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The effect of cooling rate on the fluidity of mortar made from kiln clinker

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Abstract

The effect of cooling rate on the fluidity of mortar is investigated. This study proposed a model for the early hydration of C_3A In this model, the amount of C_3A hydrated initially is almost proportional to the size of C_3A and the C_3A content. This model explained all the experimental results.

The C_4AF crystallite size calculated by the Rietveld method can be used to measure the cooling rate of clinker. These measurements are consistent with the conventional microscopical method. This method can be a tool to predict the fluidity of mortal.

Keywords: Clinker; Characterization; The Rietveld method; X-Ray diffraction

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1. Introduction

The conditions for producing commercial clinker affect the characteristics of minerals within the clinker. Many researchers including Ono [1,2] and Maki [3] have reported the conditions for producing commercial clinker by focusing on the heating profiles and the content of minor elements. Although qualitative variations in clinker would be expected to affect many properties of cements, so far there are only reports that focus on the semi-quantitative relationship between heating profile and compressive strength [1,2].

The Rietveld method has been widely used for quantitative analysis of mineral compositions of clinker and cement because the accuracy and the handling of the method are suitable for commercial use [4–14]. The relationship between the qualitative change of minerals detected from the XRD profiles and property of cements however has not been analyzed.

This paper focuses on the ferrite phase as it was found that the peak shape of ferrite is the peak that varies with cooling rate [15]. The qualitative relationship between the cooling rate of clinker and the ferrite crystallite size is established. We have evaluated cooling rate using an optical microscope and the ferrite crystallite size was evaluated using the fitted profiles by the Rietveld method. The relationship between cooling rate and the early hydration has been analyzed. The mechanism of causing the relationship has been explained and experimentally verified.

2. Experimental method

2.1. Preparation of samples

To examine the fluidity of mortar, 6 OPC clinkers were chosen from more than 20 clinker samples. These clinkers have systematic cooling rates and C_3A contents. All clinkers were produced in rotary kilns at cement plants. Chemical composition and the mineral composition of each clinker was calculated using the Bogue calculation and is displayed in Tables 1 and 2 respectively.

Cements were prepared in a laboratory mill. To avoid the effect of SO_3 content and of conversion ratio from gypsum to hemihydrate on fluidity of mortar, only gypsum was added to clinker to adjust the total amount of SO_3 content in cement to 2.8%. Blaine's specific surface area of all samples was also adjusted to approximately 3300 cm^2/g.

Furthermore, we examined the relationship between calculated crystallite size of C_4AF and cooling rate of clinker. Clinkers were crushed and sieved to 2–4 mm. They were then heated at 1450 °C for 20 min in an electric furnace followed by

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cooling at a prepared temperature for 20 min in another electric furnace to control the cooling rate.

2.2. Evaluation

Polished samples were prepared for microscopic observation and point-count procedure. Cross sections of the clinkers were prepared. They were polished to 0.3 μm. Following microscopic observation, the clinkers were etched using the appropriate method [16], and then observed. The Point-count procedure was in accordance with ASTM C 1365-98.

Mortar was prepared according to JIS R 5201 (W/C = 0.5, S/C = 3.0). An additive containing Polycarboxylic acid was added at 0.65 wt.% of cement because it accelerates the hydration of C_3A [17,18]. Mortar flow was measured according to JIS A 1171 with mini slump corn. A mortar flow of 5 min and 30 min after mixing was measured. Mortar flow is measured by measuring the diameter of the spreading mortar over a certain time.

Bruker's D8 with high-speed detector was used to gain an X-ray diffraction pattern. The data were collected from 2 theta = 10 to 65°. The step size was 0.008 or 0.13 °/step. The X-Ray tube power was 35 kV–350 mA. The maximum X-Ray peaks counts were from 60,000 to 80,000.

