at various temperatures under argon atmosphere. From the TEM observation, scale-like and honeycomb-like crystals were observed by heat treatment of the UF under argon atmosphere, whereas needle-like crystals were observed by heat treatment of the UF under air atmosphere. The scale-like and honeycomb-like crystals may be considered to be carbonaceous substances. In the case of the IL, the scale-like and honeycomb-like crystals may be considered to be carbonaceous substances, similar to the case of the UF. From the TEM observation, needle-like crystals, which were observed for the UF heat-treated under air atmosphere, were not observed.

2.3. Thermal Behavior of the UF and IL under Air after Argon. Figure 6 gives XRD patterns of the UF and IL heat-treated at 800 °C under air atmosphere again after heat-treated under argon atmosphere. The quartz and andalusite existed under all heat-treatment conditions. Because the samples were heat-treated at 800 °C under air atmosphere again after heat-treated under argon atmosphere, calcite and anhydrite was observed, similar to the case where they were heat-treated at 800 °C under air atmosphere. The troilite, which was formed under argon atmosphere, was transformed to hematite.

In the case of the IL, the quartz and andalusite existed under all heat-treatment conditions. Because the samples were heat-treated at 800 °C under air atmosphere again after heat-treated under argon atmosphere, calcite and anhydrite were observed, similar to the case where they were heat-treated at 800 °C under air atmosphere. The troilite, which was formed under argon atmosphere, was transformed to hematite. The oldhamite existed only in the IL samples under all heat-treatment conditions, similar to the case under argon atmosphere. The precipitation of the oldhamite in such coal samples as heat-treated under air atmosphere were reported in some
papers.\textsuperscript{41−43} Liang et al.\textsuperscript{41} reported that oldhamite exists in the coal samples heat-treated at 600 \degree C under air atmosphere. The data of Lu et al.\textsuperscript{42} suggested that oldhamite seems to exist in the coal samples heat-treated at 850 \degree C under air atmosphere, although weak diffraction lines around 2\theta = 45° and 65°, which may be due to oldhamite, were assigned to unknown peaks. Skhonde et al.\textsuperscript{43} reported that oldhamite exists even if high ash bituminous coal blend was undergone by combustion after gasification under SO\textsubscript{3} flow.

| Table 1 summarizes crystal phases precipitated in the UF and IL heat-treated under various atmospheres. The quartz (SiO\textsubscript{2}) and andalusite (Al\textsubscript{2}SiO\textsubscript{5}) existed under all heat-treatment conditions. Anhydrite (CaSO\textsubscript{4}), calcite (CaCO\textsubscript{3}), and hematite (Fe\textsubscript{2}O\textsubscript{3}) were observed in the UF and IL heat-treated under air atmosphere, while troilite (FeS) in closed square (■) was formed in the UF and IL heat-treated under Ar atmosphere.

Any calcium compounds did not appear in the UF heat-treated under argon, probably because they would be dissolved in an amorphous phase. The lime shown in closed circle (●) was observed in the UF and IL heat-treated under air, while oldhamite (▲) was observed in the IL heat-treated both under argon and under air atmosphere again after heat-treated under argon atmosphere. It seems that this would be attributable to the fact that the contents of Ca and S in the IL are about twice those in the UF. Once the CaS was formed under argon heat treatment, it is considered to be relatively stable under air atmosphere heat treatment. From analogy with the IL heat-treated under argon, oldhamite may be formed in the UF heat-treated under argon. However, it seems that the amounts of Ca and S in the UF would be too small for the diffraction line of oldhamite to appear in XRD.

Figure 7 shows TEM images of the UF and IL heat-treated under air atmosphere again after heat-treated under argon atmosphere.

