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# Characteristics of clinker formation in a circulating fluidized bed boiler firing Korean anthracite

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**Abstract**−To shed light on the causes of clinker formation during the initial operation period of the Tonghae circulating fluidized bed (CFB) boiler, which uses Korean anthracite as fuel, the properties of ash, sand and limestone particles and the mixtures of each gradient have been characterized. The clinkers formed in the loopseals and the fluidized bed ash cooler (FBAC) of the CFB boiler were also characterized by analyzing the composition, the surface phenomena and the crystal structure of the clinkers. As a result, the black clinker was found to come from the sand particles and the composition of the white clinker was found to be similar to that of ash particles. The cause of the clinker formation in the FBAC proved that ash was sticking to molten or sintered phases in the high temperature regions in the boiler. On the other hand, the composition of the ash changed with the particle size, showing an enrichment of $Fe_2O_3$ as the particle size decreased. Also, the ash particles between 75-100 μm contained more than 11% CaO which resulted in low initial deformation temperature of the particles. So it is possible to explain that the amount of Fe and Ca in the fine particles of the ash plays a crucial role in the formation of agglomerates in the CFB boiler.

Key words: Clinker, Agglomeration, Quartz, Mullite, Circulating Fluidized Bed Boiler

## INTRODUCTION

It is quite important to prevent the formation of clinkers in circulating fluidized bed (CFB) boilers for stable and continuous operation. The clinker, an agglomerate form of some mineral matters, is in general one of the fundamental problems in CFB boilers due to the possibilities of the instability of fluidization and the decrease of boiler utilization. Especially, poor fluidization due to the clinker formation may finally result in the complete defluidization of the bed, which means an unscheduled shutdown of the whole CFB boiler [1,2].

There are several CFB boilers in Korea. Among them, the largest one is the Tonghae CFB boiler (200 MWe×2 units) which has been firing Korean anthracite and has been commercially operated since 1998. Domestic Korean anthracite contains the many non-combustible constituents to form ash and has lower combustion efficiency compared to bituminous coal [3]. Several operational problems in the Tonghae CFB boiler have been attributed to mutual interactions of minerals in fuel. In particular, during the commissioning period of the Tonghae CFB boiler, a considerable amount of clinker was formed at fluidized bed ash cooler (FBAC) and loopseals [4]. In this period, sand was used as bed material for start-up, which may lead to the formation of agglomerates and sinters. Also, Korean anthracite may contain substantial amount of the minerals such as kaolinite, illites, quartz, pyrite and so on. With the exception of quartz, the others would be expected to decompose at the CFB operational temperature, so agglomeration of ash particles could occur when two or more particles of bed materials adhere and then form a permanent bond. The shape of clinkers in the CFB boiler could be found to be different from those of other thermal power plants. It seemed that two or three particles with different colors were adhering to a molten or sintered surface, and the bond strength of agglomeration was so weak that they could be manually separated to black and white particles. A molten surface can be formed by fusion of the mineral particles or as the result of a chemical reaction when two or more components interact [6]. The agglomeration of ash particles usually occurs if a glassy phase is present to form a bond. So the operating temperature of changing the ash composition and forming the glassy phase is of importance.

In the present paper, then, to identify the causes of clinker formation when especially occurring during the initial start-up period of the CFB boiler, the surface phenomenon, chemical composition and mineral phases of ash particles and clinkers were determined by various chemical analyses. Also, the effect of the size of the ash particles on the clinker formation was also observed and discussed to predict the clinker formation temperature and atmosphere.

## EXPERIMENTAL

### 1. Features of the Tonghae CFB Boiler and Operation Conditions

The Tonghae CFB boiler, which has been described in many previous studies, is shown in Fig. 1 [4,5]. It consists of a furnace (19 m-W ×8 m-L×32 m-H), three cyclones and loopseals, three fluidized bed heat exchangers (FBHEs) and a fluidized bed ash cooler (FBAC). The furnace of the CFB has a rectangular footprint which allows for good fuel mixing. Limestone is injected with the fuel feed chutes in two injection ports along the rear wall. Bottom ash is removed from the furnace via two ash control valves (ACV) and then is in-

