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FULL PAPER

Hydration reaction and hydrated products of low heat Portland cement-expansive additive- $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ system with/without CaCl_2

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Low heat Portland cement (LHC) containing expansive additives can reduce the temperature stress and the crack generation of concrete, therefore it can be used for producing mass concrete and high-strength concrete. However, since LHC does not contain much aluminum, it is difficult for LHC to immobilize chloride ions and be used in salt damage environments such as seashore. $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ addition to LHC can be the countermeasure, however chloride immobilization in LHC with $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ has not been researched in detail. This paper describes the influence of CaCl_2 addition on hydration of LHC containing an expansive additive and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$. In LHC containing an expansive additive, ettringite was mainly generated with and without CaCl_2 . In contrast, in LHC containing an expansive additive and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, monosulfate was generated without CaCl_2 , and Friedel's salt were generated with CaCl_2 . Therefore, LHC containing an expansive additive and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ showed potential for chloride ion immobilization.

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Key-words : Low heat Portland cement, Chloride ion, Expansive additive, $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, AFm phase, Friedel's salt

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1. Introduction

Since low heat Portland cement (LHC) contains more $2\text{CaO}\cdot\text{SiO}_2$ (C_2S) and less $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A) than ordinary Portland cement (OPC), it has high durability¹⁾ and reduces the temperature stress of concrete.²⁾ In addition, expansive additives reduce crack generation caused by drying shrinkage,³⁾ therefore LHC containing expansive additives is suitable for producing high durable concrete. However, the amount of C_3A in LHC is not sufficient to generate AFm phases. AFm phases are typical hydrated products in cement and consist of CaO , Al_2O_3 , Fe_2O_3 , and ions. $3\text{CaO}\cdot(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)\cdot\text{CaX}\cdot n\text{H}_2\text{O}$ is the formula of AFm where X means the ion and n depends on the ion. The A and F of AFm are abbreviations of aluminum and iron, respectively, and m indicates that the amount ratio of CaX to the sum of Al_2O_3 and Fe_2O_3 is 1:1. However, Fe_2O_3 is often disregarded and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaX}\cdot n\text{H}_2\text{O}$ is used to discussion. When the ion is sulfate ion, n is 12 and the phase is called monosulfate: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$. Sulfate ion in monosulfate can be exchanged for other ions (e.g., chloride, hydroxide, etc.), resulting in

transformation from monosulfate to other AFm phases. In addition, expansive additives can be mainly classified as ettringite-type and lime-type, but they do not generate AFm phases. Since AFm phases can absorb chloride ions and generate Friedel's salt: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$, they can immobilize chloride ions, which rust iron rebar.⁴⁾ Because of a lack of AFm phases, it is difficult to use LHC containing expansive additives in salt damage environments such as seashore.

Addition of $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (CA_2) is one of the countermeasures for chloride immobilization in cementitious materials. It is reported that 5–10 mass % CA_2 addition to OPC containing chloride ions generates Friedel's salt.⁵⁾ Moreover, the authors already have found the possibility of the iodine ion immobilization in cement-based materials containing LHC, an expansive additive, and CA_2 .⁶⁾ Since iodine and chlorine are both halogens, CA_2 addition to LHC could also aid in chloride immobilization. However, there are few researches on hydration of LHC containing expansive additives and CA_2 , and the research on chloride immobilization in LHC containing expansive additives and CA_2 is also required.

In this paper, the authors investigated the hydration reaction and the hydrated products of cementitious materials which consist of LHC, an expansive additive, CA_2 ,

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and CaCl₂. This will provide useful data for chloride immobilization in LHC-type materials.

2. Experimental procedures

2.1 Materials

Table 1 shows the chemical compositions of LHC (made by TAIHEIYO CEMENT CORPORATION, Japan), an expansive additive (CSA, made by Denka Company Limited, Japan), and CA₂ (made by Denka Company Limited, Japan) used in this paper. **Table 2** shows the mineral compositions of used LHC (calculated by Bogue's equation) and used CSA. CSA means calcium sulfoaluminate and it mainly consists of CaO, ye'elimite: 3CaO·3Al₂O₃·CaSO₄, and CaSO₄. Ye'elimite is a cementitious compound having high Al₂O₃/CaO ratio and it can generate ettringite. First, CaO and water generates Ca(OH)₂, resulting in the reaction between ye'elimite, Ca(OH)₂, and CaSO₄. This reaction generates ettringite resulting in restrain of drying shrinkage. CaCl₂ (Kanto Chemical Co., Ltd., special grade reagent) was used to add chloride ions.

