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Burning and nodulization process of clinker in the rotary kiln as viewed from the fine textures of the constituent minerals

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Abstract

Portland cement clinkers from the rotary kiln vary with their grain size in both chemical compositions and microscopic textures, according to the wide variation in the burning and nodulization environment in the kiln. The dense interior of large clinker nodules, first formed at high heating rates on and near the surface of the moving raw mix mass, is enriched with K_2O and SO_3 and made up from coarse-grained components of the raw mix. The alite crystals consist mostly of the M_3 phase with inclusions in the core. By contrast, the porous exterior, formed inside the mass at lower heating rates and firing temperatures, is less in K_2O and SO_3 content and made up from fine-grained components of the raw mix. The alite crystals are generally zoned with M_1 occurring in the core. Clinker nodules of medium size, similar in both the chemical composition and the fine textures of alite, are formed concurrently with the exterior of large nodules. Fine clinker nodules come from the core of the mass where the radial motion is stagnant and are formed, due to the large temperature gradient in the mass, at low heating rates and firing temperatures. Dust components comprise, besides small fragments of clinkers, separate alite and belite grains in quantity, indicating that they are separated mostly in the quenching cooler from the porous surface layers of the large clinker nodules. K_2O and SO_3, as well as the fine textures of alite, are useful as an indicator of the progress of firing and nodulization in the kiln.

Keywords: Nodulization; Chemical composition; Microscopic texture; M_1; M_3

1. Introduction

In modern cement manufacturing, the clinker nodules from the rotary kiln are characterized by extremely wide range of size distribution from large grains to fine dusts and their chemical compositions and microscopic textures vary systematically with grain size. Large grains show shell structures with compact inner and porous outer parts [1]. The fine textures of alite, subject to change depending on the heating process in the kiln as well as the characteristics of raw mix, are particularly useful to reproduce the processing conditions in the kiln. With increasing firing temperature, the constituent phase of alite changes from M_1 to M_3 and further to T_2 [2,3]. Heating rates both below and above the liquid formation temperature greatly influence the crystal morphology and the phase constitution of alite [2,4]. Minor components in clinker modify the physical properties of the interstitial liquid and thus influence the mode of alite crystallization to a considerable degree [5,6]. Such observations, when combined with the chemical composition and fine texture changes within nodules as well as with clinker size, can provide useful information on the firing and nodulization process in the kiln.

2. Experimental

About 240 kg of Portland cement clinkers from two different plants (A and B) were sampled at the outlet of the quenching cooler and sieved into 11 classes ranging from >30 to <0.15 mm ϕ. Table 1 shows the average chemical compositions of Clinkers A and B. Chemical analysis and

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Table 1
Chemical composition of clinkers used in the experiment

Clinker	Insoluble residue	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5	f-CaO	Total
A	0.07	0.72	22.09	5.35	3.06	66.03	0.96	0.30	0.22	0.58	0.26	0.16	0.12	0.66	100.58
B	–	0.16	22.40	4.95	2.49	66.10	1.91	0.81	0.22	0.28	0.32	0.16	0.12	0.62	99.90

thin section microscopy were made for each class of the clinker nodules. With Clinker A, investigations were made separately for the inner and outer parts of the nodules larger than 15 mm ϕ. The phase constitution of alite (the ratio of M_1/M_3) was determined quantitatively by the point counting technique under the polarizing microscope.

3. Results

3.1. Chemical compositions

Fig. 1 shows the size distribution of the clinker samples, A and B. Clinker A is richer in coarse grain components than Clinker B. Fig. 2 gives the variation of minor components of Clinker A with grain size. Free CaO, K_2O and SO_3 decreased monotonously with decrease in clinker size, while MgO and Na_2O remained almost constant. Clinker B also showed the similar trend.

Fig. 3 shows the variation of SO_3 content, given separately for the inner and outer parts of clinker nodules larger than 15 mm ϕ. The SO_3 contents in the exterior, much less than in the interior, are comparable with those in the nodules of medium size (15–5 mm ϕ). A complete correlation exists, as shown in Fig. 4, between K_2O and SO_3, suggesting their strong affinity in the interstitial liquid.