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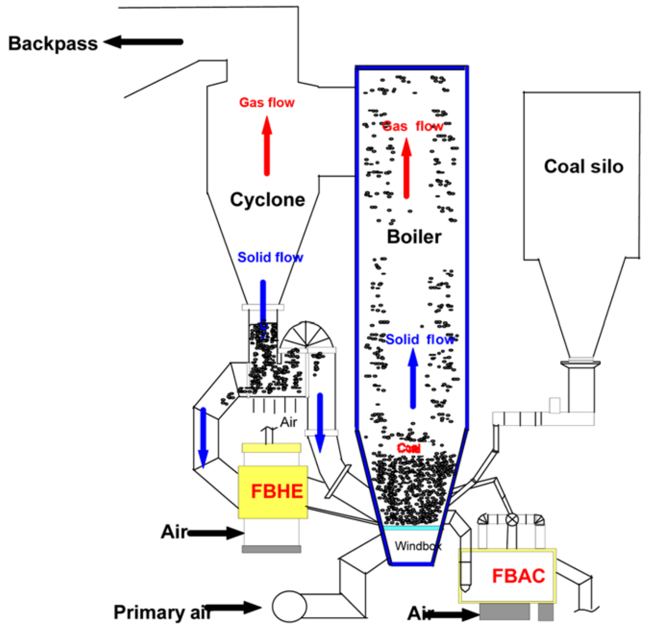



**Fig. 1. Tonghae CFB boiler feature.**

troduced into an FBAC. The loopseals serve to create a pressure seal from the positive pressure in the combustor to the negative pressure in the cyclone. This pressure seal prevents the flow of material back up the cyclone from the bottom of the combustor. The loopseal is a compact, low-velocity multi-chamber fluidization grate. In the Tonghae CFB unit, the boiler turndown requirement, coupled with the difficult to burn anthracite fuel, resulted in FBHEs. At each of the three loopseals, a stream of the solid materials is diverted and introduced into an FBHE. The FBHEs are bubbling beds containing natural circulation evaporative, superheat and reheat heat transfer surfaces. As the solids from the loopseals flow over and through the FBHE heat transfer surfaces, the ash is cooled and then returned to the combustor.

The operation conditions of the Tonghae CFB boiler at the beginning stage for start-up are shown in Table 1. At the initial operation period, the temperatures of the furnace, cyclones and loopseals were much higher than expected, which seemed to be the main cause of unstable operation and clinker formation. After that, however, the operation was stabilized by lowering the temperatures through modification of the cyclones and optimization of the operation conditions [5].

**Table 1. Operation conditions of the Tonghae CFB boiler at the commissioning period**

| Operation parameters | Conditions |
|---|---|
| Power generation [MWe] | 200 |
| Coal flow rate [kg/s] | 97-98 |
| Limestone flow rate [kg/s] | 2.2-3.5 |
| Total air flow [kg/s] | 210-218 |
| Combustor temp. [°C] | 870-890 |
| Combustor outlet temp. [°C] | 945-1015 |
| Cyclone outlet temp. [°C] | 960-1015 |
| Loopseal temp. [°C] | 920-1004 |

**Table 2. Analyses of Korean anthracite used in the Tonghae CFB boiler**

| Proximate analysis | wt% (air dry basis) | Ultimate analysis | wt% (dry basis) |
|---|---|---|---|
| Moisture | 3.3 | C | 54.7 |
| Volatile matters | 4.0 | H | 0.3 |
| Fixed Carbon | 53.7 | O | 3.8 |
| Ash | 39.0 | N | 0.2 |
| Heating value (HHV) | 4600 (kcal/kg) | S | 0.6 |
| | | Ash | 40.4 |

**2. Materials**

The analyses of Korean anthracite used in the Tonghae CFB boiler are shown in Table 2. The anthracite has comparatively rich ash and low volatile content. Despite the high ash content of coal, sand was used as bed material because the amount of coal ash particles was insufficient to make a use of bed material during the initial operation period for start-up.

The ash and clinker specimens analyzed in this study were also obtained from the Tonghae CFB boiler during initial operation period.

**3. Reagents**

The standard solution for composition analysis used in this study was obtained from Perkin-Elmer with 1,000 ppm for ICP, and $LiBO_2$ was obtained from Scientifique Claisse Inc.. Nitric acid was used without further purification and all solutions were prepared with distilled water.