2.2 Sample preparation

In this paper, four cementitious materials were investigated. Considering a previous report,⁶⁾ the amounts of LHC, CSA, and CA₂ in the materials were fixed at the ratios in **Table 3**. The amount of added CaCl₂ was fixed so that the molar ratio of CaCl₂/Al₂O₃ = 1. First, LHC, CSA, and CA₂ were thoroughly mixed, and water was poured into the mixed powder. The water-powder mass ratio was 0.60, and the paste was mixed for 10 min by hand with a stainless steel spoon. After the mixing, cement paste was poured into a 1 cm × 1 cm × 8 cm mold and then cured at 20°C in a sealed case. The humidity in the sealed case

was 100%. After 1 day curing, the hardened paste was demolded and continuously cured for 0, 2, 6, or 27 days. This means that the total curing (hydration) times of specimens were 1, 3, 7, and 28 days. After the curing, hydration of specimens was stopped by adding a large amount of acetone. Finally, the specimens were dried under a pressure of 0.02 MPa at 20°C for 24 h.

2.3 Analysis methods

The specimens made in Section 2.2 were pulverized to pass through a 90 μm sieve. To identify the hydrated products, MgO (Kanto Chemical Co., Ltd., special grade reagent) was added to the pulverized specimen as an internal standard, and the specimen was analyzed by powder X-ray diffraction (XRD) (Rigaku Co., Ltd., SmartLab-SPI/TISM). In addition, the reaction ratios of 4CaO·Al₂O₃·Fe₂O₃ (C₄AF) and CA₂ were calculated by the quantitation of the unreacted amount using the internal reference method. Diffraction peaks (2θ) for the quantitation were 12.2° for C₄AF, 25.6° for CA₂, and 42.9° for MgO. The areas of diffraction peaks were evaluated by peak fitting using the least-squares method and numerical integration of the fitted curve. The reaction ratio of each mineral in the specimen was calculated by Eq. (1).

$$\alpha_i(t) = 100 - \frac{\frac{S_i(t)}{S_{MgO}(t)} \times \frac{100}{100 - Ig. loss(t)}}{\frac{S_i(0)}{S_{MgO}(0)} \times \frac{100}{100 - Ig. loss(0)}} \times 100 \quad (1)$$

where t is the hydration time, i is the name of the mineral, $\alpha_i(t)$ (%) is the reaction ratio at t hours, $S_i(t)$ is the peak area of the mineral in the specimen that was hydrated for t hours, and $Ig. loss(t)$ (%) is the mass loss of the specimen during calcination at 1000°C.

3. Results and discussion

3.1 Identification of hydrated products

Figure 1 shows the XRD patterns of hydrated products for 1 day hydration. In the LHC-CSA system, ettringite: 3CaO·Al₂O₃·3CaSO₄·32H₂O was mainly generated. In the

Table 1. Chemical compositions of materials

(mass %)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO
LHC	63.4	26.8	2.5	3.0	2.3	0.5
CSA	67.0	1.8	5.4	0.9	19.6	0.9
CA ₂	23.9	0.6	67.7	7.1	0.0	0.3

Table 2. Mineral compositions of LHC and CSA

(mass %)	Ca ₃ SiO ₅	Ca ₂ SiO ₄	Ca ₃ Al ₂ O ₆	Ca ₄ Al ₂ Fe ₂ O ₁₀	CaSO ₄
LHC	26.6	56.8	1.6	9.2	3.9
(mass %)	CaO	Ye'elimite	CaSO ₄	Ca ₂ SiO ₄	Ca ₄ Al ₂ Fe ₂ O ₁₀
CSA	50.0	10.0	30.6	5.4	2.9

Table 3. Mixing proportions of cementitious materials

	(mass %)			(molar ratio)
	LHC	CSA	CA ₂	CaCl ₂
LHC-CSA	93.0	7.0	—	—
LHC-CSA + CaCl ₂	93.0	7.0	—	CaCl ₂ /Al ₂ O ₃ = 1.0
LHC-CSA-CA ₂	83.7	7.0	9.3	—
LHC-CSA-CA ₂ + CaCl ₂	83.7	7.0	9.3	CaCl ₂ /Al ₂ O ₃ = 1.0

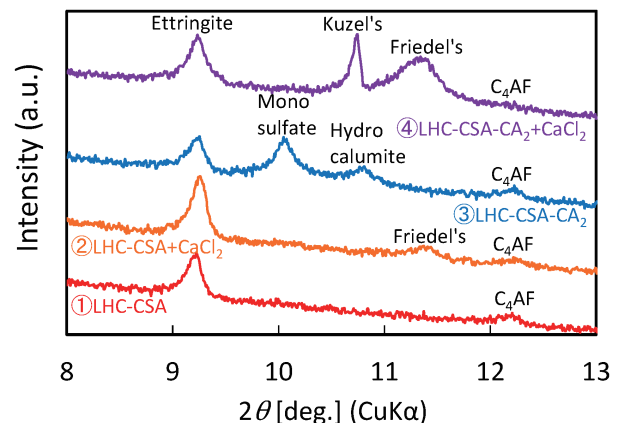


Fig. 1. XRD patterns of hydrated products for 1 day hydration.