Figs. 5 and 6 show the variation of Al_2O_3 and Fe_2O_3, respectively. With large clinker nodules, they are slightly richer in the exterior than in the interior. They increase slightly with decreasing clinker size and show broad maxima at around 1.2–0.6 mm ϕ, due probably to the gravitational segregation of clinker particles. Exactly the same trend was observed for Clinker B. The amount of the interstitial material as obtained by treating clinker with salicylic acid in methanol showed the similar trend of change with grain size. A close correlation exists between Al_2O_3 and Fe_2O_3, as shown in Fig. 7, indicating the almost constant A/F ratio regardless of the size and the part of the grains.

MgO is closely correlated with $C_3A + C_4AF$ (r=.958) and gives a broad peak at the same grain size as Al_2O_3 and Fe_2O_3. This indicates that, irrespective of the grain size, the concentration of MgO in the interstitial liquid is kept constant at elevated temperatures. Similarly, the concentration of Na_2O in the interstitial liquid is practically constant. This is in a marked contrast with K_2O, the concentration of which varies widely with grain size.

3.2. Fine textures

Fig. 8 exemplifies the macroscopic textures of large clinker nodules. Clinker A is characterized by the presence of large brownish cores, in which alite crystals are made up mostly of M_3 (Fig. 9a). The crystals usually entrap in the core, interstitial liquid, bubbles and belite crystals, indicative of unstable growth in the early stage of crystal growth. Such part of the crystals with inclusions is generally low in birefringence and consists of M_1. With normal clinker

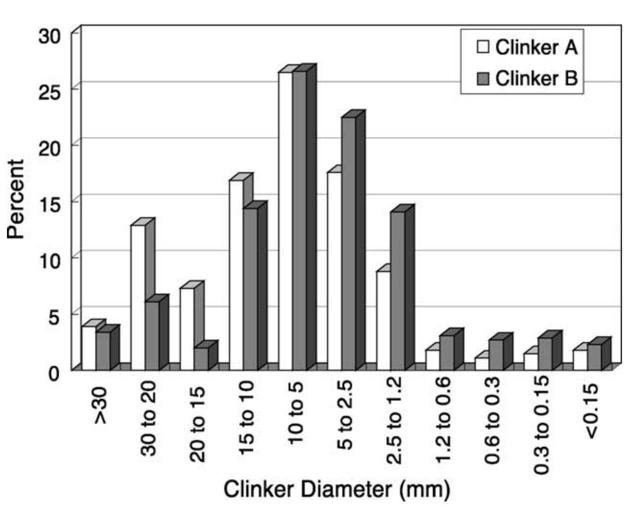


Fig. 1. Size distribution of clinker nodules from the quenching cooler.

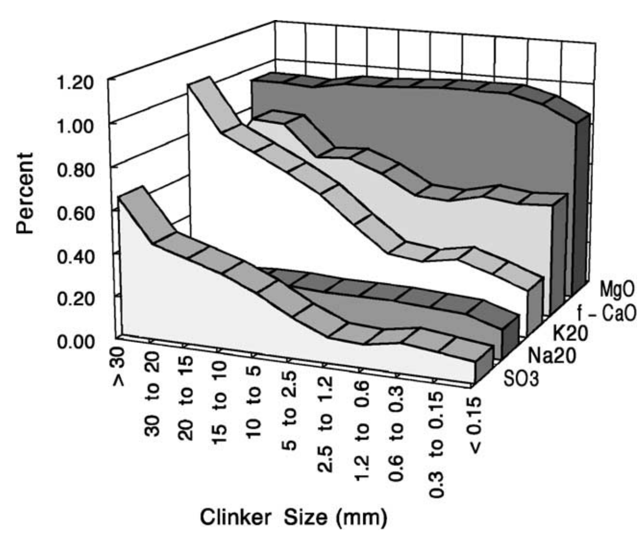


Fig. 2. Variation of minor components with clinker size (Clinker A).