Table 1. Crystal Phases Precipitated in the UF and IL Heat-Treated under Various Atmospheres

|          | UF air                  | UF Ar  | UF air after Ar | IL air                  | IL Ar  | IL air after Ar |
|----------|-------------------------|--------|-----------------|-------------------------|--------|-----------------|
| lime (CaO)| ● ● ●                   | ● ● ●  |                 | ● ● ●                   | ● ● ●  |                 |
| calcite (CaCO\textsubscript{3}) | ○ ○ ○                   | ○ ○ ○  | ○ ○ ○           | ○ ○ ○                   | ○ ○ ○  | ○ ○ ○ |
| anhydrite (CaSO\textsubscript{4}) | ○ ○ ○                   | ○ ○ ○  | ○ ○ ○           | ○ ○ ○                   | ○ ○ ○  | ○ ○ ○ |
| oldhamite (CaS) | ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ | ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ | ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ ▲ |
| andalusite (Al\textsubscript{2}SiO\textsubscript{5}) | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ |
| quartz (SiO\textsubscript{2}) | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ |
| hematite (Fe\textsubscript{2}O\textsubscript{3}) | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ | ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ |
| troilite (FeS) | ■ ■ ■                   | ■ ■ ■  |                 | ■ ■ ■                   | ■ ■ ■  |                 |

\textsuperscript{a}L: 800 \degree C, M: 1000 \degree C, H: 1200 \degree C.

Figure 5. TEM images of the UF heat-treated under argon atmosphere at temperatures 800, 1000, and 1200 \degree C.

Figure 6. XRD patterns of the UF and IL heat-treated under air atmosphere again after heat-treated under argon atmosphere.
like crystals, which were not observed for the IL heat-treated under air atmosphere, appeared. Thus, the needle-like crystals were observed in UF (air), UF (air after argon), and IL (air after argon).

TEM–EDS images were measured, as shown in Figure 8, for (a) UF heat-treated at 1000 °C under air, (b) IL heat-treated at 1000 °C under air, and (c) IL heat-treated under air atmosphere again after heat-treated under argon atmosphere at 1000 °C. The chemical composition determined by TEM–EDS measurement for UF is shown in Table S3. The results of TEM–EDS measurement seem to roughly reflect overall chemical composition of coal. Therefore, we semiquantitatively discussed chemical composition using EDS mapping data. The oldhamite seen only in the IL heat-treated under air atmosphere again after heat-treated under argon atmosphere at 1000 °C was identified from the Ca and S composition mapping in Figure 8c. It was found from TEM–EDS observation that needle-like crystals mainly consist of Si and Al (Figure 8a,c). In this case, andalusite (Al2SiO5) is assumed from the XRD data available to be one candidate for needle-like crystals. While this crystalline phase existed in both UF and IL under all heat-treatment conditions, it is doubtful whether it would be related to needle-like shape.

There are some reports on needle-like crystals mullite (3Al2O3·2SiO2: Al6Si2O13) and anorthite (CaAl2Si2O8) including Si and Al as coal ash. Moreover, it is known that andalusite transforms to mullite at high temperatures.48 Because needle-like crystals were not seen in the IL heat-treated under air atmosphere, such reported results may be arisen from the difference in ash composition of the untreated coal samples taken. The UF with more Al and less Ca relative to the IL may produce mullite rather than anorthite. Because the composition of mullite has a higher Al/Si ratio compared to andalusite, the andalusite precipitated from the UF with an Al/Si ratio higher than the IL may tend to transform to needle-like mullite-related substance. Therefore, the needle-like crystals seen in UF (air), UF (air after argon), and IL (air after argon) are assumed to be mullite-related substances, which was partially transformed from andalusite but not detectable in XRD patterns. Moreover, needle-like crystals for UF (air, 1200 °C) vanished, as shown in Figure 3. Mullite reacts with CaO to produce anorthite by heat-treating at temperatures higher than 1130 °C and 800 °C. It is consistent with our assumptions that needle-like crystals are mullite-related substances.

The needle-like crystals were not seen in UF (Ar) and IL(Ar). In addition, Ding et al.49 reported that transformation of andalusite to mullite was depressed under the carbon-embedded conditions (reduction conditions), compared to air conditions. These are not contradicting with our results.