Bruker's TOPAS version 2.1 was used for the Rietveld calculation for the mineral compositions and the crystalline size of C_4AF. TOPAS version 2.1 is software specifically for quantitative Rietveld analysis. It uses the fundamental parameter method for refinement. This method divides a peak width at half height into the machine factor, the microstrain and the crystallite size. The machine parameters were fixed by using the standard X-ray diffraction pattern of NIST LaB_6 crystals. The microstrain was fixed at a suitable value obtained from X-ray pattern fitting. It is assumed that the variation of thermal stress caused by the variation of cooling rates is small.

To calculate the crystallite size of C_4AF, clinkers were treated with salicylic methanol solution. The residues were then measured with D8. This method was used to remove the calcium silicates from the samples to reduce the noise from the crystallite information of C_3A and C_4AF. The finesses of the clinkers before acid solution were unified by controlling the milling time to ensure the finesses of the residues almost the same.

The crystallite size of C_4AF is calculated from the residue of the peak width at half height by TOPAS v2.1 and this reflects the actual crystallite size, the imperfectness of crystallite lattice, the quantity of solute in C_4AF depending on the chemical composition of liquid phase at C_4AF deposition, and the variation of lattice parameters caused by chemical zoning [19,20,21].

To evaluate the effect of the quantity of the hydrated C_3A on the variation of cooling rate of clinker, heat evolution was measured using a conduction calorimeter. The W/C ratio was 0.5 and the A/C ratio was 0.65 wt.%.

Table 1
Chemical composition of clinkers fired in rotary kiln (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
1	21.1	6.0	3.4	66.1	1.0	0.5	0.3	0.3
2	22.1	5.7	3.1	65.9	1.0	0.5	0.3	0.4
3	20.3	6.5	4.1	66.6	1.0	0.3	0.3	0.3
4	19.2	7.0	4.1	64.3	1.6	0.9	0.4	0.5
5	20.5	6.1	3.7	65.0	1.5	0.8	0.3	0.4
6	20.0	7.0	4.1	64.9	1.4	0.5	0.3	0.5

Measured with XRF by calibration line method for glass beads.

Table 2
Potential of mineral compositions of the clinkers calculated using the Bogue calculation (wt.%)

	Bogue calculation			
	C_3S	C_2S	C_3A	C_4AF
1	63.2	13.0	10.1	10.5
2	57.9	19.6	9.8	9.5
3	66.9	7.8	10.4	12.5
4	62.8	7.6	11.6	12.6
5	62.3	11.8	9.9	11.4
6	59.5	12.5	11.4	12.6

For the Bogue calculation, the compositions in Table 1 were used.

3. Results and discussion

3.1. Phase compositions

Clinker phase composition calculated using the Rietveld method and the difference between the compositions calculated using the Bogue calculation for 6 clinker types are shown in Table 3. C_3A and C_4AF contents measured by the Rietveld method tend to underestimate and overestimate those by the Bogue calculation, respectively. This is mainly caused due to the variation of the cooling rates in clinker. The ferrite phase is composed of a continuous solid solution of C_4AF–C_6A_2F. Commercial clinker is composed of a solid solution in between that of the ferrite phase. As the cooling rates of the clinker increase, the chemical compositions shift toward C_6A_2F, and the C_3A contents decrease [22]. In addition, the solid solution of MgO and alkali may change the amount of the interstitial phase [23,24]. It is expected that the MgO contents will vary by about 0.5%, scarcely changing the interstitial phase contents [24]. Similarly, the effect of alkali is small due to the small variation in alkali contents in these clinkers.

In the following discussion, the phase compositions of clinker are based on the results of the Rietveld calculation. The phase compositions calculated by the Rietveld method and the Point-count procedure was consistent within the point-count deviation.