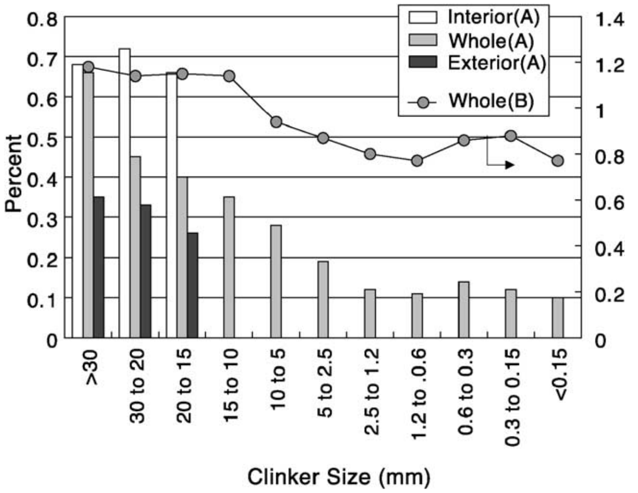


Fig. 3. Variation of SO_3 content in clinker.

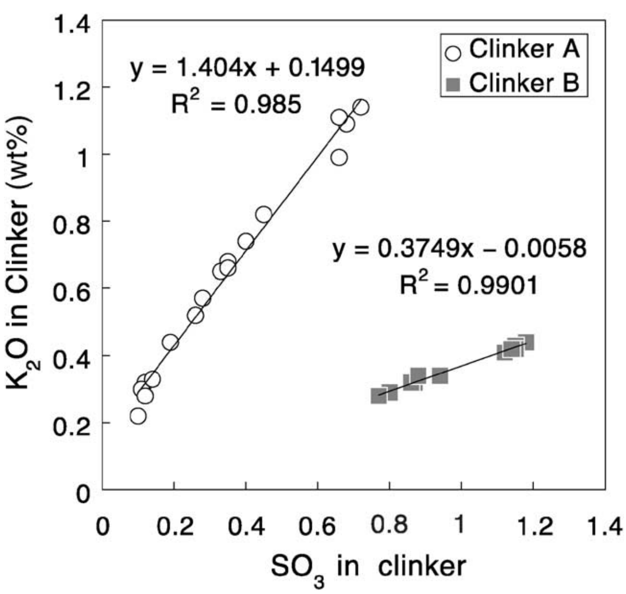


Fig. 4. Relationship between SO_3 and K_2O content in clinker.

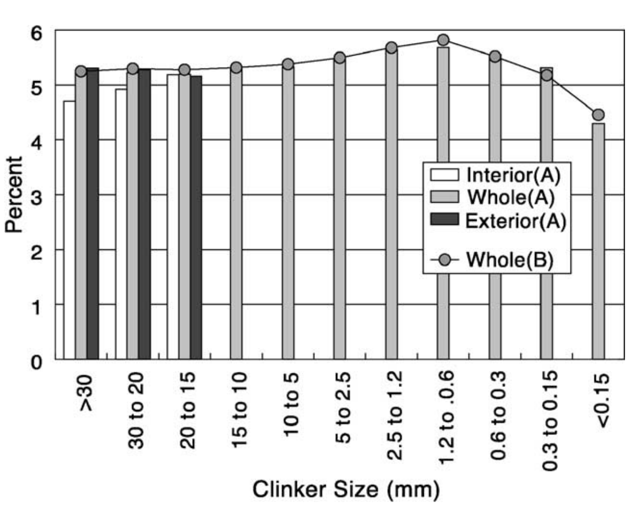


Fig. 5. Variation of Al_2O_3 content in clinker.

