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New clinker formation process by the fluidized bed kiln system

Takako Yuko*, Tatsuo Ikabata, Tatsushi Akiyama, Takanori Yamamoto, Norimitsu Kurumada

Cement/Concrete Research Laboratory, Sumitomo Osaka Cement Co., Ltd., 7-1-55 Minamiokajima, Taisho-ku, Osaka 551-0021, Japan

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Abstract

Clinkers produced by the new fluidized bed kiln are different from the commercial rotary kiln clinkers in the formation process and their characteristic qualities. In the granulating unit, the cluster of free CaO that originates in the coarse particles of limestone plays a role as a nucleus and the granulation by the adhesion of fine particles of raw materials follows. The melt phase made from siliceous raw materials encourages adhesion. Clinker minerals are almost completed to form in the granulating unit, and the consumption of free CaO and the grain growth of calcium silicate progresses in the sintering unit.

Keywords: Clinker; Microstructure; Mineralization; Granulation

1. Introduction

A new fluidized bed kiln system for cement clinkers has been developed by Sumitomo Osaka Cement (SOC) and Kawasaki Heavy Industry (KHI). The basic research and development of this system started at KHI, and a fundamental study and some basic tests on granulation and clinkering by using a 2-ton/day bench-scale plant were executed in collaboration with SOC. A pilot plant with the capacity of 20 tons/day was developed in collaboration with the Center for Coal Utilization, Japan (CCUJ). The research and development of the project was a collaboration of CCUJ and the Japan Cement Association (JCA), who funded in a scaled-up plant with a capacity of 200 tons/day. The plant has four vessels instead of the usual rotary kiln and clinker cooler. The spouted bed kiln (SBK) acts as the granulating unit and the fluidized bed kiln (FBK) acts as the sintering unit that replaces the rotary kiln. The fluidized bed quenching cooler (FBQ) and the packed bed cooler (PBC) replace the clinker cooler [1].

One of the most important points of this system is the rapid temperature rise of raw materials in the SBK from approximately 850°C to 1350°C within a few seconds. It is achieved by the highly efficient and homogeneous burning conditions in the fluidized bed. It is impossible to accomplish this by using conventional methods. Clinkers granulate in the SBK and are then sintered in the FBK at almost the same temperature. The temperatures average 1350°C. Therefore, this new type of bed reactor can produce cement clinkers at 100°C lower than conventional cement kilns.

Another important point is the flow of material. The raw materials fed into a rotary kiln are held for an equal amount of time and follow almost the same sintering process. However, in this new system, the raw materials that go through the suspension preheater are dispersed into the SBK homogeneously, and the granulation of the clinker is advanced in succession. Clinkers formed in the SBK are discharged to the FBK. The amount of clinkers discharged from the SBK equals the amount of raw materials blown into the SBK. Therefore, the average holding time in the SBK depends on the amount of raw materials blown into the SBK, and individual clinker particles have various holding times in the SBK. The smaller clinkers are discharged after a short holding time, while the larger ones are kept longer. However, the holding time in the FBK has no effect on the size of clinker.

The average size of the clinker produced by this system is about 2 mm and is much smaller than that of a rotary kiln clinker. The difference is due to the granulating process. The coalescence process in the rotary kilns reported by Petersen [2] does not proceed in this system. In the FBK, granules are separated from each other and are fluidized by a hot air stream through the distributor on the

* Corresponding author. Tel.: +81-6-6556-2260; fax: +81-6-6556-2209.

E-mail address: tyuko@sits.soc.co.jp (T. Yuko).

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bottom of the SBK. The granules in the SBK should grow only by an adhering process of raw materials to the surface of each granule in the kiln.

In this paper, we report a clinker formation process that can operate at lower temperatures than in standard rotary kilns.

2. Outline of the fluidized bed kiln system

The clinker samples characterized in this research were produced by the 200-ton/day test plant. This plant is a scaled up version of the 20-ton/day pilot plant. The schematic diagram of this plant is shown in Fig. 1. A powdered raw mix from the conventional suspension preheater with a precalciner is fed into the SBK by blowers. Clinker granules are formed in the SBK and are successively introduced into the FBK through the chutes. Small particles such as raw meals are blown back into the SBK by the counter-flow of hot air. Clinkers are completely sintered in the FBK and are discharged into the FBQ. In the FBQ, the clinkers are quenched and the heat is recovered. Finally, the clinkers fall into the PBC. The burners are located in the SBK and the FBK.