3.2. Effect of the cooling rate on mortar flow

The effect of C_3A content on fluidity of mortar is shown in Fig. 1. C_3A content and the fluidity of mortar usually show a strong correlation, but this figure does not show such a strong correlation. In general, the fluidity of mortar is effected by various characteristics of cement. For example, phase composition, minor minerals (alkali compounds or periclase or free

Table 3
Phase compositions of the clinker calculated using the Rietveld calculation and the difference in the values compared to those calculated using the Bogue calculation (wt.%)

	The Rietveld method				Δ (Bogue–Rieveld)			
	C_3S	C_2S	C_3A	C_4AF	C_3S	C_2S	C_3A	C_4AF
1	64.8	13.3	9.8	11.3	−1.6	−0.3	0.3	−0.8
2	57.6	21.7	10.0	9.9	0.3	−2.0	−0.2	−0.4
3	68.9	6.1	10.4	13.8	−1.9	1.7	0.0	−1.3
4	64.7	9.9	10.2	14.7	−1.9	−2.2	1.5	−2.0
5	65.2	12.6	7.3	14.0	−2.9	−0.8	2.6	−2.7
6	59.8	14.8	9.3	14.7	−0.3	−2.4	2.1	−2.1

lime), containing gypsum and hemihydrate, fineness, type of additive, etc. We carefully controlled the finishing process to unify these factors except for the variable of C_3A content. Microscopical observation was conducted on the clinker.

The microstructure of interstitial phase of Clinkers 1, 3, and 4 are shown in Fig. 2. Clinker 1 shows a fine structure matrix of minute aluminate and ferrite indicating rapid cooling [16]. In contrast, Clinker 4 shows a coarse structure matrix indicating slow cooling [16], and Clinker 3′s structure is in between 1 and 4. That is to say, the cooling rate of Clinkers 1, 3, and 4 qualitatively changes rapidly, intermediately, and slowly respectively.

With both Figs. 1 and 2 in mind, a model of early hydration is proposed.

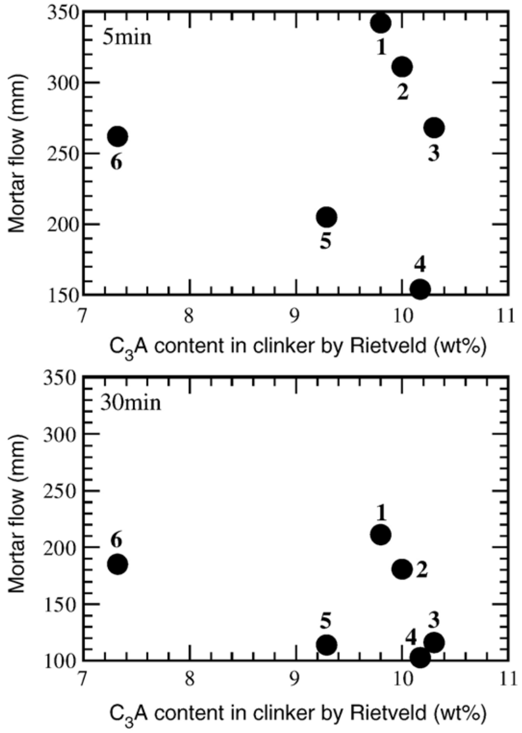

Fig. 1. Effect of C_3A content in kiln clinker on the fluidity of mortar. The number symbols correspond to the sample numbers in Tables 1, 2, and 3.

3.3. Model of early hydration

To explain the deviation in Fig. 1, we propose a simple model of early hydration of C_3A, as shown in Fig. 3. This model assumes the relationship between microtexture of the interstitial phase of clinkers and its early hydration are connected to the fluidity of mortar. To simplify the model, slowing of C_3A hydration by ettringite formation [25] and possible effects of solid solution of minor elements, such as SiO_2, on the reactivity of C_3A [26] are not considered in the model.

The model assumes following two phenomena. One is that C_3A particles are consumed until the reacting interface reaches

