Hydration Analysis of Rapid-hardening Mortars with Amorphous Calcium Aluminate Additives

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ABSTRACT

We investigated the relation between the physical properties and the hydrated-phase composition of rapid-hardening mortars that consist of ordinary portland cement (OPC), anhydrite, and amorphous calcium aluminate additives. X-ray diffraction/Rietveld method was used for hydration analysis. The characteristic of the rapid-hardening mortar was changed with variation in the CaO to Al_2O_3 molar ratio on amorphous calcium aluminate. Hydration analysis data suggested that these molar ratio affected to the rate of ettringite and matrix C-S-H phase formation. At the same time, the rate of anhydrite hydration was also affected. As a result, compressive strengths and long-term length change of mortars were changed. Therefore, it was necessary for satisfactory performance of rapid-hardening mortar to apply appropriate CaO to Al_2O_3 molar ratio of amorphous calcium aluminate.

1. Introduction

In Japan, rapid-hardening mortars are utilized for construction that must be completed within a limited timeframe, such as emergency highway repairs. There are many types of rapid-hardening mortars used throughout the world. In Europe, alumina cement is used for this type of mortar[1, 2], while amorphous calcium aluminate is used in Japan[3, 4]. These mortars are made of portland cement, amorphous calcium aluminate, and anhydrite[5]. As amorphous calcium aluminate has a much higher hydration activity than crystalline calcium aluminate[6], it is a suitable component for rapid-hardening mortar.

To improve the durability of constructions made from cement is considered to be important for obtaining low life-cycle cost. The above types of rapid-hardening mortars are based on the formation of ettringite, and have excellent characteristics for use in construction; however, unreacted anhydrite within such mortars can lead to damage of the construction project because of the extended delay in ettringite formation. Accordingly, understanding the hydration mechanism of rapid-hardening components is very important in terms of obtaining the desired durability.

In this context, we investigated the relation between the physical properties of rapid-hardening mortars and the chemical composition of amorphous calcium aluminate.

With the aim of ensuring both safety and excellent physical properties, we investigated the relation between the physical properties of mortar and the chemical composition of amorphous calcium aluminate used as a rapid-hardening component. In particular, we carried out a hydration analysis using X-ray diffraction (XRD)/Rietveld method.

2. Experimental

Materials

1) Amorphous calcium aluminate
Table 1 shows the chemical composition of amorphous calcium aluminate. The samples which had seven CaO/Al_2O_3 molar ratio levels were prepared. The starting materials of these samples were reagent-grade $CaCO_3$, Al_2O_3, and SiO_2 powders, and the powders were mixed by ball mill. To obtain calcium aluminate clinkers, the mixtures were sintered for 1 hour at 1650°C in a laboratory electric furnace and cooled quickly in air. After cooling, all clinkers were confirmed as amorphous materials by XRD analysis. Amorphous calcium aluminate powder was obtained by grinding these clinkers using a ball mill to achieve a Blaine specific surface area of 580 ± 20 m^2/kg.

Table 1 Chemical composition of amorphous calcium aluminate

	CaO (%)	Al_2O_3 (%)	SiO_2 (%)	CaO/Al_2O_3 (molar ratio)
Amor-CA	40.0–54.0	57.0–43.0	3.0	1.4–2.3

2) Cement and Anhydrite
We used JIS R 5210 ordinary portland cement with a Blaine specific surface area of 330 m^2/kg and 600 m^2/kg of natural anhydrite.

Test method of mortars

Table 2 shows the mix proportion of rapid-hardening mortars analyzed in this study. Citric acid was used as a set retardant. The mortar specimens were prepared by mixing 50% of this cement mixture and 50% silica sand at 20°C with 80% R.H.. This mix proportion was adopted for obtaining good fluidity and rapid hardening performance. All mortars had good

workability. Mortar bars of dimensions 40 x 40 x 160 mm were used. After de-molds(24 h), specimens were cured in water at 20˚C. Seven class specimens with amorphous calcium aluminate which had varied chemical composition were prepared.

The compressive strengths of these mortars were measured using the JIS R 5201 test method, and the length-change rates of the mortars were measured using a dial gage.