**4. Apparatus and Procedure**

Composition analyses were performed by inductively coupled plasma atomic emission spectroscope (ICP-AES; Spectro-P, Spectro Co.). Crystalline phases present in the ash, clinker and agglomerate samples were determined by X-ray diffractometer (XRD; Ultima +2200, Rigaku). The thermal characteristics were analyzed by differential thermal analyzer (DTA; SDT 2910, TA Instruments) and surface phenomena were obtained by scanning electron microscope (SEM; JSM 6360, JEOL). The ash fusion temperature with size fraction was determined by ash fusion temperature determinator (AF 600; Leco Co.).

## RESULTS AND DISCUSSION

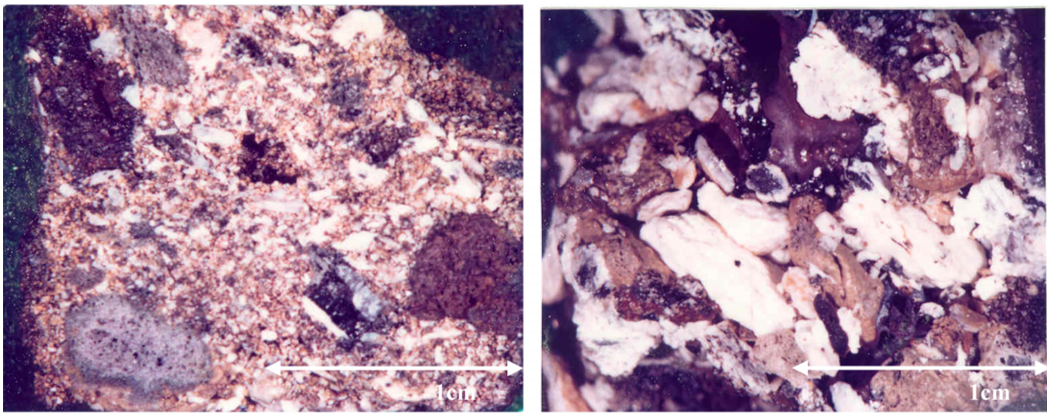
**1. Technical Problems During Initial Operation of the CFB Boiler**

During the initial operation of the CFB, there were some problems such as formation of clinker in the loopseals, agglomeration of bed ash in the FBAC and so on [4]. At this stage, stable fluidization of solid particles could not be achieved due to the formation of clinker in the loopseals and the FBAC because of higher operation temperature than expected. The anthracite used in the operation included more fine particles, which produced a residue to finer ash particles after combustion and this may cause the formation of clinker. On the other hand, the coarse particles of the coal which caused poor fluidization may be the main reason for agglomeration in FBAC.

After the commissioning period, the Tonghae CFB was successfully operated via some modification and optimization of the unit [5].

**2. Optical and SEM Analyses of the Clinkers**

Stereozoom microscope feature of clinkers from initial operation




(a) (b)

**Fig. 2. Stereozoom microscope feature (bar=1 cm); (a) loopseal clinker (b) FBAC clinker.**

stage of the CFB boiler is presented in Fig. 2. They were agglomerated to each other with different colors and manually separated. Fig. 2(a) was from the loopseals and Fig. 2(b) was from the FBAC. The loopseals clinker covered with sand and partially molten surface. The FBAC clinker bond was so weak that the clinker was composed of black and white particles. The enlarged SEM images of molten surface and particles are shown in Fig. 3 and 4, which have given valuable information regarding the interactions between mineral particles in the boiler. Fig. 3 and Fig. 4 show the liquid-glassy phase, which can be reacted with the ash particles at this operation temperature. This glassy bond may be the evidence of internal fusion of fine particles of sand and ash. The agglomeration of ash particles in the fluidized bed usually takes place if a liquid phase is present to make a bond between particles. Also, glassy bonds containing significant amount of CaO can be found when limestone has been added to the furnace for sulfur capture. Therefore, the aluminosilicate glass can be easily formed when Si and Ca in the bed particles such as sand, ash and limestone exist [6]. On the other hand, numerous pores and molten phases were observed in the loopseal clinker as shown in Fig. 3. These pores, which decrease thermal conductivity of the particles, have a significant influence on the growth of deposit [7]. Also, the black clinkers from the FBAC had liquid phases and some pores as shown in Fig. 4(a). This may be come from large amount of Fe content in the particles as expressed in Table 3, which could make the agglomeration potential higher in the boiler.