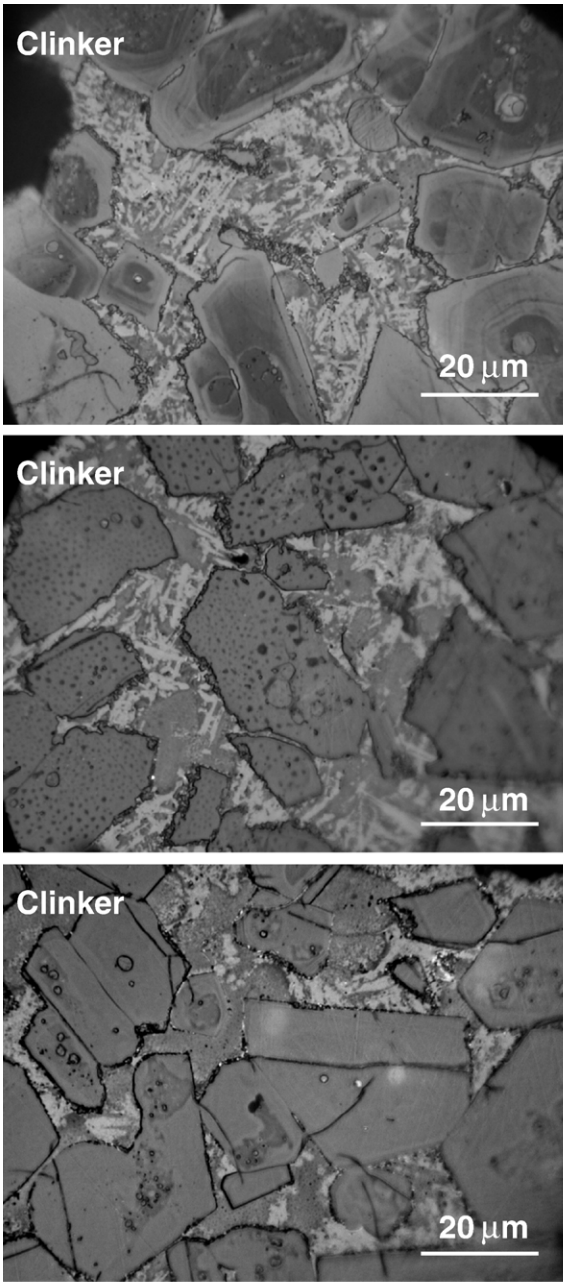

Fig. 2. Microtexture of clinker 1, 3, and 4. The dark and bright parts of interstitial phase are C_3A and ferrite phases, respectively.

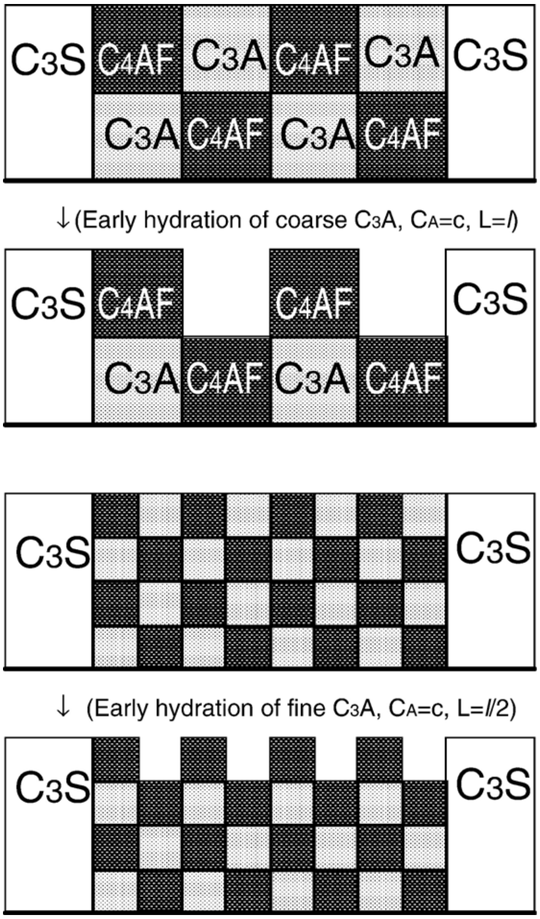

Fig. 3. Schematic model for the early hydration of C_3A: effect of C_3A grain size on the amount of hydrated C_3A.

another phase such as C_4AF. The other is that C_3A and C_4AF particles are almost same size because they precipitate as an eutectic texture. The latter assumption is represented by the following equation:

$$L_c = L_f \tag{1}$$

where, L_c is the average size of C_3A; L_f is the average size of C_4AF.