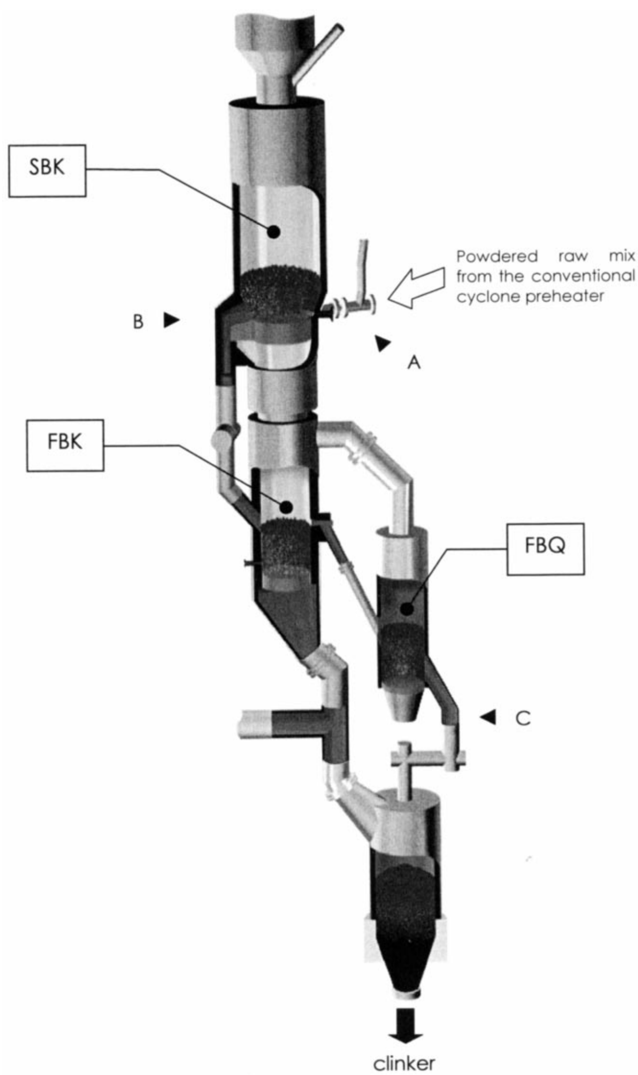

Fig. 1. Schematic diagram of the fluidized bed kiln system. A to C show the sampling points.

Table 1
The chemical compositions of the raw material and the clinkers from the SBK and the FBQ

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
Raw material[a]	21.40	5.57	2.81	65.38	1.95	0.57	0.20	0.83
Clinker from the SBK	21.84	5.32	2.59	64.74	2.00	0.87	0.26	0.74
Clinker from the FBQ	22.07	5.50	2.61	64.89	2.01	0.69	0.22	0.52

3. Production conditions and sampling

The feed rate of raw mix was 10 tons/h that corresponded to 60% of the plant's capacity. The raw mix was carried from a rotary kiln plant; therefore, the chemical composition and fineness were the same as that used in a commercial rotary kiln. Operating temperatures were continuously measured by thermocouples arranged in the plant. Average temperatures were 857°C, 1320°C, 1340°C, and 784°C in the precalciner, SBK, FBK, and FBQ, respectively. The

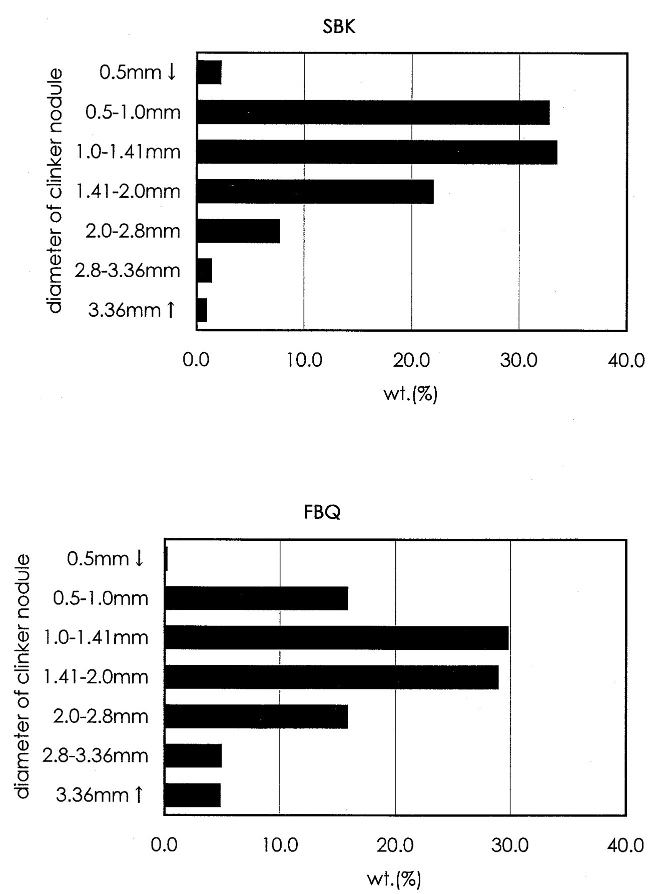

Fig. 2. Clinker size variations.

average holding times were 1.2 h in the SBK and 37 min in the FBK. Samples were simultaneously taken from points A, B, and C in Fig. 1. The raw material was also taken from the feeder at the same time. Table 1 shows the chemical compositions of the raw material and the samples from points B and C.

4. Distribution of components with clinker granule size

Clinkers produced by this system have a characteristically spherical shape of various sizes. Fig. 2 shows the size distribution of clinkers sampled from points B and C in Fig. 1 for the SBK and the FBQ, respectively. The granule size of clinkers produced in this system is about 1–3 mm in diameter. The size depends on the production conditions such as chemical composition of raw mix, burning temperature, and holding time. In previous studies of the rotary kiln, it was shown that the relation between the chemical composition and the clinker size was very useful in estimating the clinker formation mechanism [3]. In the SBK, the clinker size increased with holding time, so the clinker size reflects the holding/reaction time. The composition change with clinker size directly reflects the reaction process. The analysis was carried out by the JIS R 5202 wet method. Results are shown in Figs. 3 and 4.