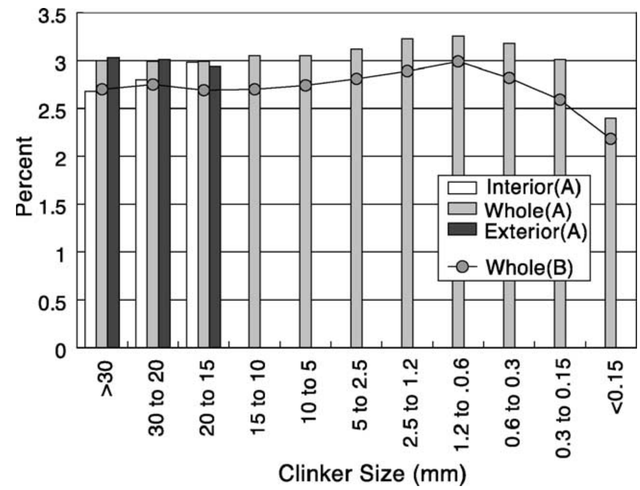


Fig. 6. Variation of Fe_2O_3 content in clinker.

processing, the unstable growth of alite tends to occur under the high concentration of SO_3 and high heating rates [2,4]. In the exterior, the alite crystals are usually zoned with M_3 overgrowing M_1 and they are well faceted and appear smooth in appearance without inclusions (Fig. 9b). Some are composed of M_1 and M_3 mixed in patches. Those crystalline textures indicate that the alite was grown stably throughout under low heating rates and firing temperatures. With Clinker B, the brownish cores are small and scattered throughout the nodule. Table 2 summarizes the textural features of the interior and exterior parts.

As regards the size distribution of alite crystals, the interior is rich in large crystals (Fig. 10), due partly to the size segregation that leads to the concentration of coarse-grained components of the raw mix in the surface layer of the moving mass [1]. However, no appreciable difference was

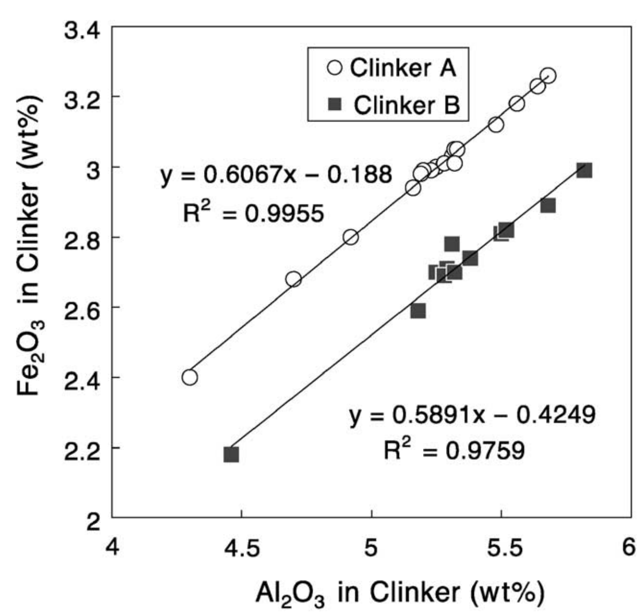
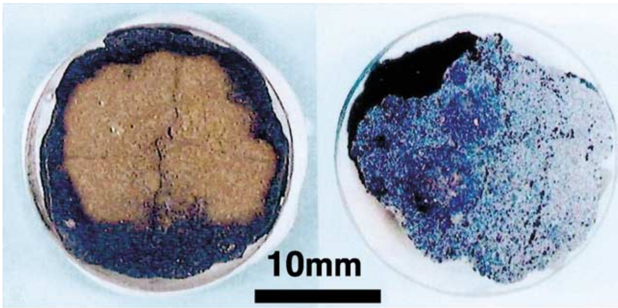


Fig. 7. Relationship between Al_2O_3 and Fe_2O_3 content in clinker.



(a) Clinker A (b) Clinker B

Fig. 8. Section of Clinkers A (a) and B (b) of coarse clinker nodules (30–25 mm ϕ).