The volume of the reacting C_3A (R_V) is obtained by the following equation:

$$R_V = aC_AL_c \tag{2}$$

where, a is the specific surface area of cement; C_A is a proportion of C_3A surface area to cement.

The volume fraction of C_3A (C_V) is equal to C_A despite the shapes and quantity of particles.

$$C_A = C_V \tag{3}$$

Eqs. (2) and (3) lead to (4).

$$R_V = aC_VL_c \tag{4}$$

The total weight of initially hydrated C_3A (R_W) is obtained by the following equation:

$$R_W = dR_V \tag{5}$$

where, d is the density of C_3A.

The weight fraction of C_3A (C_W) to whole cement is obtained by the following equation:

$$C_W = kC_V \tag{6}$$

where, k is the conversion factor between the volume fraction to the weight fraction. So k is a function of densities and contents of C_3A minerals. The differences between densities among C_3A minerals are small which is indicated by the small variation of the chemical and phase compositions in this study (See Table 3). Therefore the variation of k is small.

Eqs. (4), (5) and (6) lead to (7).

$$R_W = ad/kC_WL_c \tag{7}$$

Together with Eqs. (1) and (7), conclusive Eq. (8) is determined.

$$R_W = ad/kC_WL_f \tag{8}$$

Therefore, this model indicates the weight of C_3A hydrated initially in the cement paste (R_W) and is almost proportional to the size of the C_4AF particles (L_f) and the weight fraction of C_3A (C_W).

Eq. (8) explains the deviations in Fig. 1 qualitatively. Rapid cooling causes a fine texture in the interstitial phase. Eq. (8) suggests the amount of reactive C_3A within the fine texture is relatively small.

3.4. Semiquantification of the cooling rate

In this section, experimental tests were conducted to establish the semi-quantitative measurements of cooling rate using the Rietveld method.

The Rietveld method can calculate various parameters. These are scale factor, lattice parameters, atom position, crystallite size, lattice strain, preferred mineral orientation, etc. The method fits the theoretical profile to the measured profile by calculating parameters. Some parameters should be fixed at suitable values because there are correlations among the parameters. Strong correlations indicate too many parameters to account for the calculated charts. In this study, we selected independent parameters for fitting. All the correlation coefficients were smaller than 70%.

Among the previously mentioned factors, crystallite size is an available measurement of the cooling rate of clinker. Rapid cooling caused small C_4AF crystallite size as shown in Fig. 4. (In this figure, the low and high cooling temperatures indicate rapid and slow cooling as described in the Section 2.1.) Slow cooling rate caused large crystallite size.

Calculated crystallite size can use as a semi-quantitative measure for cooling rate, also observed by optical microscope as shown in Fig. 5. Slow cooling causes coarse texture of the

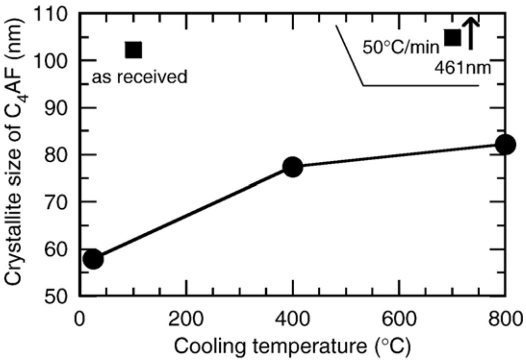

Fig. 4. Effect of cooling rate of clinker on calculated C_4AF crystallite size. Kiln clinker is reheated and cooled at shown temperatures with an electric furnace. Silicates in clinker were removed with salicylic acid methanol solution.

interstitial phaseand rapid cooling causes a fine texture in the phase. [16]

Crystallite size increases as cooling rate slows. This is mainly caused by the following reasons. C_4AF is able to grow over a long period of time, solid solubility of Al_2O_3, SiO_2 and MgO decreases and chemical zoning of C_4AF tends to disappear.

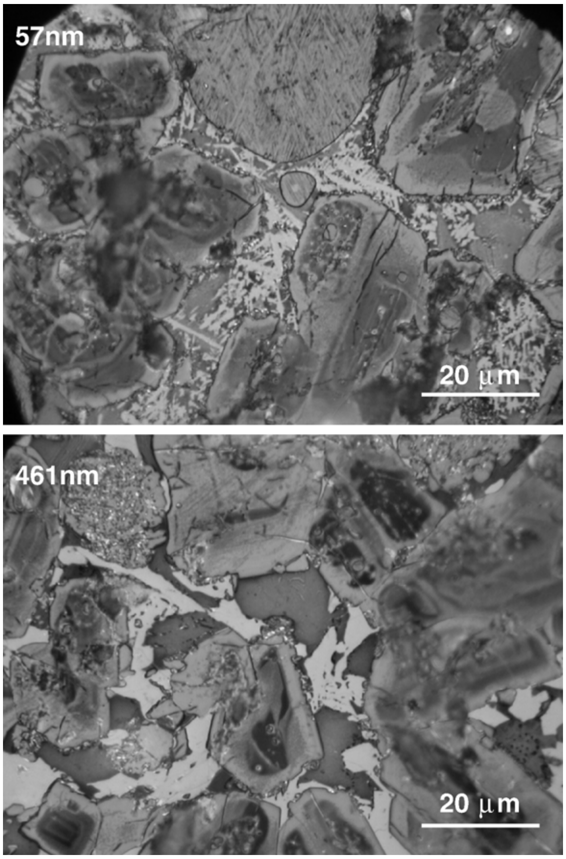

Fig. 5. Photomicrographs indicating the effect of cooling rate on the microstructure of the interstitial phase in clinkers corresponding with Fig. 4. Figures of upper left of each photo indicate the calculated C_4AF crystallite size of C_4AF. The clinker was polished and etched with Nital for silicates, and with KOH water solution for C_3A.

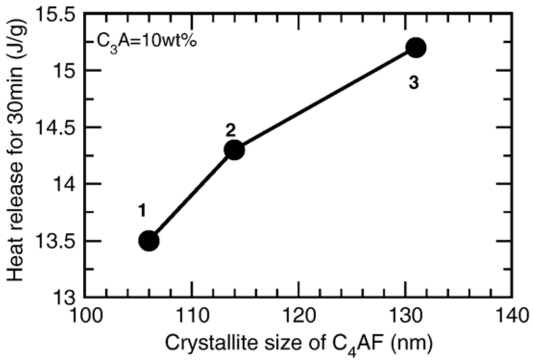

Fig. 6. Effect of cooling rate on heat release over 30 min. after the mixing of cement pastes made from the clinkers corresponding to Table 1. The weight ratios of materials in cement pasts: W/C and PA/C were 0.5 and 0.65%, respectively.

3.5. Effect of cooling rate on heat evolution and the fluidity of mortar

(As mentioned in the previous section, the calculated C_4AF crystallite size can be a useful measurement for the cooling rates of clinker. Also, the model mentioned in the Section 3.3 was verified.)

Fig. 6 shows heat evolution in clinker increases with decreasing cooling rate. The C_3A contents in all clinkers used in this test were approximately the same (=10 wt.%). This result indicates that the calculated C_4AF crystallite size is strongly associated with the initial heat released in cement pastes where the initial C_3A contents was the same in each clinker. This supports the model in Section 3.3 and Eq. (8).

The fluidity of mortar increases as cooling rate increases, shown in Fig. 7. This test also used the clinkers where the C_3A contents were approximately the same. These results strongly indicate that the fluidity of mortar has a negative correlation with calculated crystallite size, also interpreted in the same model. The coarse texture of the interstitial phase accelerates the initial hydration and lowers the fluidity of mortar.