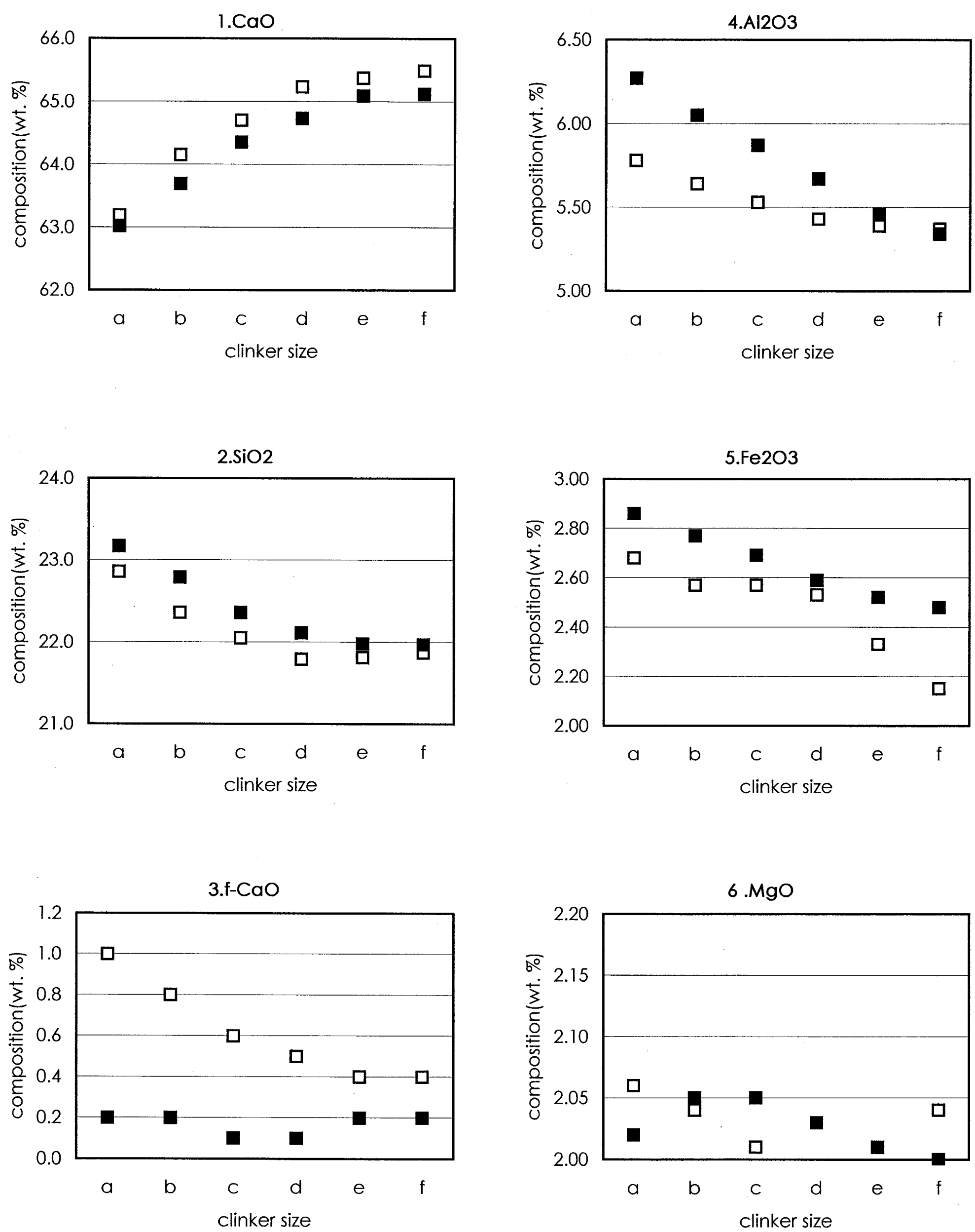

Fig. 3. Chemical composition change with clinker size (1: major elements): (a) 0.5–1.0 mm, (b) 1.0–1.41 mm, (c) 1.41–2.0 mm, (d) 2.0–2.8 mm, (e) 2.8–3.36 mm, (f) >3.36 mm. Open symbol: SBK clinkers and solid symbol: FBQ clinkers.

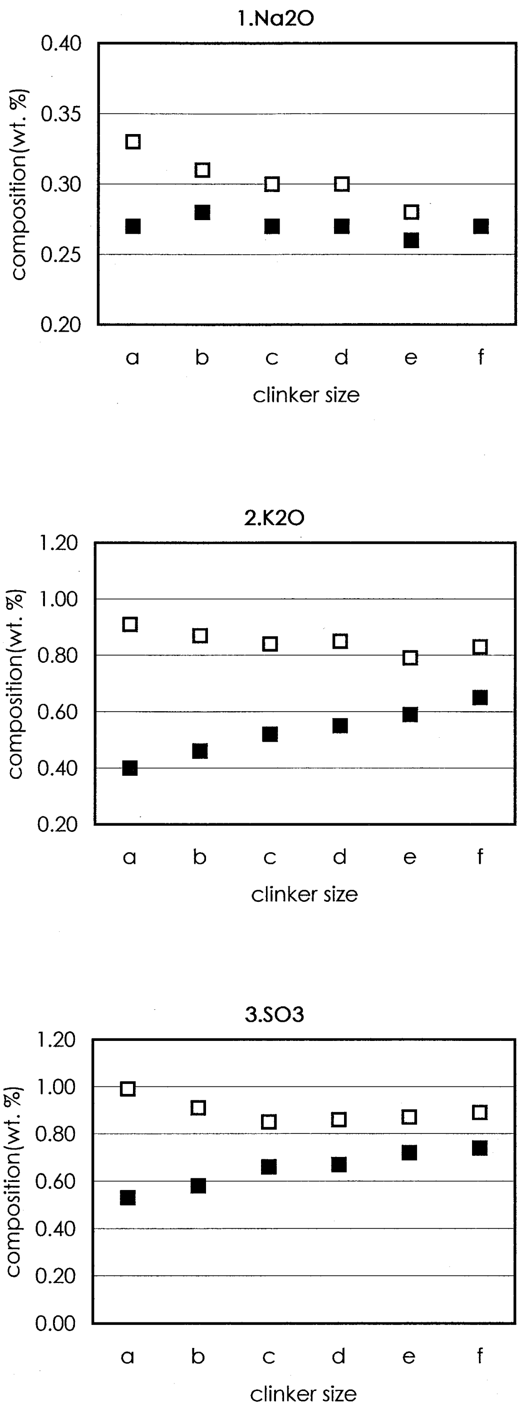

Fig. 4. Chemical composition change with clinker size (2: minor elements): (a) 0.5–1.0 mm, (b) 1.0–1.41 mm, (c) 1.41–2.0 mm, (d) 2.0–2.8 mm, (e) 2.8–3.36 mm, (f) >3.36 mm. Open symbol: SBK clinkers and solid symbol: FBQ clinkers.

4.1. Major elements

CaO content increased and SiO_2 content decreased with the size of the clinker produced by the FBK as shown in Fig. 3, which means that belite is predominant in the smaller granules and alite is predominant in larger ones. The distributional characteristics of calcium silicates will be described later in detail.

The main components of the liquid phase, Al_2O_3 and Fe_2O_3, decreased with clinker size, that suggesting that these components were more predominant in smaller granules and that the nucleation of the granule needs a sufficient quantity of liquid. The same tendency was reported on the rotary kiln clinker, which is caused by enrichment of these components in the periphery of the clinker [3]. However, the tendency was more marked for the fluidized bed kiln. Liquid phase distribution will be described later in detail.

4.2. Minor elements

The changes of the main elements with the clinker size mentioned above were almost the same for the clinkers in the SBK and the FBK. However, the contents of Na_2O, K_2O, and SO_3 were quite different, as shown in Fig. 4, on account of the influence of their volatilization. In the SBK, Na_2O, K_2O, and SO_3 decreased with the increase of the clinker size. In the FBK, Na_2O showed very low content and almost the same amount regardless of the clinker size, but K_2O and SO_3 increased with the clinker size. The amount of each element was always smaller than in the SBK. The volatilization takes place on the surface after the migration of elements from the inside. Therefore, the decrease of the element by volatilization in the inner part of the larger clinkers reduces. Then, the average density of the element increases with the clinker size. On the other hand, Na_2O may have a faster diffusion coefficient than the volatilization rate on the surface.

In the case of MgO, a non-volatile component, no difference depend on the clinker size was produced between the SBK and the FBK.

4.3. Free CaO

The content of free CaO changed from 1.0% to 0.4% with the clinker size in the SBK and was almost constant at 0.2% in the FBK as shown in Fig. 3(3). The clinker size reflects the holding time in the SBK. The inside of the larger clinker was burned for a longer time, so the free CaO decreased. However, in the FBK, the holding time was independent of the clinker size. In the SBK, free CaO mainly remained in the periphery of the clinker for every size and was consumed at the same rate in the FBK. Therefore, the free CaO content of the clinker in the FBK was independent of clinker size.

5. Microstructure of clinker

Fig. 5 shows photomicrographs of clinkers in this system. They have fewer pores and an extremely low occurrence of large pores when compared to clinkers produced in rotary kilns. Clinkers often have belite clusters in the core.