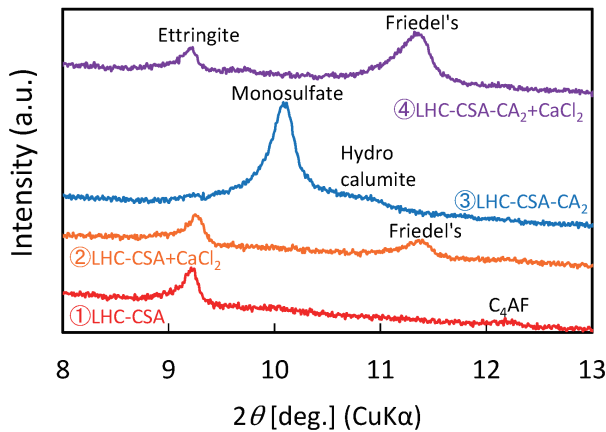


Fig. 2. XRD patterns of hydrated products for 28 days hydration.

LHC-CSA + CaCl₂ system, ettringite and Friedel's salt were generated. The peak of ettringite in this system was larger than that in the LHC-CSA system. In addition, since the peak of Friedel's salt in the LHC-CSA + CaCl₂ system was small, the amount of Friedel's salt may be small. On the other hand, in the LHC-CSA-CA₂ system, ettringite and monosulfate were generated. Hydrocalumite: 3CaO·Al₂O₃·Ca(OH)₂·12H₂O was also generated. However, since the peak of hydrocalumite was small, the amount may be small. The authors consider that the restraint of hydrocalumite generation was caused by the coating of aluminum hydroxide gel, similar to the OPC-CA₂ system in a previous report.⁷⁾ In the LHC-CSA-CA₂ + CaCl₂ system, ettringite, Friedel's salt, and Kuzel's salt: 3CaO·Al₂O₃·Ca(Cl₂SO₄)_{0.5}·11H₂O were generated. The peak of ettringite was larger and the peak of C₄AF was smaller than those in the LHC-CSA-CA₂ system.

Figure 2 shows the XRD patterns of hydrated products for 28 days hydration. The LHC-CSA system generated ettringite, and the LHC-CSA + CaCl₂ system generated ettringite and Friedel's salt, as well as the result for 1 day hydration. On the other hand, in the LHC-CSA-CA₂ system, the peak of ettringite disappeared and the peak of monosulfate became larger than 1 day. In the LHC-CSA-CA₂ + CaCl₂ system, the peak of Kuzel's salt disappeared and the peak of Friedel's salt became larger than 1 day. Incidentally, the peak area of Friedel's salt was 2.5 times larger than that for 1 day hydration.

From these results, it is revealed that ettringite was mainly generated in the LHC-CSA system, but AFm phases, such as monosulfate or hydrocalumite, were not generated for any hydration time. Therefore, it will be difficult for the LHC-CSA system to immobilize chloride ions. Actually, the LHC-CSA + CaCl₂ system generated Friedel's salt, but its amount was small. On the other hand, in the LHC-CSA-CA₂ system, monosulfate and hydrocalumite were generated, and the amount of monosulfate increased with increasing hydration time. Actually, a large amount of Friedel's salt was generated in the LHC-CSA-CA₂ + CaCl₂ system, therefore the LHC-CSA-CA₂ system may be able to immobilize chloride ions.

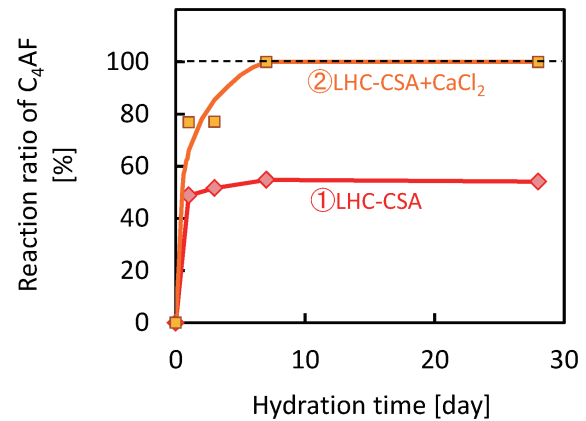


Fig. 3. Reaction ratios of C₄AF.