Table 2 Mix proportion of test mortars

Mix proportion			W/C
OPC	Amorphous Calcium Aluminate	Anhydrite	
80%	8%	12%	35%

2.3 Hydration analysis

The XRD/Rietveld method[7, 8] was used for the quantitative analysis of rapid-hardening cement upon hydration. Specimens of paste were prepared for this analysis. The mix proportion in Table 2 was adopted for these pastes without silica sand. The number of pastes was as same as the number of mortar specimens. The samples for quantitative analysis were prepared by crushing these specimens such that hydration was stopped after a prescribed time (3, 9, and 24 hours) by mixing the specimens with a large quantity of acetone. The samples were then filtered under reduced pressure and dried in air at 40˚C. After drying, the samples were finely powdered by hand. We then added 30% corundum with an average particle size of 3 micro meters.

XRD data were obtained using a Rigaku MultiFlex diffractometer with a Cu X-ray tube. Measurements were carried out at 2 theta values ranging from 5˚ to 70˚, with a step width of 0.03˚.

For the Rietveld analysis, we used the software SIROQUANT [TM]. Nine refinement phases were used: alite (monoclinic $3CaO.SiO_2$), belite (beta-$2CaO.SiO_2$), C_3A ($3CaO.Al_2O_3$, sum of cubic and orthorhombic phases), C_4AF ($4CaO.Al_2O_3.Fe_2O_3$), ettringite, anhydrite, calcite, and portlandite.

The ignition loss of samples was determined by heating the samples at 1000˚C for 1 hour. The mineral compositions of samples determined using the XRD/Rietveld method were converted into the compositions of unhydrates from the value of ignition loss.

A conduction calorimeter was used to evaluate the hydration activity of amorphous calcium aluminates. These measurements were adopted for a water-to-sample ratio of 10.

3. Results

3.1 Compressive strength of the mortar

Figure 1 shows the compressive strengths of different rapid-hardening mortars. The most important property of rapid-hardening mortars is that a high strength is obtained at an early age.

The compressive strength of rapid-hardening mortars changed with variations in the CaO/Al_2O_3 (C/A) molar ratio used in amorphous calcium aluminates. The greatest compressive strength was recorded at three hours (early age) for mortar mixed with amorphous calcium aluminate with a C/A molar ratio of about 1.8. However, all mortars showed similar strengths over 1 day for all values of C/A molar ratio. Moreover, only minor strength development was observed from 1 to 28 days for mortars that used amorphous calcium aluminates with a C/A molar ratio of less than 1.7. In contrast, we recorded a very high compressive strength at 28 days for mortar with amorphous calcium aluminate with a C/A molar ratio in excess of 1.8.
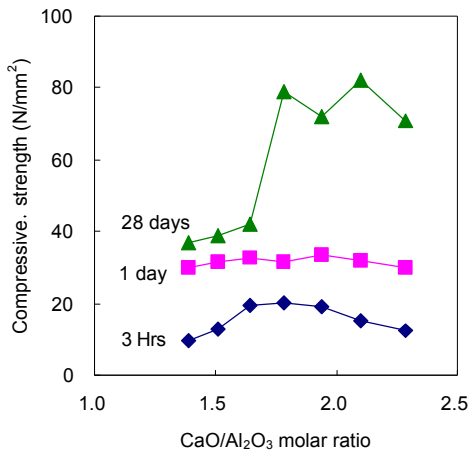

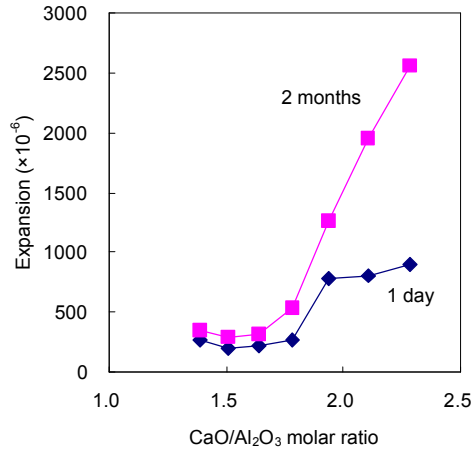Fig. 1. Compressive strengths of analyzed mortars.

Fig. 2. Length-change ratio of mortars. (expansion)

3.2 Length-change ratio of analyzed mortars

Figure 2 shows the length-change ratio of analyzed mortars. The length change is important as an index of durability. The length-change ratio was

low for all ages and for all mortars that used amorphous calcium aluminate with a C/A molar ratio of less than 1.8; however, the length-change ratio increased with age for mortar s that us ed amorphous calcium aluminate with a C/A molar ratio of more than 1.8. For amorphous calcium aluminate with a C/A molar ratio of more than 1.8, the length-change ratio of th e mortar increased with increasing C/A molar ratio.

3.3 Analysis of the hydration process of pastes

3.3.1 Ettringite

Figure 3 shows the amounts of ettringite measured using the XRD/Rietveld method. For amorphous calcium aluminate with a low C/A molar ratio, little ettringite formed within the paste at an early age, but it developed in large quantities after 9 hours. The amount of ettringite that formed in the paste during the interval from 9 to 24 hours was the same for all molar ratios of C/A.
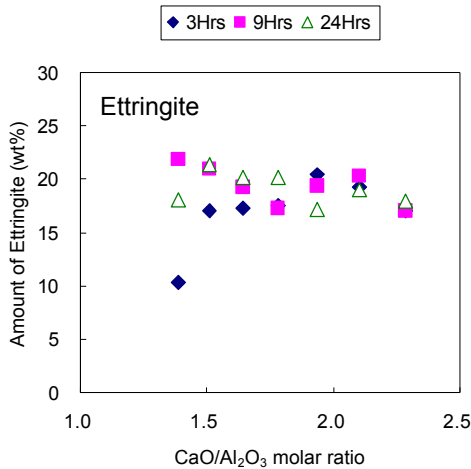
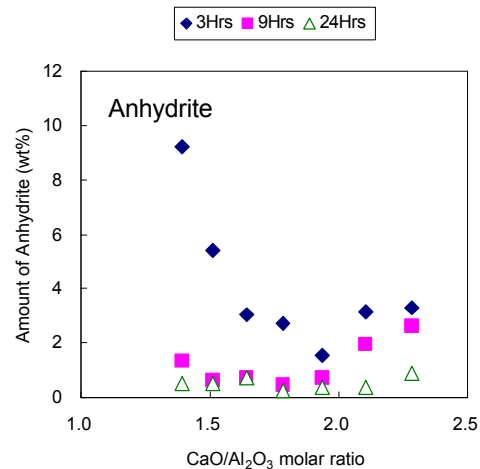Fig. 3. Amount of ettringite in analyzed pastes.

Fig. 4. Amount of anhydrite in analyzed pastes.

3.3.2 Anhydrite

Figure 4 shows the amount of anhydrite in pastes, as measured using the Rietveld method. For amorphous calcium aluminate with a low C/A molar ratio, the amount of reactive anhydrite was low at early ages, and the amount of anhydrite in the paste decreased rapidly over time. For amorphous calcium aluminates with a high C/A molar ratio, the hydration speed of anhydrite hydration was slow.

3.3.3 Minerals within ordinary portland cement

Figures 5 –8 show the amounts of alite, belite, C_3A, and C_4AF within ordinary portland cement, respectively. The degree of hydration of alite increased over time and increased with increasing C/A molar ratio of amorphous calcium aluminate. In terms of belite and C_4AF, we observed no significant changes in content with changing molar ratio. In contrast, the amount of unhydrated C_3A decreased with progressive hydration.
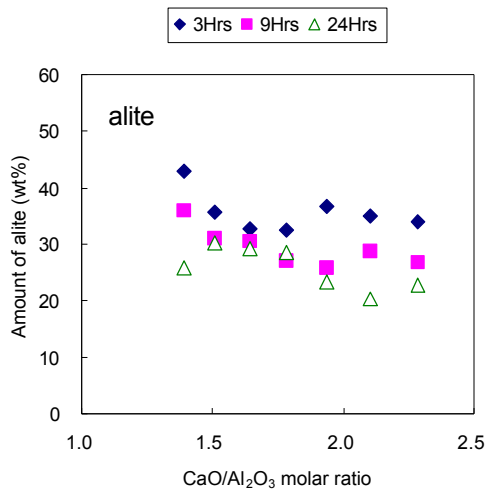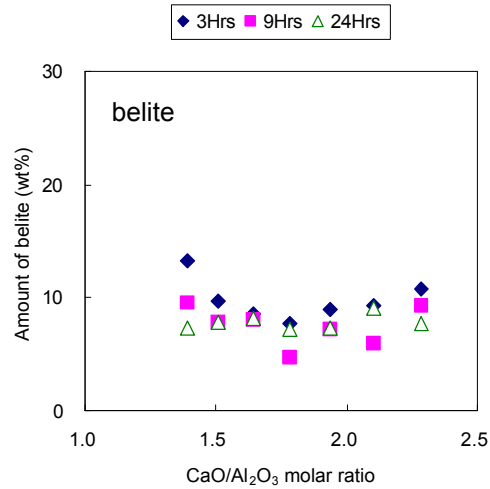
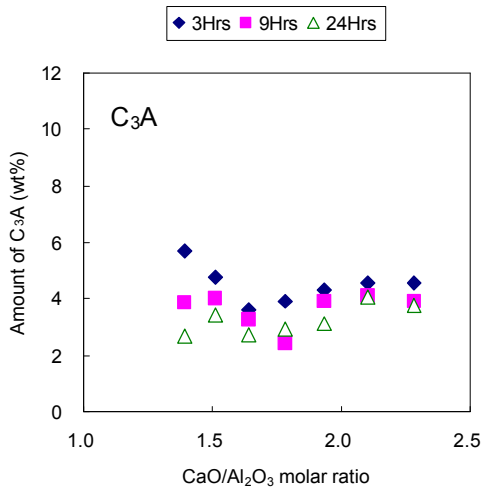Fig. 5. Amount of alite.
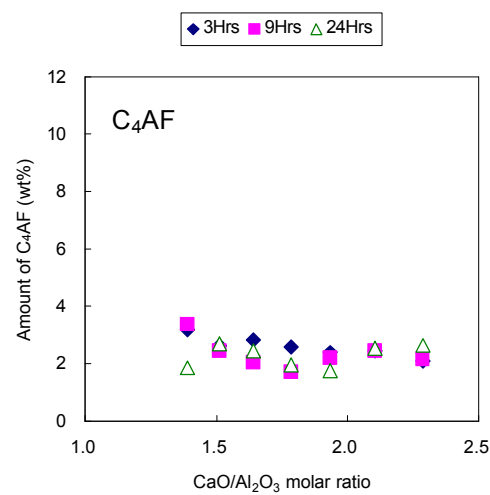
Fig. 6. Amount of belite.

Fig. 7. Amount of C_3A.

Fig. 8. Amount of C_4AF.

Figure 9 shows the ignition loss of analyzed pastes. The trend of ignition loss versus C/A molar ratio is similar to that for ettringite.
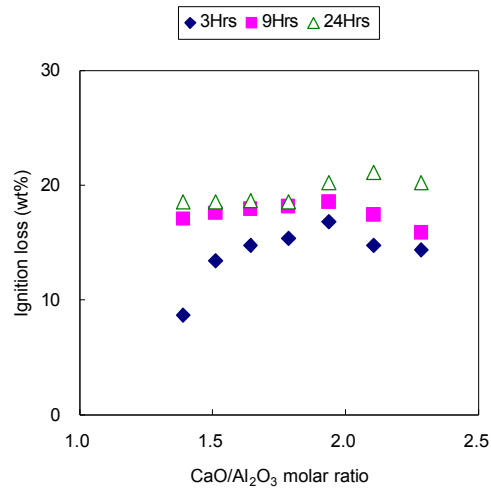

Fig. 9. Ignition loss of analyzed pastes.

3.3.4 Hydration activity of amorphous calcium aluminate

Figure 10 shows the hydration heat behavior of amorphous calcium aluminates analyzed in this study. The hydration activity of amorphous calcium aluminate increased with increasing C/A molar ratio.
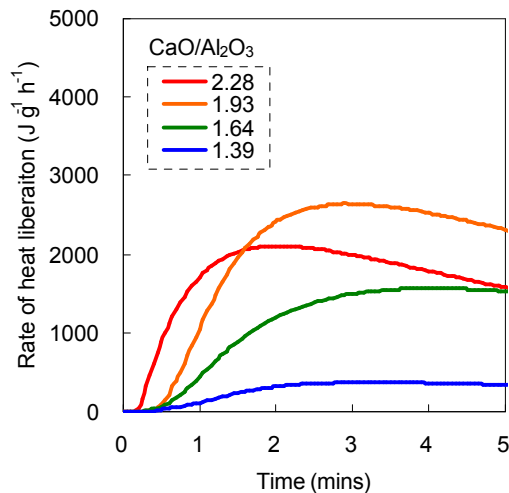

Fig. 10. Hydration heat of analyzed amorphous calcium aluminates.