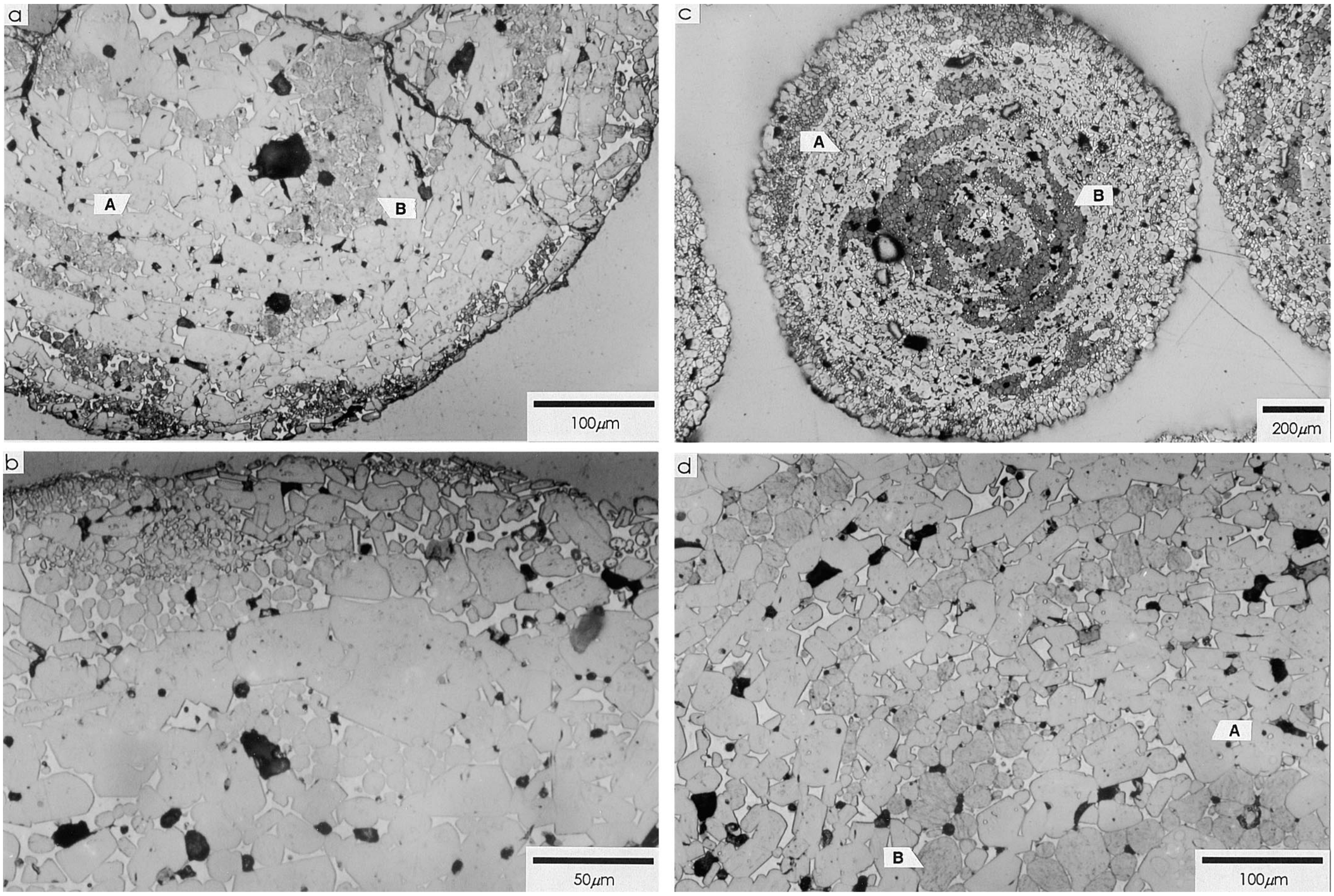

Fig. 5. Photomicrographs of clinkers (A: alite, B: belite). (a,b) Clinker in the SBK. (c,d) Clinker in the FBQ. Alite and belite crystals are arranged in concentric circular. The liquid-rich layer with thickness of 50 μm is shown in the upper part of (c).