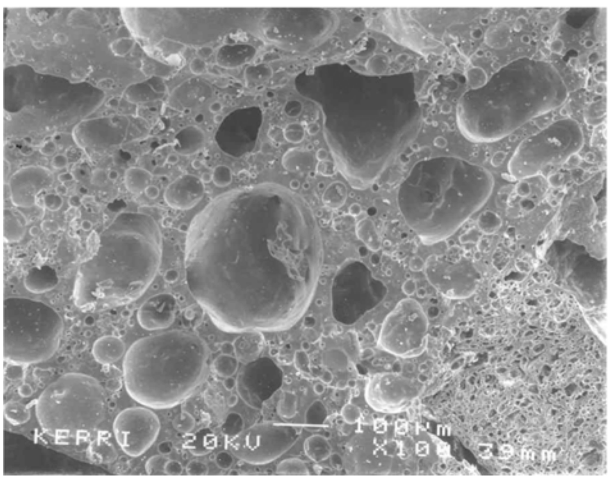
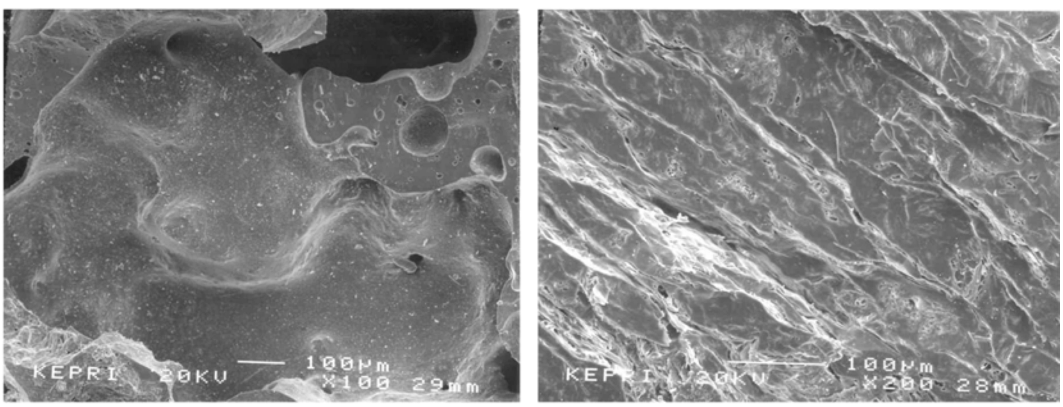



**Fig. 3. SEM image of loopseal clinker (bar=100 μm).**

**3. Chemical Composition and Mineral Phases of the Clinkers**

The chemical compositions of black and white particles of the clinkers were compared to data obtained for fly ash, sand and lime-




(a) (b)

**Fig. 4. SEM image of FBAC clinker; (a) black particle (bar=100 μm), (b) white particle (bar=100 μm).**

**Table 3. Concentration analysis of the solid materials in the CFB boiler by inductively coupled plasma atomic emission spectroscopy (ICP-AES)**

| Sample | | % (w/w) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $Fe_2O_3$ | $TiO_2$ | $Na_2O$ | $K_2O$ |
| 1. Fly ash | | 52.09 | 31.95 | 3.27 | 0.82 | 5.26 | 1.90 | 0.16 | 3.83 |
| 2. Sand | | 79.26 | 13.10 | 1.11 | 1.03 | 3.61 | 0.47 | 2.03 | 3.77 |
| 3. Limestone | | 1.75 | 1.22 | 50.97 | 2.05 | 0.24 | 0.04 | 0.05 | 0.37 |
| 4. Clinker (White) | FBAC | 53.63 | 35.16 | 0.52 | 0.36 | 1.16 | 2.73 | 0.08 | 3.42 |
| | Loopseal | 58.37 | 34.87 | 0.46 | 0.36 | 0.95 | 1.56 | 0.11 | 3.85 |
| 5. Clinker (Black) | FBAC | 66.91 | 21.06 | 1.02 | 1.11 | 4.80 | 1.06 | 0.08 | 2.88 |
| | Loopseal | 69.46 | 19.62 | 0.52 | 1.44 | 6.00 | 0.95 | 0.10 | 3.42 |

stone from the Tonghae CFB boiler as shown in Table 3. The majority of the black particles consisted of $SiO_2$, $Al_2O_3$ and $Fe_2O_3$. The MgO and $Fe_2O_3$ levels were relatively high, while the level of $Al_2O_3$ was lower than that of other samples. On the other hand, the levels of composition of white particles were typical of fly ash. This suggests that the sand used for bed material and limestone used for reducing the SOx make the black particles of the clinker, which means the sand particles react with limestone and then agglomerate with ash particles.