4. Discussion

The hydration behavior of the rapid-hardening cement that contained amorphous calcium aluminate was greatly influenced by the C/A molar ratio[4]. This hydration behavior is considered to reflect the combined reactiveness properties of the different minerals.

To explain the hydration behavior of this rapid-hardening cement, three factors are assumed : (1) the hydration activity of amorphous calcium aluminate increases rapidly with increasing C/A molar ratio, (2) the rate of dissolution of each of the main minerals into water occurs in the order of amorphous calcium aluminate > alite > anhydrite, and (3) the hydration of alite progressed with the formation of ettringite, as its formation was necessary to supply Ca ions to other minerals.

In considering these factors, the hydration behavior of the rapid-hardening cement can be explained as follows.

. C/A molar ratio of less than 1.7
In this range, ettringite formation was slow because the rate of supply of Ca and Al ions was low due to the low activity of amorphous calcium aluminate. Accordingly, the hydration of alite made minimal progress, although the final ettringite formation was substantial because large amounts of Al were supplied from amorphous calcium aluminate. As the hydration of alite did not progress significantly, the long-term compressive strength of the mortar was poorly developed. The hydration of alite was probably obstructed by surplus Al ions.

Little anhydrite remained, as the dissolution rate of anhydrite exceeded that of amorphous calcium aluminate in this C/A molar range. Accordingly, the long-term expansion of the mortar was also minor.

. C/A molar ratio of approximately 1.8
In this range, ettringite formation became active and the mortar developed a high compressive strength at an early age. The rate of supply of Ca and Al ions from amorphous calcium aluminate matched the supply rate of SO_4 ions from anhydrite. Moreover, the long-term strength of the mortar was high, as the obstruction of alite hydration described above was circumvented by the small amount of surplus Al. The long-term expansion of the mortar was only minor, as no anhydrite remained in the sample.

. C/A molar ratio above 1.9
Ettringite formation was active in this range because of the rapid supply of Ca and Al ions from amorphous calcium aluminate. However, the

reactive speed of the anhydrite was slower than that of the above systems. We attribute this phenomenon to the following factors.

First, obstruction of the hydration of alite and amorphous calcium aluminate occurred because a gel phase formed from the excess supply of Ca and Al ions from the more active hydrated amorphous calcium aluminate. This excess supply of Ca and Al ions resulted from an imbalance between the rate of supply of Ca and Al ions from amorphous calcium aluminate and that of SO_4 ions from anhydrite. Second, the diffusion of SO_4 ions from anhydrite decreased with the progressive formation of the cement paste matrix associated with the accelerated hydration of alite and the formation of ettringite.

In either case, long-term expansion of the mortar resulted from the remaining anhydrite and the stiffening matrix of paste with progressive hydration of alite.

Therefore, it was necessary for satisfactory performance of rapid-hardening mortar to apply appropriate chemical composition of amorphous calcium aluminate.

5. Summary

We investigated the relation between the physical properties of mortar and the hydration of rapid-hardening cement with an amorphous calcium aluminate additive.

.   The characteristic of the rapid-hardening cement was changed with variation in the C/A molar ratio of amorphous calcium aluminate. The mortar that used an amorphous calcium aluminate with a C/A molar ratio of approximately 1.8 showed a high compressive strength at an early age and a low length-change ratio. However, the mortar that used amorphous calcium aluminate with a C/A molar ratio below 1.7 did not achieve sufficient compressive strengths at 3 hours or at 28 days. For a C/A molar ratio above 1.9, the mortar had high long-term compressive strength but insufficient short-term compressive strength. In addition, the length-change ratio of mortar was low for C/A molar ratios below 1.8, and increased with increasing C/A molar ratio for C/A molar ratios above 1.9.
.   For amorphous calcium aluminate with a C/A molar ratio below 1.7, small amounts of ettringite were recorded at an early age; the reaction rates of alite and anhydrite were also low. For amorphous calcium aluminate with a C/A molar ratio above 1.9, a large amount of ettringite formed at an early age, but the reaction rate of anhydrite was low. It is

considered that this trend was related to an increase in the length-change rate of the mortar.

Consequently, it was necessary for satisfactory performance of rapid-hardening mortar to apply appropriate CaO to Al_2O_3 molar ratio of amorphous calcium aluminate.

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