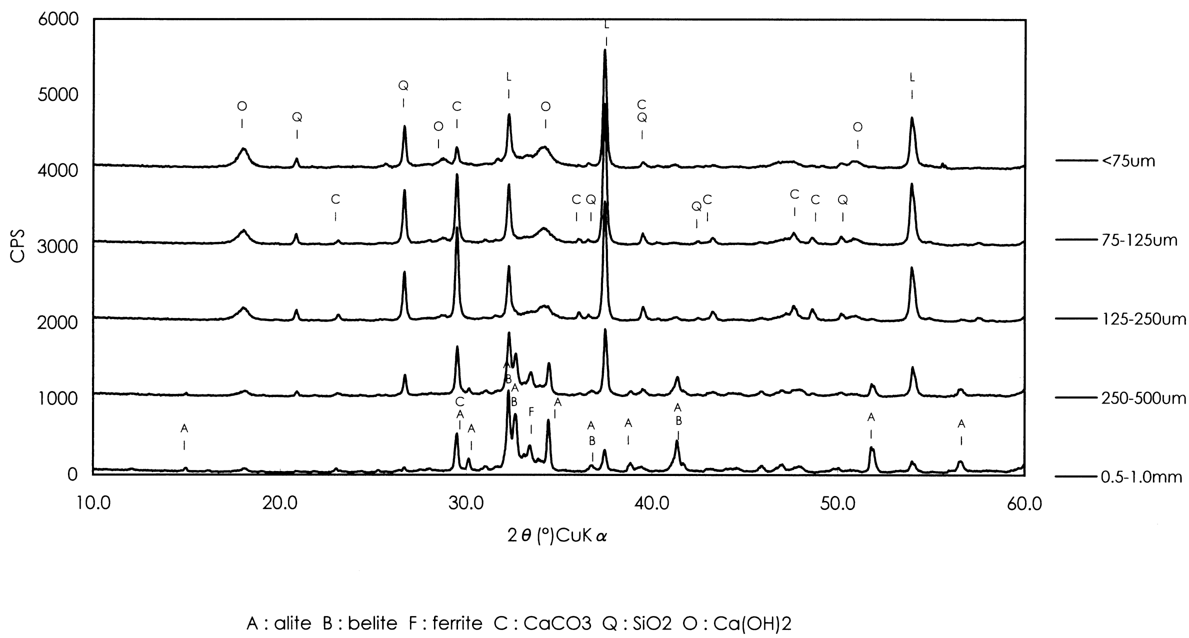

Fig. 6. XRD patterns of sample in the preheater.

Belite also frequently formed a concentric circular cluster in the outer part of clinker, but the amount was less than that of the belite clusters in the core. The sizes of alite and belite in the FBK were slightly larger than in the SBK but were smaller than that of the rotary kiln clinker. This may be due to a lower sintering temperature in the FBK.

Free CaO was mainly observed in the core and periphery, but the FBK clinkers have very little amount of free CaO in the periphery. In the core, they form clusters and have substantial grain size. In the periphery, they have relatively small grain size. Probably these free CaO in the periphery are almost used up in the FBK.

Small clinkers were rich in belite in comparison with large clinkers. This was due to the volume of the outer part that consisted mainly of alite with concentric circular structure increased with the clinker size, suggesting that the siliceous raw materials were consumed in the earlier stage of clinker formation.

Aluminate and ferrite phases are characteristically fine grained in most clinkers. These interstitial phases tend to concentrate on the periphery of clinkers. The thickness of concentrated interstitial phases are almost constant in all sizes of clinkers, and Al and Fe contents decrease with clinker size, as shown in Fig. 3(4) and (5). The concentra-

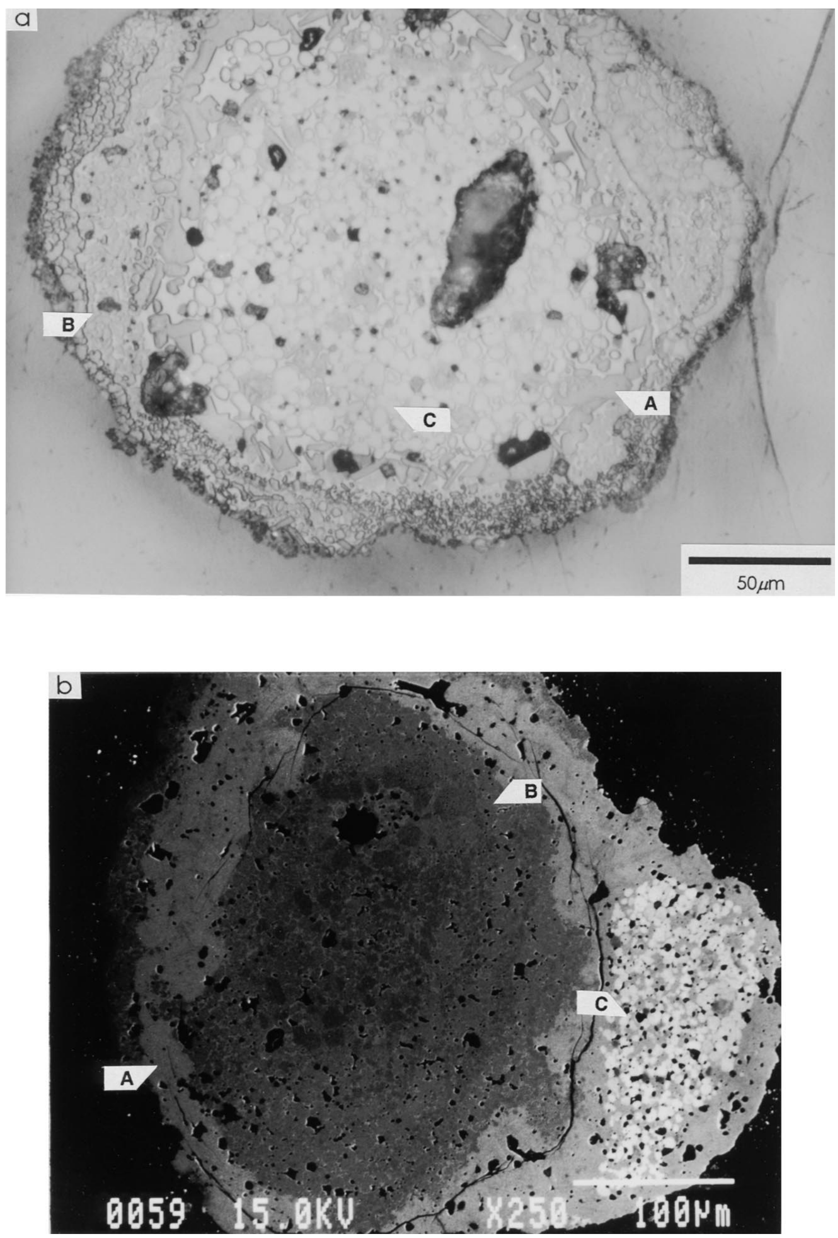

Fig. 7. Photomicrographs of small particles blown up from the SBK (A: alite, B: belite, C: free CaO). (a) Small particle having free CaO cluster in the core (optical photomicrograph: reflected light). (b) Small particle consisted of belite and free CaO clusters covered with alite crystals (back-scattered electron image).