While the needle-like crystals were not formed in the presence of lime as in IL (Air) with an Al/Si ratio lower than UF, these crystals were formed in the presence of oldhamite instead of lime as in IL (Air after argon). Because most of the carbon is burnt at 600 °C under air atmosphere, and lime is in contact with other species of ash such as mullite-related substance before neutralization by the acid components (sulfuric acid, etc.), it was easy for needle-like crystals to be formed for the UF-treated under air atmosphere, as the UF contains an amount of lime lower than IL. On the other hand, C suppresses the reaction between species of ash under Ar atmosphere and H2 reacts with pyrite to generate H2S and troilite. The lime is neutralized by H2S to form oldhamite, which would lead to the loss of the ash-dissolving ability. The sulfur in FeS2 was also migrated to Ca compounds (CaS or CaSO4) by heat-treating.49 This was also supported by the fact that, in EDS measurement, the distributions of Ca and S were almost the same as each other. It is therefore assumed that the crystallization of the Al2O3–SiO2 system would progress by heat-treating under air atmosphere again after heat-treating under argon. Such is more likely to happen, because the content of sulfur in the IL was much higher than that in the UF.

3. CONCLUSIONS

In this study, changes in the behavior of ash components in the two bituminous coal samples (UF and IL) with varying the treating atmosphere and temperature were investigated using TG–DTA, XRD and TEM measurements. The quartz (SiO2) and andalusite (Al2SiO5) existed under all heat-treatment conditions. Anhydrite (CaSO4), calcite (CaCO3), and hematite (Fe2O3) were observed in the UF and IL heat-treated under air atmosphere, while troilite (FeS) was formed in the UF and IL heat-treated under argon atmosphere. All the crystalline phases in heat-treated UF were observed in heat-treated IL. The lime was observed in the UF and IL heat-
From the TEM observation, needle-like crystals, which were not seen in the untreated samples, were observed in the UF heat-treated under air atmosphere, while such crystals were not seen in the IL heat-treated under air atmosphere. The needle-like crystals seen in UF (Air), UF (Air after argon), and IL (Air after argon) were found from TEM−EDS and XRD observation to mainly consist of SiO$_2$ and Al$_2$O$_3$, suggesting that they would be mullite-related substances. The composition of mullite-related substances has a higher Al/Si ratio, compared to andalusite. Therefore, it is likely that the andalusite phase formed from the UF would transform to needle-like mullite-related substance because the UF has an Al/Si ratio higher than the IL. On the other hand, the needle-like crystals were not formed for the IL heat-treating under air probably because of the presence of lime and the IL having a lower Al/Si ratio relative to the UF. However, the needle-like crystals were found for the IL heat-treated under air after Ar treatment, suggesting that lime was neutralized by the hydrogen sulfide formed under argon treatment to eventually form oldhamite, which promoted the formation of the needle-like crystals.

4. EXPERIMENTAL SECTION

4.1. Coal Samples and Heat Treatment. Bituminous coal samples, UF and IL, were purchased from Argonne National Laboratory. Ultimate and proximate analysis of these coal samples are shown in Table S2. Ash contents of the UF and IL are 13.03 wt % and 14.25 wt %, respectively.

Ash components of these coal samples are shown in Table S2. Roughly, the UF has a higher carbon content (86%), a higher Al$_2$O$_3$ content, a lower CaO content, and a lower SO$_3$ content, compared to the IL. Heat treatment of the UF and IL was performed at 800−1200 °C under air, argon, or argon to air atmosphere and was cooled in the furnace.

4.2. Characterization of Coal Samples Using TG−DTA, XRD, TEM, and TEM−EDS. The original as-received (AR) and pulverized coal samples were subjected to the following measurements: Thermal gravimetric (TG) and differential thermal analyses (DTA) measurement of coal samples using Shimadzu DTG-60AH was performed under air or argon atmosphere with the following conditions: flow rate of 100 mL/min, temperatures of 800−1200 °C at a heating rate of 10 °C/min, without retention at target temperature, and by furnace cooling. Further, TG−DTA measurement of the UF and IL heat-treated up to 800−1200 °C under argon atmosphere was also performed at 800 °C at a heating rate of 10 °C/min, without retention at the target temperature and by furnace cooling under air atmosphere to eventually investigate the oxidation process.