3.2 Influence of CaCl₂ addition on reactions of C₄AF and CA₂

Figure 3 shows the reaction ratios of C₄AF in the LHC-CSA and LHC-CSA + CaCl₂ systems. In the LHC-CSA system, the reaction ratio of C₄AF was about 55% and independent of the hydration time. On the other hand, in the LHC-CSA + CaCl₂ system, the reaction ratio of C₄AF was above 70% even for short hydration time, and all of C₄AF reacted in 7 days hydration. These results correspond to the results in Figs. 1 and 2. Incidentally, in the LHC-CSA-CA₂ and LHC-CSA-CA₂ + CaCl₂ systems, the peaks of C₄AF were observed for 1 day hydration, but were not observed for 3 days hydration. Therefore, it can be said that all of C₄AF reacted in 3 days hydration in the two systems containing CA₂. In addition, the peak of C₄AF in the LHC-CSA-CA₂ + CaCl₂ system was smaller than that in the LHC-CSA-CA₂ system (Fig. 1). From these results, it is revealed that the C₄AF reaction is accelerated by CaCl₂ addition.

The results in Sections 3.1 and 3.2 conclude that CaCl₂ addition resulted in Friedel's salt generation, an increase in the amount of ettringite, and acceleration of C₄AF hydration. The authors consider that these three influences are related to a reaction between the gel-like coating on C₄AF particles and the added chloride ions. The authors have proposed a model for restraint of C₃A hydration in C₃A-CaSO₄·2H₂O system in which aluminate gel-like coating containing SO₄²⁻ is generated on the C₃A particle surface.^{8,9)} In this model, the aluminate gel-like coating restrains C₃A hydration and finally decomposes with ettringite generation, resulting in acceleration of C₃A hydration. The authors consider that a similar phenomenon occurred in the C₄AF hydration in this paper, i.e. the following model is proposed. First, the gel-like coating containing SO₄²⁻ was generated on the C₄AF particle surface, resulting in the restraint of C₄AF hydration in the LHC-CSA and LHC-CSA-CA₂ systems. In contrast, when CaCl₂ was added to these two systems, Friedel's salt was generated by a reaction between the gel-like coating and the added chloride ions. This reaction resulted in the disappearance of the gel-like coating and the acceleration of

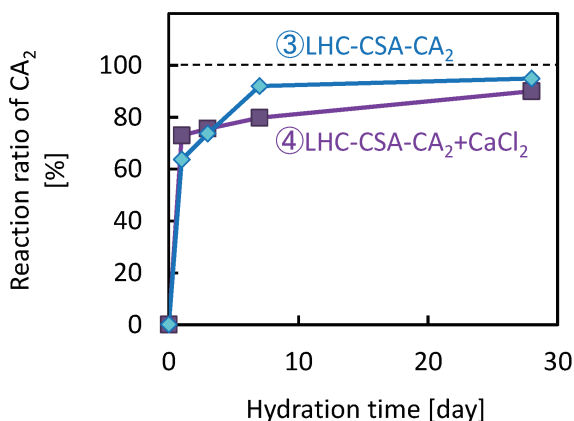


Fig. 4. Reaction ratios of CA₂.

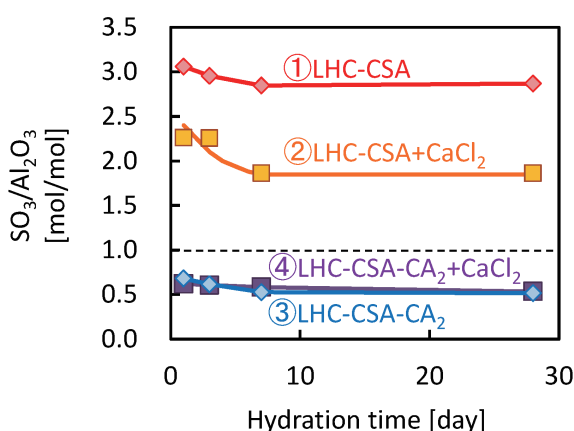


Fig. 5. Changes of SO₃/Al₂O₃ reacted ratios.

C₄AF hydration. In addition, the decomposition of the coating eluted SO₄²⁻ to the liquid phase. