# Clinkerization of Portland Cement Raw Meal in the Microwave Processing System

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Three kinds of carbons, natural coal, activated carbon and pet coke were used as susceptors and heating sources, and heating patterns and sintering processes between the microwave fields and the conventional electric furnace were studied. The heating patterns in the microwave fields were different from the electric furnace. The microwave system showed very efficiently to heat 1450$^{o}$C the raw meal and influenced by the kinds of carbons. The microwave heating patterns showed the heating time 1/8 of the electric furnace for activated carbon, 1/4 for pet coke and 1/3 for natural coal. The clinkerizations in the microwave fields were also different from the electric furnace. The crystal sizes of calcium silicates sintered in the microwave system were smaller than those in the electric furnace. The phase transformation from beta form of dicalcium silicate to gamma form was much more occurred during the cooling process in the samples sintered in the microwave system

*Keywords : Microwave processing, Portland cement, Susceptors, Carbon, Petroleum, Clinkerization*

## 1. Introduction

Microwave heating system is very attractive in the chemical compounds manufacturing due to fast heating, less contamination and energy saving process. Therefore, many studies have been carried out on the application of microwave to ceramic materials sintering. [1,2,3]

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Some researches[4,5] were reported on the microwave sintering of Portland cement and clinker minerals. The results showed that the microwave enhanced sintering reaction of clinker minerals due to different clinkerization mechanism from the conventional one and microwave sintering process was faster and caused formation of Alite mineral at lower temperature compared with conventional heating system.

Microwave energy is caused from the interaction between microwave and materials which have dielectric properties. Some ingredients in materials interact with microwave in the electric and magnetic field, which is called as susceptors. Carbon, Silicon carbides, Silicon nitrides and magnetite are well known susceptors. S. Long et al.[6] showed that the iron in the microwave fields enhanced clinkering reaction, resulting in faster sintering process.

In the Portland cement coal and ferrite are generally supplied to raw meal as fuel and ingredient of clinker minerals. The role of coal in the cement manufacturing process is to help calcination of limestone in the preheater and clinkerization in the sintering zone of kiln. In the microwave fields the carbon in the cement clinker meal acts as a susceptor and roles as a heating source.

In the study, three kinds of carbons, natural coal, activated carbon and pet coke were used as susceptors in the industry raw meal of Portland cement, and heating patterns and sintering processes between the microwave fields and the conventional electric furnace were studied.

## 2. Experimental

### 2.1 Raw materials

The raw meal used in the study was industry meal in the cement manufacturing plant. The chemical and mineral compositions are shown in the Table 1. This raw meal is a typical type I Portland cement raw meal. The susceptors such as activated carbon(reagent grade), petroleum coke(by-product of oil refinery) and coal were added to the raw meal in the range from 0 to 15 wt.% shown in the Table 1. The proximate analysis results and chemical compositions of ashes of susceptors are shown in the Table 2 and Table 3, respectively.

Table 1. Formulation of cement clinker of raw meal

(wt.%)

| Chemical compositions | | | | | Modulus* | | | Mineral composition | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | LOI | LSF | SM | IM | $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ |
| 13.92 | 3.16 | 2.19 | 42.05 | 0 | 95.15 | 2.60 | 1.44 | 40.98 | 9.41 | 4.67 | 6.65 |

LSF (Lime saturation factor), SM (Silica modulus), IM (Iron modulus)

Table 2. Results of proximate analysis of three kinds of carbons

(wt.%)

| | Fixed carbon | Volatile matter | Ash | CV(Kcal/Kg) |
|---|---|---|---|---|
| Activated carbon | 100 | | | |
| Petroleum coke | 88.1 | 10.9 | 0.8 | 8,691 |
| Coal | 52.0 | 28.2 | 15.4 | 6,218 |

Table 3. Chemical compositions of ashes of three kinds of carbons.

(wt.%)

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|
| Activated carbon | - | - | - | - | - | - | - | - |
| Petroleum coke | 24.5 | 15.8 | 22.5 | 11.9 | 1.5 | 13.4 | 2.31 | 0.63 |
| Coal | 41.6 | 18.1 | 9.1 | 19.4 | 1.1 | 5.2 | 0.52 | 0.96 |

## 2.2 Sintering setups of microwave and conventional system

Microwave sintering system was reported as elsewhere [7]. The microwave sintering system has 2.45Gz and multimode, and its maximum power intensity is 6kW. The temperature was measured using a pyrometer. The raw meals of cement clinkers were sintered in the insulation package which was reported elsewhere[8] as shown Fig. 1. Electric furnace sintering system was a typically conventional electric furnace with temperature control system up to 1,600 $^{o}$C.