The XRD data for the fly ash and clinkers are shown in Table 4. The major crystalline phases identified in the FBAC and loopseal clinkers and fly ash were quartz ($SiO_2$) and mullite ($3Al_2O_32SiO_2$).

**Table 4. Mineral phase analysis of the clinkers and the fly ash in the CFB boiler by X-ray diffractometry (XRD)**

| Sample | Major | Minor | Trace |
|---|---|---|---|
| FBAC | Quartz ($SiO_2$) | Mullite ($Al_6Si_3O_{13}$) | Cristobalite |
| Loopseal | Quartz ($SiO_2$) | Mullite | Albite |
| | | | Lime |
| | | | Hematite |
| Fly ash | Quartz ($SiO_2$) | Mullite | Kalsilite |
| | | | Gypsum |
| | | | Microline |

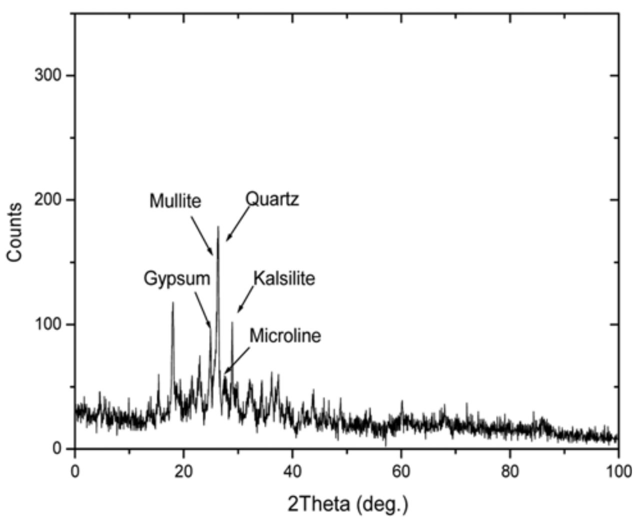



**Fig. 5. XRD spectrum of circulating fluidized bed boiler fly ash.**

A small amount of cristobalite was also detected in the FBAC clinker [8]. This is the high temperature form of quartz, and cristobalite ($SiO_2$) is generally formed with increasing the sintering temperature [9]. Fig. 5 shows the mineral phases of fly ash from CFB. Kalsilite ($KAlSiO_4$),

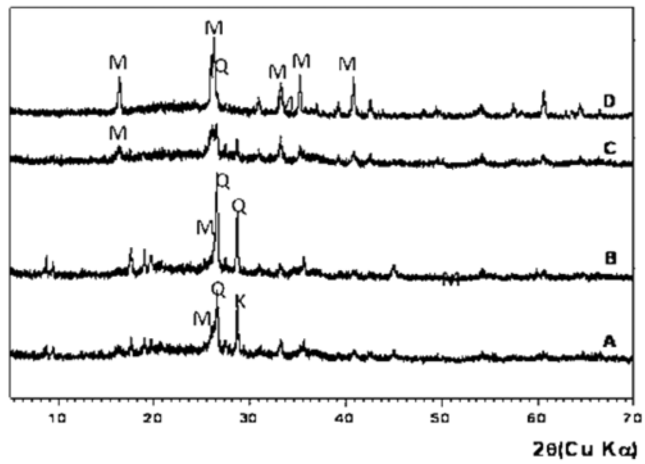



**Fig. 6. XRD spectrum of the fly ash from the CFB boiler (A: 815 °C, B: 900 °C, C: 1,000 °C, D: 1,200 °C, M: Mullite, Q: Quartz, K: Kalsilite).**

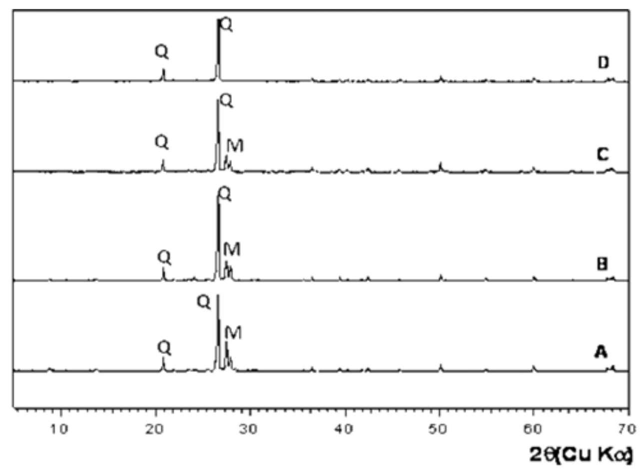



**Fig. 7. XRD spectrum of the sand from the CFB boiler (A: 815 °C, B: 900 °C C: 1,000 °C, D: 1,200 °C, Q: Quartz, M: Microcline).**