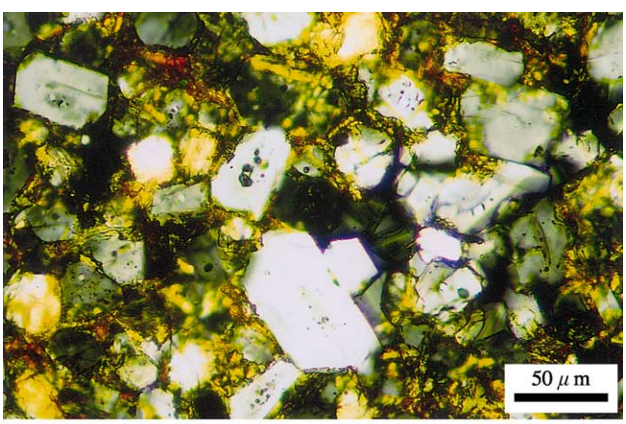
Table 2
The textural features of the interior and exterior parts of clinker

	Textural features	Interior	Exterior
Alite	Constituent phase	$M_1 < M_3$	Zoned
	Inclusions	Abundant (core)	Scarce
	Grain size	Large	Small
	Content	Low	High
Belite	Grain size	Large	Small
	Content	High	Low
	Occurrence	Clustered	Dispersed

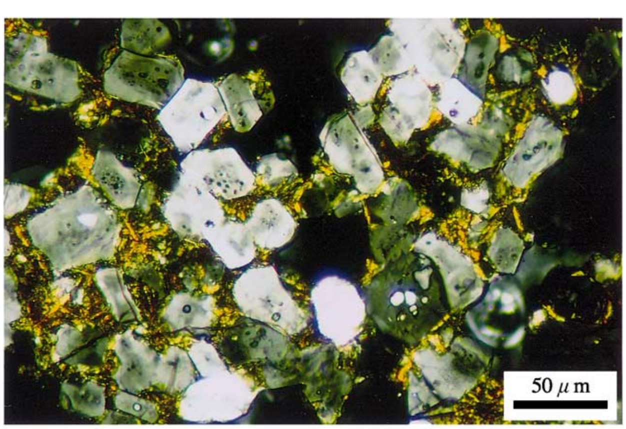
recognized in aspect ratio between the two parts. In the interior, belite crystals form clusters, while in the exterior they are uniformly scattered throughout the grains. This evidences the concentration of coarse quartz grains in the surface layer of the raw mix mass due to the size segregation.

In the clinker nodules of medium size (15–5 mm ϕ), the shape, size and phase constitution of alite are comparable with those in the exterior of large clinker nodules (Fig. 11). Further decrease in clinker size is accompanied by the increase in the ratio of M_1/M_3 with hybrid patchy crystals prevailing over zoned crystals (Fig. 12). This clearly shows that the alite was formed at much lower heating rates and firing temperatures.

The dust components below 0.15 mm ϕ comprise, besides small fragments of clinkers, isolated alite and belite crystals in quantity. Zoned and patchy alite crystals from the



(a) Interior



(b) Exterior

Fig. 9. Alite in the interior (a) and exterior (b) of coarse clinker nodules (20–15 mm ϕ, Clinker A). Transmitted light. Crossed polars.

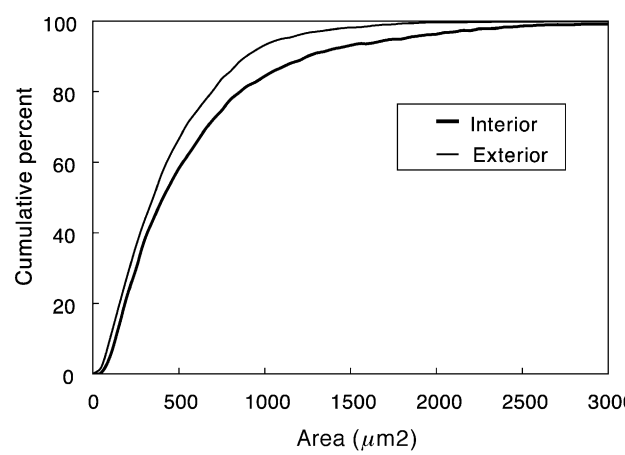


Fig. 10. Grain size distribution of alite for the inner and outer parts of coarse clinker nodules (30–20 mm ϕ, Clinker A). Grain size as represented by area.