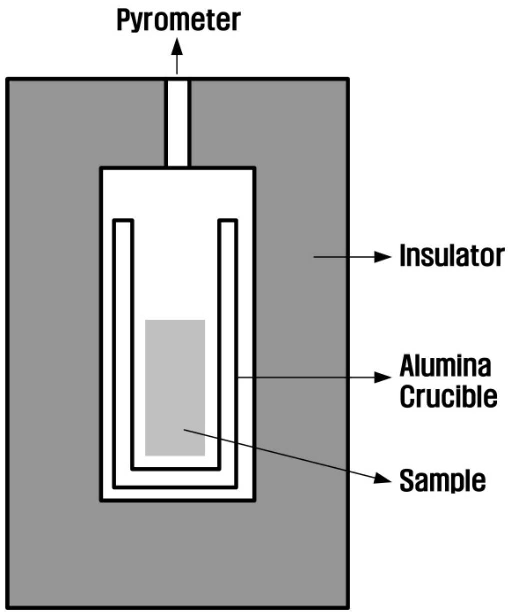



Fig. 1. Insulation package for sintering samples in the microwave sintering system. [8]

2.3 Experimental processing

The three kinds of carbons as susceptors were added to the raw meal ranging from 0 to 15 wt.%. The samples were pelletized with $\phi$ 1 x 0.3 cm. The samples in the microwave sintering system were not heated at 950$^{o}$C for calcinating limestone, but some samples in the conventional sintering system were calcinated at 950$^{o}$C for 10 min. The heating rate in the conventional sintering system was 10$^{o}$C/min. All samples in the both sintering systems were heated at 1,450$^{o}$C for 10 min., and then characterized. The preparations of samples are shown in the Table 4.

Table 4. Preparations of samples in the microwave and conventional sintering systems.

| Systems | Susceptors (wt.%) | | Calcination(min., 950°C) | Sintering(min., 1,450°C) |
|---|---|---|---|---|
| Microwave system | Activated carbon | 5 | 0 | 10 |
| | | 10 | 0 | 10 |
| | | 15 | 0 | 10 |
| | Petroleum coke | 5 | 0 | 10 |
| | | 10 | 0 | 10 |
| | | 15 | 0 | 10 |
| | Coal | 10 | 0 | 10 |
| | | 15 | 0 | 10 |
| Conventional system | None | | 0 | 10 |
| | | | 10 | 10 |

## 3. Results and discussion

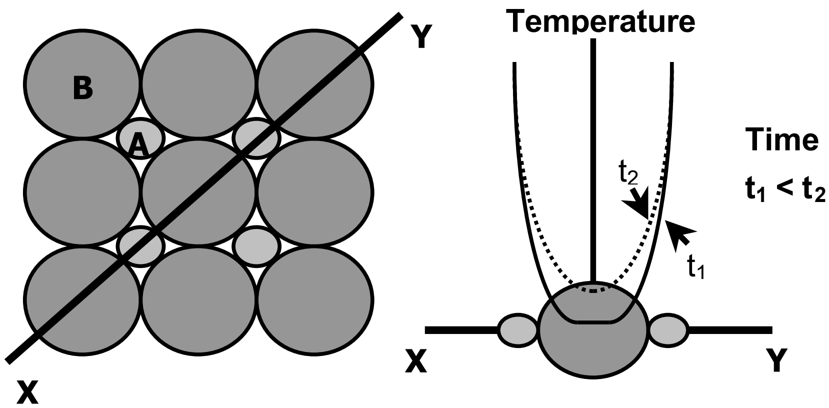
### 3.1 Burning and heating profile

Carbon acts as a susceptor in the microwave system and roles as a heating source as shown in Fig. 2. Upper material is carbon and lower one is raw meal of cement clinker. The carbon interacts with microwave and burns, resulting in raising temperature the carbon itself and then raw meal. Therefore, the temperature gradient between carbon and raw meal occurred in the microwave sintering system. The temperature of this raw meal containing carbon is not uniform inside the sample, which is called anisothermal. This anisothermal sintering process may be explained in Fig. 3.

(A) (B) (C)

(A) susceptor (upper) and raw meal (lower) (B) at beginning stage
(C) at sintering temperature

Fig. 2. Interaction between susceptor microwave and temperature raising phenomena in the microwave fields.