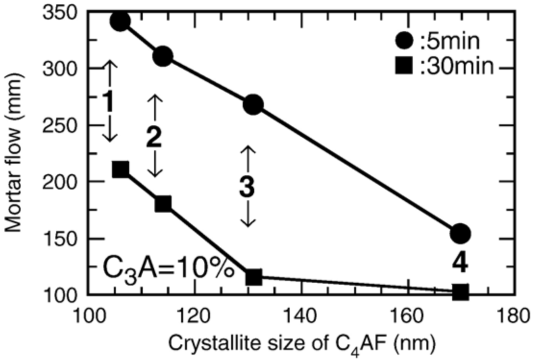

Fig. 7. Effect of cooling rate on fluidity of mortar made from the clinkers corresponding to Table 1. The Fluidity was evaluated by the diameter of spreading mortar. The weight ratios of materials in mortar: W/C, S/C, and PA/C were 0.5, 3, and 0.65%, respectively.

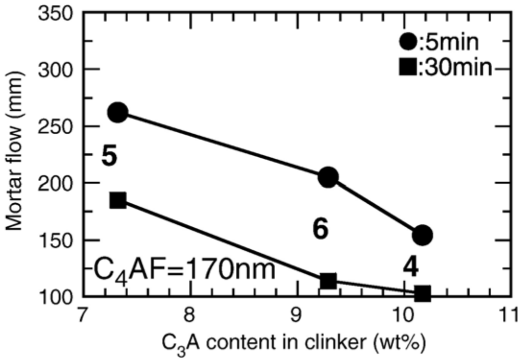

Fig. 8. Effect of C_3A content in kiln clinker on fluidity of mortar made from the clinkers corresponding to Table 1. The Fluidity was evaluated by the diameter of spreading mortar. The weight ratios of materials in mortar: W/C, S/C, and PA/C were 0.5, 3, and 0.65%, respectively.

In addition, C_3A content and the fluidity of mortar indicates a negative correlation as shown in Fig. 8. Calculated C_4AF crystallite size is approximately the same (=170 nm).

The Eq. (8) provides a complete explanation of Figs. 6, 7, and 8. An increase in cooling rate causes a decrease in the amount of C_3A initially hydrated. As shown in Fig. 2, the microscopic C_3A grain size decreases with an increase in the cooling rate of clinkers. Therefore, the initial heat flow decreases with increasing cooling rate as shown in Fig. 6. The mortar flow is improved with a decrease in reacting C_3A and the formation of ettringite as shown in Fig. 7. Similarly, the decrease in reacting C_3A and formation of ettringite caused by the low content of C_3A in cement improves mortar flow, shown in Fig. 8.

4. Conclusion

This study proposed a model for the early hydration of C_3A. In this model, the amount of C_3A hydrated initially is almost proportional to the size of C_3A and the C_3A content. The size of C_3A was substituted by C_4AF.

This model then is able to explain all the experimental results. Heat evolution decreased with an increase in cooling rate. Fluidity of mortar increased with increasing cooling rate and with decreasing C_3A content.

The C_4AF crystallite size calculated by the Rietveld method can be used to measure the cooling rate of clinker. These measurements are consistent with the conventional microscopical method. The rapid cooling rate of clinker causes the fine texture of the interstitial phase and the small C_4AF crystallite size.