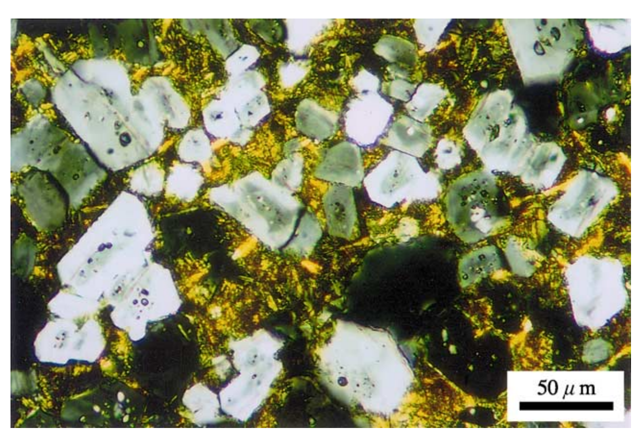


Fig. 11. Alite in clinkers of medium size (15–10 mm ϕ, Clinker A). Transmitted light. Crossed polars.

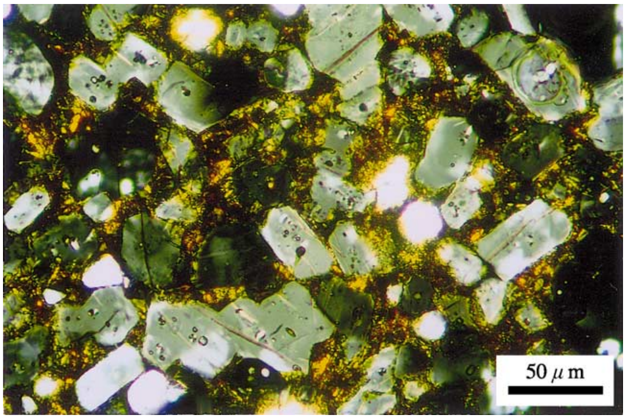


Fig. 12. Alite in fine clinker nodules (1.2–0.6 mm ϕ, Clinker A). Transmitted light. Crossed polars.

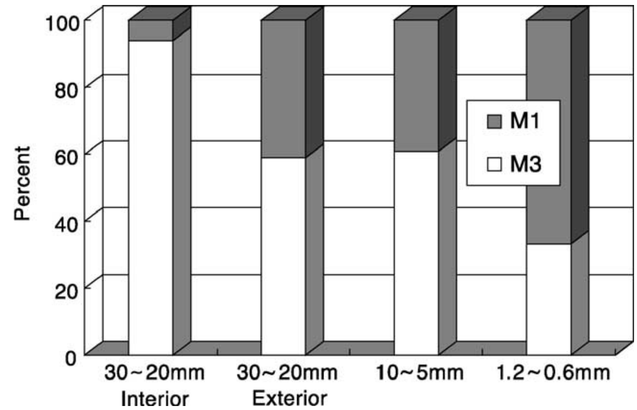


Fig. 14. Proportion of M_1 to M_3 in Clinker A determined by point counting technique.

different stages of clinkering are mixed together (Fig. 13). These observations suggest that the dust components are mostly formed in the quenching cooler separated from the porous surface layers of large clinker nodules.

Fig. 14 shows the quantitative phase constitution of alite obtained by point counting technique. The alite crystals in the core of the large clinker nodules consists mostly of M_3, while those in the exterior are rich in M_1. The M_1/M_3 ratio increases with decreasing grain size. This confirms the results of microscopic observations mentioned above.

4. Discussion

Alkalis and SO_3 in the kiln gas react in the preheater cyclones to form alkali sulfates of low melting points, which encourage the agglomeration of raw materials in the cyclones [7]. The subsequent size segregation in the transition zone of the kiln makes the raw materials enriched with alkali sulfates concentrate on and near the surface the raw mix mass [1], where the precipitation of alite and nodulization start on a large scale on the occurrence of the interstitial liquid in the raw mix. The active radial motion of the raw mix such as cascading and rolling leads to the formation of large nodules, i.e. the interior of large clinker nodules. Thus, the products are rich in alkalis and SO_3.