A: susceptor, B: raw meal

Fig. 3. Temperature gradient between susceptor and raw meal

As showing in Fig.3, the carbon interacts with microwave and raises temperature itself, and then increases temperature of raw meal. The temperature gradient between carbon and raw meal occurred and then is getting smaller as increasing temperature with time. Therefore, the carbonation process of the limestone in the raw meal is not necessary.
As the carbon acts as a heating source, the temperature of raw meal increases very fast, compared with the conventional heating system. Fig. 4 shows the heating profiles of three kinds of carbons in the microwave fields and conventional sintering system.

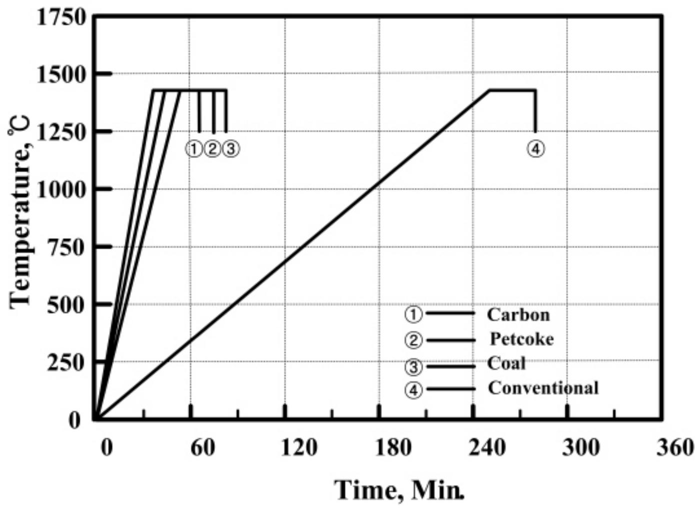


Fig. 4. Heating profiles of three kinds of carbons (10wt.%) in the microwave fields and conventional sintering system.

The intensity of interaction between three kinds of carbons and microwaves is in the increasing order, coal, pet coke and activated carbon. This intensity of interaction is related to the contents of carbon in the three kinds of susceptors. The heating process of the microwave sintering system is very short, compared with the conventional sintering system; the heating time in the microwave system 1/8 of the conventional sintering system for activated carbon, 1/4 for petroleum coke and 1/3 for natural coal

3.2 Clinkerization

Calcination reaction is very important process in the sintering process of cement clinker because the sintering process easily helps form clinker minerals in the sintering zone of the rotary kiln, which significantly influences clinker production amounts. As mentioned above, the calcination process is not needed in the microwave sintering system in the case of existing carbons.
In the study the free CaO contents were measured after sintering samples in order to investigate calcination and clinkerization of the raw meals. Table 5 shows the free CaO contents of samples after sintering at 1,450°C

for 10 min.

The free CaO contents of samples in the microwave systems show very low, especially 0.83 wt.% for 10% of activated carbon, 0.94 wt.% for 10% Pet coke and 2.12 wt.% for 10% coal. In the conventional sintering process 4.71 wt.% CaO was measured in the sample after calcinations and sintering process.

Table 5. Free CaO contents of the samples after sintering at 1,450°C for 10 min.

| Systems | Samples | Calcination at 950 °C (min) | Sintering at 1,450 °C (min) | Free CaO (wt.%) |
|---|---|---|---|---|
| Microwave sintering system | Activated carbon 10% | - | 10 | 0.83 |
| | Pet Coke 10% | - | 10 | 0.94 |
| | Coal 5% | - | 10 | 2.12 |
| | Coal 10% | - | 10 | 1.52 |
| | Coal 15% | - | 10 | 1.21 |
| Conventional sintering system | Controlled | - | | 5.99* |
| | | - | 10 | 4.92 |
| | | 10 | - | 5.41 ** |
| | | 10 | 10 | 4.71 |

* Sample was heated up to the 950°C at 10°C/min

** Sample was heated up to the 1,450°C at 10°C/min

Fig. 5, Fig. 6 and Fig. 7 show X-ray patterns of samples after heating at 950°C according to various kinds of carbon susceptors in the microwave sintering system and samples after calcinating at 950°C for 10 min. in the conventional sintering systems.

The samples sintered in the microwave system show lower contents of free CaO than them in the conventional system. The samples also show that the intermediate mineral phase, $C_{12}A_7$, appear at higher contents of activated carbon and petroleum coke which are intensively interactive with microwaves. The figures indicate that the peak of limestone appear in the samples sintered in the conventional system. The micro sintering system enhances calcination and clinkerization of raw meal, compared with the conventional sintering system even though the heating time is short.