For the sample XRD measurement, 0.7 g each of the coal samples was heat-treated in 100 mL/min under air or argon atmosphere up to 800−1200 °C at a heating rate of 10 °C/min, without retention at target temperature and by furnace cooling. The UF and IL samples heat-treated under argon atmosphere was again heat-treated at 800 °C at a heating rate of 10 °C/min, without retention at target temperature and followed by furnace cooling under air atmosphere. XRD patterns were measured in order to examine the crystal structures of ash in the coal samples heat-treated under air or argon atmosphere. The XRD measurement system (Ultima IV, Rigaku) with the use of Ni-filtered Cu Kα radiation ($\lambda = 0.15405$ nm) was used for coal samples (sample amount 0.10 g) held on the glass plates under the following conditions: $2\theta =$ treated under air, while oldhamite was observed only in the IL heat-treated under argon and air atmosphere again after heat-treated under argon atmosphere, probably because contents of Ca and S in the IL were larger than those in the UF. Once CaS was formed under argon heat treatment, it would be maintained even under air atmosphere heat treatment, because of its high thermal stability.
10–70°, sampling width of 0.02°, scan speed of 4°/min, voltage of 40 kV, current of 20 mA, radiation slit of 2/3°, radiation column limitation slit of 10.00 nm, scattering slit of 2/3°, detecting slit of 0.45 nm, and offset angle of 0°.

Transmission electron microscopy (TEM) measurement of the samples heat-treated by TG–DTA measurement under air, argon, or argon to air atmosphere was performed using transmission electron microscope JEM-1011 (JEOL Co. Ltd.). Transmission electron microscope equipped with TEM-EDS for the selected samples was performed using field emission electron microscope JEM-2100F (JEOL Co. Ltd.).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04311.

Ash compound assigned by JCPDS card files, value in parentheses: relative intensity of the strongest three diffraction lines, proximate and ultimate analysis of UF and IL, ash contents: UF (13.03 wt %) and IL (14.25 wt %), sulfur content: UF (0.74 wt %) and IL (2.38 wt %), chemical compositions in weight percent of ash, silicon content: UF (44.73 wt %) and IL (43.70 wt %), aluminum content: UF (24.07 wt %) and IL (18.30 wt %), and calcium content: UF (4.19 wt %) and IL (7.90 wt %) (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Tadanori Hashimoto — Division of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu-City, Mie 5148507, Japan; orcid.org/0000-0003-2887-7536; Email: hasimoto@chem.mie-u.ac.jp

Atsushi Ishihara — Division of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu-City, Mie 5148507, Japan; orcid.org/0000-0002-6390-8898; Email: ishihara@chem.mie-u.ac.jp

**Authors**

Kentaro Takai — Division of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu-City, Mie 5148507, Japan

Hung Viet Quang Nguyen — Division of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu-City, Mie 5148507, Japan; Center of Severe Materials and Environment, Vietnam Academy of Science and Technology, Hanoi 10072, Vietnam

Masakatsu Nomura — Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04311

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

A part of this work (TEM–EDS) was supported by Nagoya University microstructural characterization platform as a program of “Nanotechnology Platform” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Authors thank Shunsuke Koyabu, Karin Uemura and Dr. Hiroyuki Nasu for their helpful work.

**ABBREVIATIONS**

UF, Upper Freeport; IL, Illinois #6; M, moisture content; V, volatile matter content; A, ash content; FC, fixed carbon content; AR, as-received; DAF, dry and ash free; ND, not detected

**REFERENCES**

(1) Yang, S.; Song, G.; Na, Y.; Qi, X.; Yang, Z. Experimental study on the recovery of sodium in high sodium fly ash from thermochemical conversion of Zhundong coal. *Fuel* 2018, 229, 22–33.

(2) Wang, Y.-w.; Wang, Z.-q.; Huang, J.-j.; Fang, Y.-t. Improved catalyst recovery combined with extracting alumina from Na₂CO₃ catalyzed gasification ash of a high-aluminums coal char. *Fuel* 2018, 234, 101–109.

(3) Rathnayake, M.; Julliagawithawong, P.; Tantgermsirikul, S.; Toochinda, P. Utilization of coal fly ash and bottom ash as solid sorbents for sulfur dioxide reduction from coal fired power plant: Life cycle assessment and applications. *J. Cleaner Prod.* 2018, 202, 934–945.

(4) Simha, P.; Ramathan, A.; Thawani, B.; Jain, P.; Hussain, S.; Ganesapillai, M. Coal fly ash for the recovery of nitrogenous compounds from wastewater: Parametric considerations and system design. *Arabian J. Chem.* 2019, 12, 5049–5061.

(5) Masuka, S.; Gwenni, W.; Rakuni, T. Development, engineering properties and potential applications of unfired earth bricks reinforced by coal fly ash, lime and wood aggregates. *J. Build. Eng.* 2018, 18, 312–320.

(6) Singh, N.; M, M.; Arya, S. Utilization of coal bottom ash in recycled concrete aggregates based self compacting concrete blended with metakaolin. *Resour., Conserv. Recycl.* 2019, 144, 240–251.

(7) Tabit, K.; Waqif, M.; Sa’di, L. Anorthite-cordierite based binary ceramics from coal fly ash and steel slag for thermal and dielectric applications. *Macromol. Chem. Phys.* 2020, 254, 123472.

(8) Zhao, Y.; Zhang, J.; Zheng, C. Transformation of aluminum-rich minerals during combustion of a bauxite-bearing Chinese coal. *Int. J. Coal Geol.* 2012, 94, 182–190.

(9) Zhou, C.; Liu, G.; Yan, Z.; Fang, T.; Wang, R. Transformation behavior of mineral composition and trace elements during coal gangue combustion. *Fuel* 2012, 97, 644–650.

(10) Raaj, S. S.; Arumugam, S.; Muthukrishnan, M.; Krishnamoorthy, S. Characterization of coal blends for effective utilisation in thermal power plants. *Appl. Therm. Eng.* 2016, 102, 9–16.

(11) Terzic, A.; Peto, L.; Mjatovic, N.; Stojanovic, J.; Kragovic, M.; Milicic, L.; Andric, L. The effect of alterations in mineral additives (zoelite, bentonite, fly ash) on physico-chemical behavior of Portland cement based binders. *Constr. Build. Mater.* 2018, 180, 199–210.

(12) Galbreath, K. C.; Toman, D. L.; Zygarlick, C. J.; Pavlish, J. H. Trace Element Partitioning and Transformations During Combustion of Bituminous and Subbituminous U. S. Coals In a 7-kW Combustion System. *Energy Fuels* 2000, 14, 1265–1279.

(13) Shen, J.; Hu, H.; Xu, M.; Liu, H.; Xu, K.; Zhang, X.; Yao, H.; Naruse, I. Interactions between molten salts and ash components during Zhundong coal gasification in eutectic carbonates. *Fuel* 2017, 207, 365–372.

(14) Fehse, F.; Rosin, K.; Schröder, H.-W.; Kim, R.; Spöttle, M.; Repke, J.-U. Influence of briquetting and coking parameters on the lump coke production using non-caking coals. *Fuel* 2017, 203, 915–923.

(15) Sharma, A.; Kyotani, T.; Tomita, A. Quantitative evaluation of structural transformations in raw coals on heat-treatment using HRTEM technique. *Fuel* 2001, 80, 1467–1473.
(16) Kashiwakura, S.; Takahashi, T.; Nagasaki, T. Vaporization behavior of boron from standard coals in the early stage of combustion. Fuel 2011, 90, 1408–1415.

(17) Castro-Marcano, F.; Winans, R. E.; Chupas, P.; Chapman, K.; Calo, J. M.; Watson, J. K.; Mathews, J. P. Fine Structure Evaluation of the Pair Distribution Function with Molecular Models of the Argonne Premium Coals. Energy Fuels 2012, 26, 4336–4345.

(18) Wang, C. a.; Huddle, T.; Lester, E. H.; Mathews, J. P. Quantifying Curvature in High-Resolution Transmission Electron Microscopy Lattice Fringe Micrographs of Coals. Energy Fuels 2016, 30, 2694–2704.

(19) Li, H.; Ninomiya, Y.; Zhongbing, D.; Ming Xu, Z. Application of the FactSage to Predict the Ash Melting Behavior in Reducing Conditions. Chin. J. Chem. Eng. 2006, 14, 784–789.

(20) Zhang, Z. i; Wu, X.; Zhou, T.; Chen, Y.; Hou, N.; Piao, G.; Kobayashi, N.; Itaya, Y.; Mori, S. The effect of iron-bearing mineral ash deposition on mineral coal combustion. Proc. Combust. Inst. 2011, 33, 2853–2861.

(21) Liu, Y.; Cheng, L.; Zhao, Y.; Ji, J.; Wang, Q.; Luo, Z.; B; Y. Transformation behavior of alkali metals in high-alkali coals. Fuel Process. Technol. 2018, 169, 288–294.

(22) van Dyk, J. C.; Waanders, F. B.; van Heerden, J. H. P. Quantification of oxygen capture in mineral matter during gasification. Fuel 2008, 87, 2735–2744.

(23) Tsuchi, H.; Shirai, H.; Matsuda, H.; Rajoo, P. Emission characteristics of NOx and unburned carbon in fly ash on ash-high coal combustion. Fuel 2011, 90, 850–853.

(24) Sakasihni, K.; Saito, I.; Ishom, F.; Watanabe, I.; Mochida, I.; Okuyama, N.; Deguchi, T.; Simazaki, K. Characterization and elution behaviors of organically associated minerals in coals during acid treatment and solvent extraction. Fuel 2002, 81, 1471–1475.

(25) Murakami, K.; Sato, M.; Tsubouchi, N.; Ohtsuka, Y.; Sugawara, K. Steam gasification of Indonesian subbituminous coal with calcium carbonate as a catalyst raw material. Fuel Process. Technol. 2015, 129, 91–97.

(26) Ke, X.; Li, D.; Zhang, M.; Jean, C.-h.; Cai, R.; Cai, J.; Luy, J.; Yang, H. Ash formation characteristics of two Indonesian coals and the change of ash properties with particle size. Fuel Process. Technol. 2019, 186, 73–80.

(27) Taniguchi, M.; Kamikawa, Y.; Yamamoto, K. Comparison of staged combustion properties between bituminous coals and a low-rank coal: Fiber-shaped crystallized carbon formation, NOx emission and coal burnout properties at very high temperature. Combust. Flame 2013, 160, 2221–2230.

(28) Saikia, B. K.; Ward, C. R.; Oliveira, M. L. S.; Hower, J. C.; De Leao, F.; Johnston, M. N.; O’Brien, A.; Sharma, A.; Barah, B. P.; Silva, L. F. O. Geochemistry and nano-mineralogy of feed coals, mine overburden, and coal-derived fly ashes from Assam (North-east India): a multi-faceted analytical approach. Int. J. Coal Geol. 2015, 137, 19–37.

(29) Yoshie, R.; Taya, Y.; Ichiyamaghi, T.; Ueki, Y.; Naruse, J. Emissions of particles and trace elements from coal gasification. Fuel 2013, 108, 67–72.

(30) Liu, Y.; Cheng, L.; Ji, J.; Zhang, W. Ash deposition behavior in co-combusting high-alkali coal and bituminous coal in a circulating fluidized bed. Appl. Therm. Eng. 2019, 149, 520–527.

(31) Silva, L. F. O.; Moreno, T.; Querol, X. An introductory TEM study of Fe nanominerals within coal fly ash. Sci. Total Environ. 2009, 407, 4972–4974.

(32) Guo, L.; Zhan, M.; Wang, Z.; Zhang, Y.; Dong, P. Comparison of bituminous coal and lignite during combustion: combustion performance, coking and slagging characteristics. J. Energy Eng. 2019, 92, 802–812.

(33) Engin, B.; Atakil, H. Air and oxygen-fuel combustion kinetics of low rank lignites. J. Energy Inst. 2018, 91, 311–322.

(34) Tang, Q.; Sheng, W.; Li, L.; Zheng, L.; Miao, C.; Sun, R. Alteration behavior of mineral structure and hazardous elements during combustion of coal from a power plant at Huainan, Anhui, China. Environ. Pollut. 2018, 239, 768–776.

(35) Jing, Z.; Rodrigues, S.; Strouinia, E.; Li, M.; Wood, B.; Underschultz, J. R.; Estler, J. S.; Steel, K. M. Use of FTIR, XPS, NMR to characterize oxidative effects of NaClO on coal molecular structures. Int. J. Coal Geol. 2019, 201, 1–13.

(36) Fu, B.; Liu, G.; Sun, M.; Hower, J. C.; Mian, M. M.; Wu, D.; Wang, R.; Hu, G. Emission and transformation behavior of minerals and inorganic trace elements (HTEs) during coal combustion in a circulating fluidized bed. Environ. Pollut. 2018, 242, 1950–1960.

(37) Ban, Y.-P.; Yan-hua, T.; Jie, W.; Meng-xin, H.; Gu-si, T.; WANG-Yan; Run-xia, H. E.; Ke-duan, Z.; Quan-sheng, L. Effect of inorganic acid elution on microcrystalline structure and spontaneous combustion tendency of Shengli lignite. J. Fuel Chem. Technol. 2016, 44, 1059–1065.

(38) Zhao, H.; Li, Y.; Song, Q.; Wang, X.; Shu, X. Drying, re-adsorption characteristics, and combustion kinetics of Xilingol lignite in different atmospheres. Fuel 2017, 210, 592–604.

(39) Zhao, J.; Meng, J.; Chen, L.; Wang, T.; Song, J.; Zhang, Y.; Shu, C.-M.; Zeng, Q. Correlation analysis of the functional groups and exothermic characteristics of bituminous coal molecules during high-temperature oxidation. Energy 2019, 181, 136–147.

(40) Yuan, Z.; Shen, Y.; Yuan, H.; Sui, A.; Zhu, N.; Lou, Z. A collaborative approach to in-situ oxy sulfides and oxynitrides fixation in flue gas and energy recycling: Co-combustion of spent bleaching earth and coal. J. Cleaner Prod. 2020, 258, 120622.

(41) Liang, P.; Jiang, W.-M.; Zhang, Y.-Q.; Wang, X.-H.; Zhu, J.-L. Effect of circulating ash on sulfur conversion characteristics in the coal polygeneration process. Fuel Process. Technol. 2016, 150, 16–22.

(42) Lu, G.; Shen, Q.; Cheng, F. Sulfur fixation characteristics of single coal briquette particle during the process of combustion in different atmospheres. J. Cleaner Prod. 2020, 270, 122392.

(43) Skhonde, M. P.; Strydom, C. A.; Bust, J. R.; Schober, H. H. Sulphur capturing by an inertinite rich high ash bituminous coal during conversion in a pilot packed bed reactor. J. Anal. Appl. Pyrolysis 2011, 91, 205–209.

(44) Williams, R. P.; van Riessen, A. Determination of the reactive component of fly ashes for geopolymber production using XRP and XRD. Fuel 2010, 89, 3683–3692.

(45) Matjie, R. H.; French, D.; Ward, C. R.; Pistorius, P. C.; Li, Z. Behaviour of coal mineral matter in sintering and slagging of ash during the gasification process. Fuel Process. Technol. 2011, 92, 1426–1433.

(46) Gong, B.; Tian, C.; Xiong, Z.; Zhao, Y.; Zhang, J. Mineral changes and trace element releases during extraction of alumina from high aluminum fly ash in Inner Mongolia China. Int. J. Coal Geol. 2016, 166, 96–107.

(47) Ghasemi-Kahrizsangi, S.; Gheisari Dehsheikh, H.; Karamian, E.; Ghasemi-Kahrizsangi, A.; Yadie Hosseini, S. The influence of Al2O3 nanoparticles addition on the microstructure and properties of bauxite self-flowing low-cement castables. Ceramic Int. 2017, 43, 8813–8818.

(48) Mazel, F.; Gonon, M.; Fantozzi, G. Manufacture of mullite substrates from andalusite for the development of thin film solar cells. J. Eur. Ceram. Soc. 2002, 22, 453–461.

(49) Ding, D.; Ye, G.; Li, N.; Liao, G.; Tian, X.; Chen, L. Andalusite transformation and properties of andalusite-bearing refractories fired in different atmospheres. Ceramic Int. 2019, 45, 3186–3191.