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References

[1] Y. Ono, Microscopy for the Quality Control of Cement, J. Res. Onoda Cement Co., (Taiheiyo Cement Co.) 32 (104) (1980) 110–112.
[2] Y. Ono, Ono's Method Fundamental Microscopy of Portland Cement Clinker, Central Research Laboratory, Chichibu Onoda Cement Co., (Taiheiyo Cement Co.), 1994 9–11.
[3] I. Maki, M. Hattori, Influence of minor components on the fine texture of alite in Portland cement clinker, Il Cement 86 (2) (1989) 89–100.
[4] J.C. Taylor, L.P. Aldridge, Full-profile rietveld quantitative XRD analysis of Portland cement: standard XRD profiles for the major phase tricalcium silicate (C_3 S: $3CaO.SiO_2$), Powder Diffr. 8 (3) (1993) 138–144.
[5] H. Moller, Standard less quantitative phase analysis of Portland cement clinkers, World Cem. 26 (9) (1995).
[6] J. Neubauer, H. Hoellmann, H.W. Meyer, Quantitative X-Ray analysis of opc clinker by rietveld refinement, Proc. 10th ICCC 3 (1997) 3v007.
[7] H. Motzet, H. Poellmann, U. Konig, J. Neubauer, Phase quantification and microstructure of a clinker series with lime saturation factors in the range of 100, Proc. 10th ICCC 1 (1997) 1i039.
[8] J.C. Taylor, I. Hinczak, C.E. Matulis, Rietveld full-profile quantification of Portland cement clinker: the importance of including a full crystallography of the major phase polymorphs, Powder Diffr. 15 (1) (2000) 7–18.
[9] A.G. De la Torre, M.A.G. Aranda, Accuracy in rietveld quantitative phase analysis of Portland cements, J. Appl. Cryst. 36 (2003) 1169–1176.
[10] U. Costa, M. Marchi, Mineralogical composition of clinker by bouge and rietveld: the effect of minor elements, Proc 11th ICCC (2003) 11.
[11] NIST USA, Powder diffraction analysis of hydraulic cements: ASTM rietveld round robin results on precision, Powder Diffr. 20 (2005) 97–100.
[12] T. Fullmann, G. Walenta, Die Quantitative Rietveld-Phasenanalyse in industrieller Anwendung, ZKG Intl. 56 (5) (2003) 45–53.
[13] Quantitative XRD-Analysis in Automated Cement Laboratories, Requirements for sample preparation, ZKG Intl. 56 (5) (2003) 54–62.
[14] Proc. Intl. Symp. Quantitative Phase and Elemental Analysis in Cement industry, Karlsruhe, Germany, sponsored by Bruker AXS GmbH, Sept (2004).
[15] A.I. Boikova, Chemical composition of raw materials as the main factor responsible for the composition structure and properties of clinker phases, Proc. 8th ICCC 1 (1986) 19–33.
[16] D.H. Campbell, Microscopical Examination and Interpretation of Portland Cement Clinker, 2nd Edi.PCA, US, 1999.
[17] J. Kang, J. Lee, E. Sakai, M. Daimon, Influence of superplasticizers on the hydration of $3CaO{\cdot}Al_2O_3$, Cem. Sci. Tech. 53 (1999) 71–77 (Japanese).
[18] J. Kang, Y. Ohba, E. Sakai, M. Daimon, Influence of superplasticizers on the hydration in $Ca_3Al_2O_6$–$CaSO_4$–CaO system, Cem. Sci. Tech. 54 (2000) 22–27 (Japanese).
[19] M. Ichikawa, S. Ikeda, Y. Komukai, Effect of cooling rate and Na_2O content on the character of the interstitial materials in Portland cement clinker, Cem. Concr. Res. 24 (6) (1994) 1092–1096.
[20] K. Miyazawa, K. Tomita, Supplementary paper I-64 on the color change of Portland cement, Proc. 5th ICCC (1) (1969) 252–261.
[21] A. I Boikova, Chemical composition of raw materials as the main factor responsible for composition structure and properties of clinker phases, Proc 8th ICCC (1) (1986) 19–33.
[22] M. Ichikawa, Characters and processes conditions of clinker minerals related with strength and color of cements, Dr. thesis of Nagoya institute technology 86-87 (1997), in Japanese.
[23] I. Maki, Nature of the prismatic dark interstitial material in Portland cement clinker, Cem. Concr. Res. 3 (3) (1973) 295–313.
[24] T. Itoh, T. Yamagoshi, M. Yuge, Relationship between the quality of the cement and the amount, crystal structure of alite determined by Rietveld method, Cem. Sci. Tech. 57 (2003) 2–29 (Japanese).
[25] H.F.W. Taylor, Cement Chemistry, 2nd Edition, Tomas Telford Services Ltd, 1997 183.
[26] J. Neubauer, Private Communication, In our opinion the introduction of silicon into aluminate and ferrite phase is pronounced by fast cooling. Maybe this effect will support the decrease in reactivity, 2006.