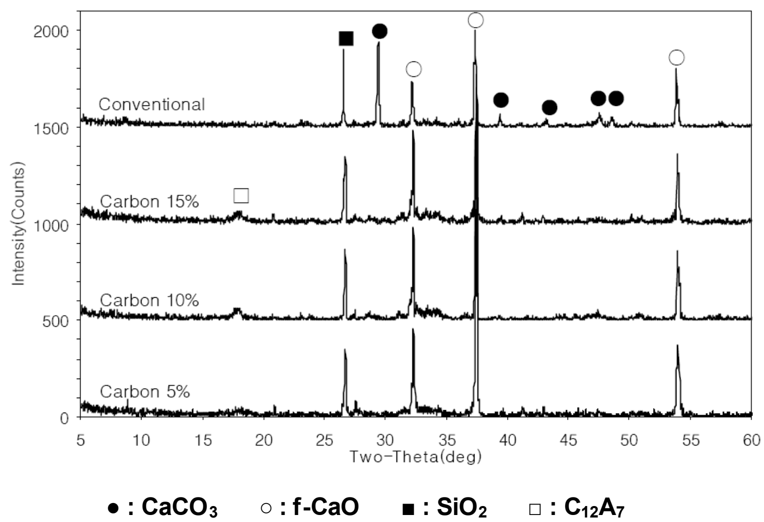



Fig. 5. X-ray patterns of samples containing activated carbon after heating at 950°C, compared with conventional sintered sample at 950 °C for 10 min.

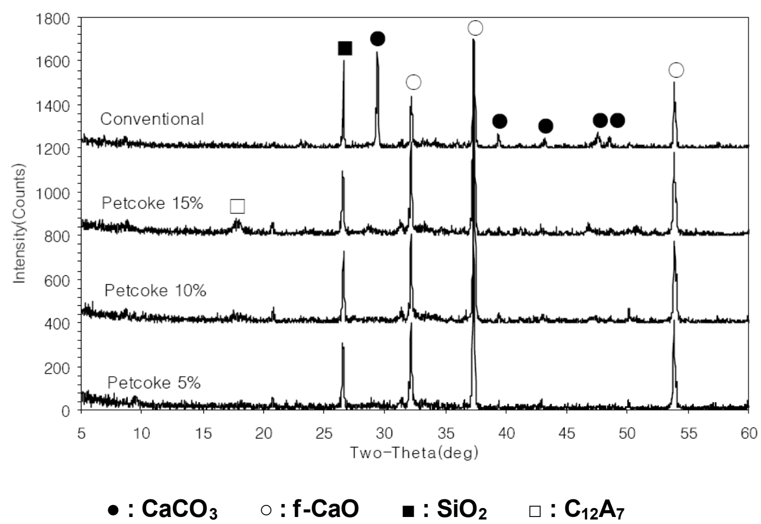
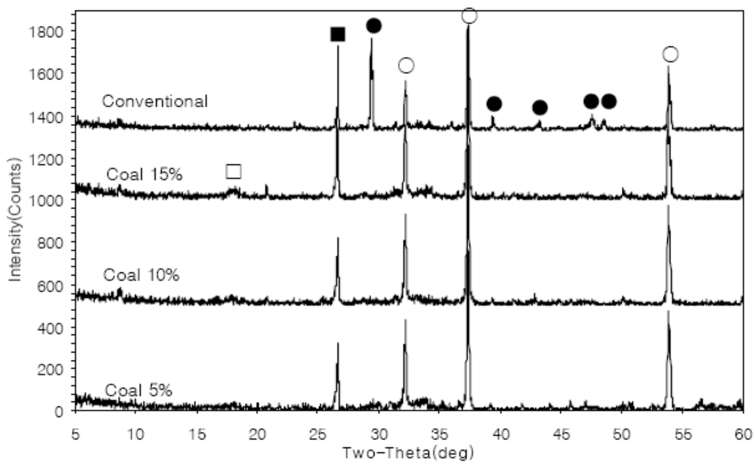
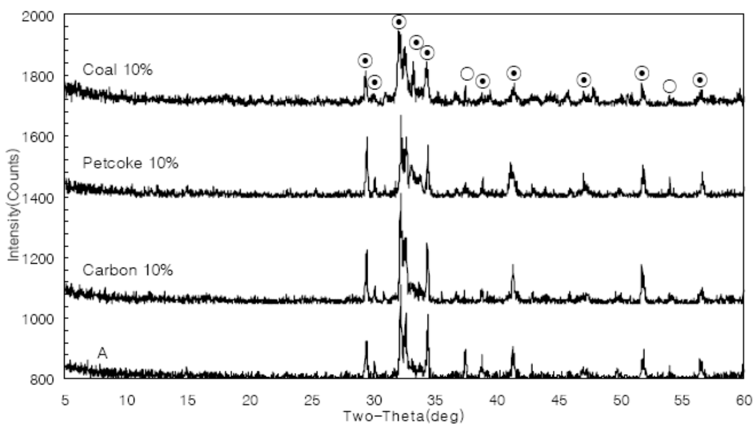



Fig. 6. X-ray patterns of samples containing pet coke after heating at 950°C compared with conventional sintered sample at 950 °C for 10 min.