**Table 5. Mineral phase analysis of the solid materials in the CFB boiler by X-ray diffractometry (XRD)**

| | Condition | DTA peak (°C) | | Description |
|---|---|---|---|---|
| | | 1st | 2nd | |
| Coal ash | | 999 | - | |
| Sand | | 573 | 1,329 | 573 °C→quartz ($\alpha\rightarrow\beta$)transition |
| Limestone | | 683-768 | - | $CO_2$ decomposition |
| Ash : Sand : Limestone (23 : 15 : 3) | 1,000 °C | 392 | 573 | 390 °C→$Ca(OH)_2$ |
| | 1,200 °C | 392 | 573 | 573 °C→quartz ($\alpha\rightarrow\beta$)transition |
| Ash : Sand (252 : 100) | 1,000 °C | 573 | - | quartz ($\alpha\rightarrow\beta$)transition |
| | 1,200 °C | 573 | - | |
| Ash : Limestone (200 : 16) | 1,000 °C | 389 | - | 390 °C→$Ca(OH)_2$ |
| | 1,200 °C | 392 | - | |
| Sand : Limestone (15 : 3) | | 573, 635-732 | 1,327 | quartz ($\alpha\rightarrow\beta$)transition<br>$CO_2$ decomposition |
| Clinker (White) | FBAC | - | - | The DTA peak of high temperature area is similar to that of ash |
| | Seal pot | - | - | |
| Clinker (Black) | FBAC | 573 | - | 573 °C→quartz ($\alpha\rightarrow\beta$)transition |
| | Seal pot | 573 | - | |

**Table 6. Chemical composition of the fly ash with size fraction by inductively coupled plasma atomic emission spectroscopy (ICP-AES)**

| Size fraction (μm) | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|
| <45 | 46.90 | 32.75 | 4.20 | 5.49 | 0.69 | 0.18 | 5.09 | 1.83 |
| 45-75 | 46.17 | 30.85 | 4.52 | 8.07 | 0.67 | 0.17 | 4.29 | 1.63 |
| 75-100 | 43.50 | 29.59 | 4.40 | 11.56 | 0.69 | 0.16 | 4.43 | 1.49 |
| 100-150 | 46.23 | 32.52 | 3.59 | 7.51 | 0.66 | 0.17 | 4.81 | 1.53 |
| >150 | 49.46 | 33.56 | 3.69 | 3.50 | 0.68 | 0.20 | 4.43 | 1.61 |

gypsum ($CaSO_4$), microline ($KAlSi_3O_8$) were detected in fly ash. These crystal phases are often found at low temperature fly ash.

The characteristics of sand and ash sintered at different temperatures (815 °C, 900 °C, 1,000 °C, 1,200 °C) were investigated to predict the causes of clinker. As indicated in Table 3, the proportion of $SiO_2$ in black parts of clinkers was more than that of white parts of clinkers. High Si content in sand may significantly contribute to glass formation. The XRD data for the sand and ash are shown in Figs. 6 and 7. As shown, the amount of quartz in ash decreased on sintering, whereas quartz in sand increased on sintering. This means that quartz in sand reacts with K, Na, Ca in limestone, ash and sand to form feldspar, which might be the key role of agglomeration [10].