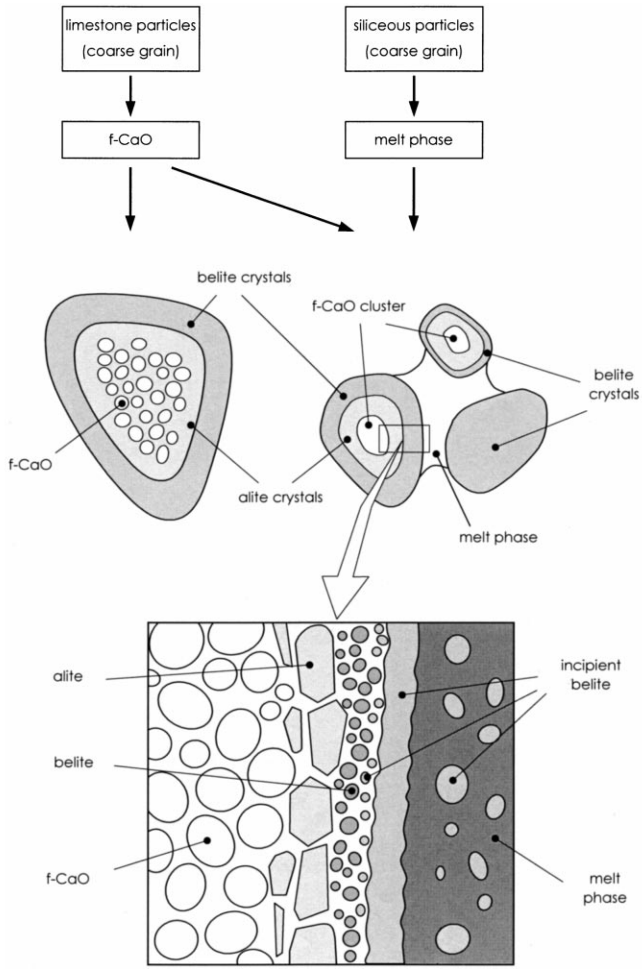

Fig. 8. Schematic model of nucleation process in the FBK system. Nucleation process in the SBK: The coarse particles of limestone change to the free CaO clusters. The siliceous particles melt and adhere on the cluster of the free CaO. Some of these clusters are connected by the siliceous melt. Free CaO and siliceous melt react and form the primary silicates.

tion of interstitial phases in the surface of clinkers probably promotes adhesion of calcareous particles and rapid dissolution of free CaO to form calcium silicates.

As shown in Fig. 5b, clinkers in the SBK were often covered with a liquid-rich layer containing fine calcium silicates and free CaO (underdeveloped minerals) with thicknesses of 10–100 μm independent of the granule size. Inside of the layer, free CaO was not observed and the grain size of the calcium silicates increased suddenly to as large as those of clinkers in the FBK, which shows the rapid reaction to mineralization on the periphery of clinkers. This layer was not observed in the clinkers from the FBK.

6. Speculation of the nucleation process

The nucleation process in the SBK cannot be predicted by the results mentioned above. Because small particles were blown back into the SBK from the discharge chutes by hot air, the sample collected at point B in Fig. 1 contained no particles that showed the beginning of the granulation. It was difficult to take out samples from the SBK directly, but the samples at point A contained small particles blown up from the SBK.

Fig. 6 gives the X-ray powder diffraction patterns of the sample at point A. The peaks of clinker minerals were observed in the particles over 250 μm in size. As the temperature in the preheater was too low to form clinker minerals, they were consequently the particles from the SBK. The cross-sections of these particles were observed by optical and electron microscopes. They mainly consisted of free CaO or belite clusters in the core of the particles covered by other phases, and sometimes a set of these clusters were connected by the melt phase as shown in Fig. 7. The chemical compositions of these melt phases