● : $CaCO_3$ ○ : f-CaO ■ : $SiO_2$ □ : $C_{12}A_7$

Fig. 7. X-ray patterns of samples containing coal after heating at 950°C compared with conventional sintered sample at 950 °C for 10 min.




: $C_3S/C_2S$ ○ : f-CaO

Samples, coal, pet coke, carbon, sintered in the microwave system

Sample,A, sintered in the conventional system

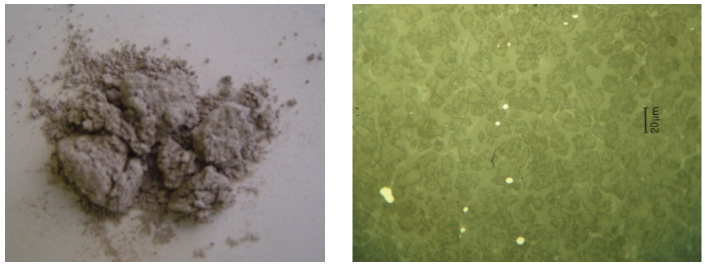
Fig. 8. X-ray patterns of samples containing coal after heating at 950°C compared with conventional sintered sample at 950 °C for 10 min.

Fig. 8 shows X-ray patterns of samples containing 10 wt.% three kinds of susceptors after heating at 1,450°C for 10 min. in the microwave system, compared with samples conventionally sintered at 1,450 °C for 10 min.

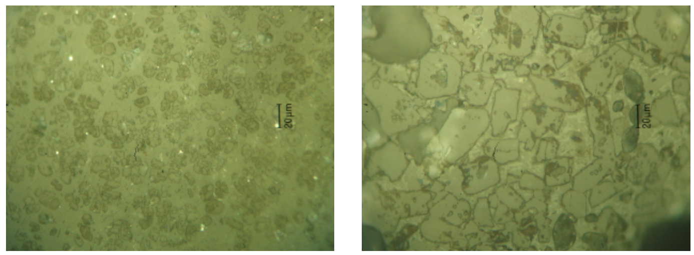
The samples sintered in the microwave system indicated dusting phenomenon during the cooling process in the air.

Fig. 9 shows SEM microscopes of samples sintered in the microwave system and conventional system. All samples show that four major clinker minerals, alite, belite, calcium aluminate and calcium ferroaluminate, were formed regardless of sintering system, but the sizes of calcium silicates are dependent on the sintering system. The samples sintered in the microwave sintering system show very smaller sizes of calcium silicates than those in the conventional sintering system.

Dusting phenomenon was shown in the almost samples sintered in the microwave sintering system. This dusting phenomenon is attributed to stabilization of dicalcium silicate; phase transformation from beta type at high temperature stable form to gamma type at low temperature stable form.[9] For the conventional sintering system dicalcium silicate was created and grown during the heating process which was longer time than the microwave sintering system, and was very well crystallized and stable during the cooling process, even though free CaO exists much in the system. Therefore, no dusting phenomenon was occurred in the conventional sintering system. For the microwave sintering system the dicalcium silicate easily formed due to roles of carbons which raised temperature rapidly, but not enough time for growing the crystal which was stable form, resulting in very fine crystals in the clinker as shown in Fig. 9. So, most of the samples sintered in the microwave sintering system showed phase transformation from beta to gamma type of dicalcium silicate during the cooling process.



(A) Dusting phenomenon (B) 10wt% Pet coke



(C) 10wt .% Coal (D) Conventionally sintered

(A), (B), (C) : samples sintered in the microwave system,

D) : sample sintered in the conventional system

Fig. 9 shows SEM microscopes of samples sintered in the microwave system and conventional system.

## 4. Conclusions

1. Carbon interacts with microwaves and roles as a heating source, and causes anisothermal sintering mechanism in the raw meal.
2. Carbon heated up rapidly in a Microwave field and the microwave system showed very efficiently to heat 1450$^{o}$C the raw meal and influenced by the kinds of carbons.
3. The microwave heating patterns showed the heating time 1/8 of the electric furnace for activated carbon, 1/4 for pet coke and 1/3 for natural coal.
4. The crystal sizes of calcium silicates in the microwave system were smaller than the electric furnace. The phase transformation from beta form of dicalcium silicate to gamma form was much more occurred during the cooling process.

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