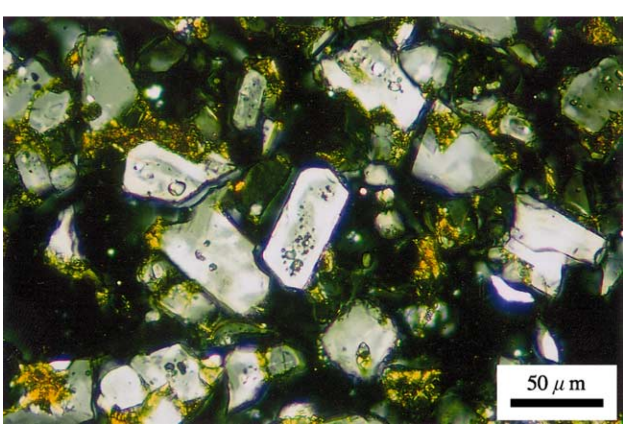


Fig. 13. Dust components (<0.15 mm ϕ, Clinker A). Transmitted light. Crossed polars.

With the axial movement of the mass, clinkering and nodulization proceed toward the inside of the mass low in K_2O and SO_3 content and rich in fine-grained components of the raw mix. The products accumulate thick on the clinker nodules previously formed and constitute the exterior of large clinker nodules.

It is presumable, from the similarities in both the fine textures of alite and the SO_3 concentration in clinker, that the nucleation and growth of medium-sized clinkers occur concurrently with the formation of the exterior of large clinker nodules. Because of the strong temperature gradient within the mass, the medium-sized clinkers are formed under lower heating rates and firing temperatures.

In the core of the mass, the radial motion is stagnant and fine clinker nodules are formed in quantity under much lower heating rates and temperatures. The concentration of both K_2O and SO_3, which decreased monotonously with decrease in clinker size, turned to increase slightly at around 0.6–0.3 mm ϕ. This increase comes presumably from the incorporation of small fragments separated from the surface layers of large clinker nodules rich in K_2O and SO_3 in the quenching cooler. Generally, the grains less than 0.6 mm ϕ were not spherical but irregular in shape. These suggest that the clinker nodules larger than 0.6 mm ϕ were formed exclusively by nodulization. The concentration of K_2O and SO_3, as well as the fine textures of alite, can thus provide a good indicator of the firing and nodulization process in the rotary kiln.

The marked difference in behavior between K_2O and Na_2O can be ascribed to their role in the interstitial liquid. K^+ and SO_4^{2-}, strong in affinity and large in ionic radii as compared with the other corresponding cations and anions, tend to be excluded from the liquid to form a separate liquid phase rich in those components, whereas Na^+, comparable with Ca^{2+} in ionic radius, can remain as a constituent of the interstitial liquid with its concentration kept practically constant.

The textures of Clinker B suggest the short burning zone in the kiln with high heating rates. The nodules initially produced on the surface of the raw mix mass remain small due to the short residence in the burning zone and they are quickly overgrown thick with fine clinker grains formed inside the mass and stick together to give large aggregates, which are consequently weak in bond and porous.

5. Summary

(1) Nodulization begins in the surface layer of the moving raw mix mass where alkalis and SO_3 are most concentrated and rich in coarse components of the raw mix. Clinker nodules formed inside the mass under lower heating rates and firing temperatures constitute the exterior of large clinker nodules.

(2) Medium-sized clinkers are nucleated and grown concurrently with the exterior of large clinker nodules.

(3) Small and fine clinker nodules occur in the core of the moving mass under the conditions of low heating rates and firing temperatures.

(4) Dust components, rich in separated alite and belite crystals, are formed mostly from the weakly sintered surface layers of large clinker nodules.

(5) SO_3 and K_2O decrease monotonously with decreasing clinker size and can be used as an indicator of the progress of firing and nodulization in the kiln.

(6) The concentration of MgO and Na_2O in the interstitial liquid is kept constant irrespective of clinker size.

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