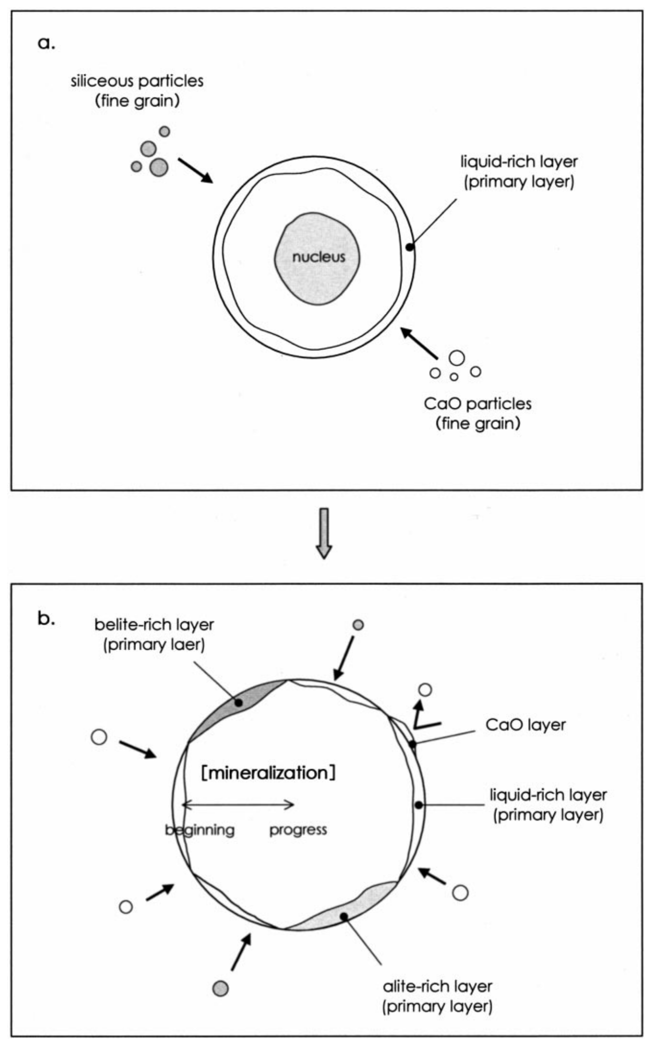

Fig. 9. Schematic model of granulation process in the FBK system. Granulation process in the SBK: The fine particles of raw materials adhere to the surface of the nucleus. However, CaO particles cannot adhere to the already adhered CaO or formed calcium silicates until they are covered with liquid phase. The raw materials react soon and form the primary layer. The mineralization and grain growth of silicates progresses with granulation.

varied, but they were mainly composed of Si, Ca, and Al. A cluster of free CaO was always covered by four layers. The first layer consisted of alite crystals, and the second one consisted of small belite crystals. The third one was incipient belite crystals. These incipient belites had no intracrystalline structure such as lamella and showed very low impurity contents in comparison with ordinary belite crystals. Finally, the outer layer consisted of the melt phase composed of Si, Ca, and Al.

From the results of the X-ray powder diffraction patterns and microscopy, the nucleus of the clinker seems to be about 250 μm in diameter and formed by a free CaO cluster or a set of several free CaO or belite clusters covered by calcium silicates and the melt phase. The outer melt layer plays an important role in increasing the particle size. The newly supplied and dispersed raw materials adhere to the outer layer of the nucleus and change into clinker minerals.

7. Conclusion

Figs. 8 and 9 show the schematic model of the clinker formation process in the fluidized bed kiln system.

After the raw meal is fed into the SBK, the siliceous particles melt immediately and adhere to the clusters of free CaO that originated in the coarse particles of limestone or they cause the adhesion of these clusters. Free CaO and siliceous melt react at once, forming calcium silicate phases at the contact area. At this stage, calcium silicates form as layering around the free CaO cluster in the order of CaO–alite–belite–incipient belite–melt phase as shown in Fig. 8. These particles (over 250 μm in size) act as a primary nucleus for granulation.

Granulation starts with the adhesion of fine particles of raw materials around the primary nucleus. Fig. 9 shows the progress of the granulation of clinkers with liquid-rich layers of 10–100 μm thickness on the surface. Adhered particles immediately become the primary layer that consists of fine calcium silicates and free CaO as shown in Fig. 9b. The advantage of this granulation is the restriction of the thickness of the CaO layer adhering to the clinker surface. If the surface is covered with CaO or produced calcium silicates that have weak adhesion, CaO particles cannot adhere to them. Therefore, the CaO layer is very thin, and the diffusion distance of the calcium ion to the reaction field becomes short. As a consequence, alite and belite clusters make a concentric circular fringe pattern as shown in Fig. 5. After that, mineralization and grain growth of calcium silicates progress with granulation.

After being discharged into the FBK, clinkers are sintered and free CaO is consumed. The grain growth of alite and belite progress a little more.

As mentioned above, in this system, clinker minerals from raw materials are almost completely formed on the periphery of clinkers in the SBK. The reasons for rapid mineralization in lower temperatures are inferred as follows.

1. Rapid temperature rise provides no time for grain growth of free CaO: Fine CaO has a high activation for reaction with silicate.
2. Restriction of the layer thickness of CaO particles adhered to the clinker surface: Diffusion length of Ca^{2+} to the reaction field is short because the thickness is very thin.
3. High concentration of the liquid phase in the periphery of clinkers: This encourages dissolution of free CaO and diffusion of Ca^{2+}.

Acknowledgments

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References

[1] M. Hara, N. Kurumada, I. Hashimoto, T. Watanabe, Development of fluidized bed cement kiln system by scale-up plant. 8th Conference on Coal Utilization Technology, 1998, Japan, pp. 239–253.
[2] I.F. Petersen, A model for the size distribution of rotary kiln cement clinker: Part 1, World Cem Technol 11 (9) (1980) 435–439.
[3] I. Maki, T. Tanioka, T. Hibino, Formation of portland clinker nodules in rotary kilns and fine textures of constituent phases, Il Cem 86 (1) (1989) 3–10.