**4. Thermal Analyses of the Solid Materials**

Table 5 shows the thermal analysis results of the ash, sand, limestone, clinkers and the mixed samples of them sintered at 1,000 °C and 1,200 °C with the mixture ratio according to the boiler operating conditions. Sand was observed to exhibit a DTA endothermic event at 573 °C, which is characteristic of the $\alpha\leftrightarrow\beta$ quartz transformation peak. For the limestone, the decomposition peak of $CO_2$ was observed between 683 °C and 768 °C. The mixed specimens (ash, sand, limestone) showed the endothermic peaks at 392 °C and 573 °C, which are characteristics for the formation of $Ca(OH)_2$ and quartz transformation [10]. The quartz peak at 573 °C and decarbonation peak between 635 °C and 732 °C were also observed in the mixed sample of the sand and the limestone. Also, the melting peak was observed at 1,327 °C. The peak patterns of the white clinkers were similar to that of the ash. The black parts showed the $\alpha\leftrightarrow\beta$ quartz transformation peak. This provided the experimental evidence for explaining the causes of clinker formation. The black parts of clinker originated from sand, which is the main effect of clinker formation.

**5. Effect of the Ash Size on the Clinker Formation**

The chemical composition of the ash with particle size distribution is shown in Table 6. The ash particles over 150 μm contained more than 49% $SiO_2$, which means that the larger ash particles contained more quartz than finer ash particles. The ash particles below 100 μm contained more than about 1% $Fe_2O_3$, and over 100 μm have more Ca contents. From this it may be confirmed that the proportion of hematite and CaO to other minerals is much higher in the finer size fraction, especially the size range of 45-100 μm, than

**Table 7. Ash fusion temperature of the fly ash with size fraction by Ash fusion temperature determinator (AFD)**

| Size fraction (μm) | IDT | FT |
|---|---|---|
| <45 | 1333 | 1550 |
| 45-75 | 1307 | 1498 |
| 75-100 | 1301 | 1393 |
| 100-150 | 1305 | 1493 |
| >150 | 1550 | 1550 |

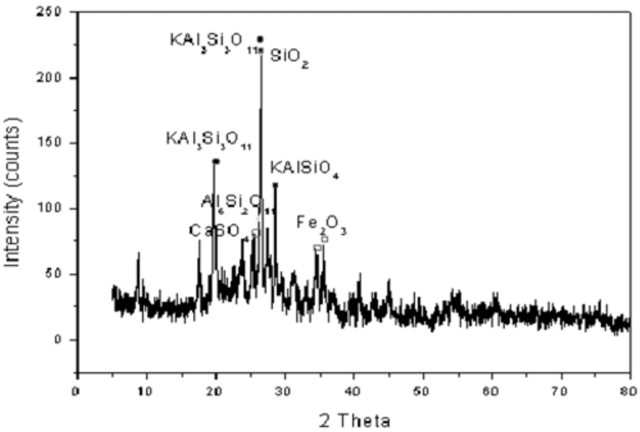



**Fig. 8. XRD patterns of the fly ash (<45 μm ash).**

the coarser ones.

Table 7 also shows the changes of ash fusion temperatures with size fraction. The initial deformation temperature of the ash particles below 150 μm dropped in 200 °C for the ash fractions of larger than 150 μm. Especially, the ash particles between 75-100 μm showed the lowest initial deformation (1,301 °C) and fluid (1,393 °C) temperatures. This result is related to the amounts of fluxing component such as Ca in the ash particles between 75-100 μm as shown in Table 6. The ash particles with higher content of Ca and Fe show the most rapid melting phenomena [11].

The XRD analysis, presented in Fig. 8, indicates that the ash particles below 45 μm show high intensity for hematite. This highlights the importance of the fine ash particles with high Fe content [11].

## CONCLUSION

The causes of clinker formation and the mineral interactions during the commissioning period of the Tonghae CFB boiler were studied. The characteristic of the black clinker particles was more similar to that of the sand used as bed media, and the property of the white clinker particles was more similar to that of the ash. It can be concluded that the causes of the clinker in the FBAC and loopseals were highly related to the particle size and chemical composition of ash. As the results from chemical composition, XRD and SEM, we could predict that ash was sticking to molten or sintered phases in the high temperature regions in the CFB boiler. The composition of the ash changed with the particle size, showing an enrichment of $Fe_2O_3$ as the size of particles decreased. The amount of Fe and Ca has been shown to be concentrated in the finer size fractions of ashes. From this it may be explained that the Fe and Ca bearing minerals acts as a flux playing a key role in the formation of agglomerates. The ash particles below 150 μm in size had low initial deformation temperature, which explained that the finer ash fractions significantly influenced the formation of aluminosilicate bonds in clinker.

Analytical development work presented above can be used to provide insight into the mechanisms of agglomerations and gain a better understanding of physical and chemical processes that produce the clinker in initial operation stage of circulating fluidized bed boiler.

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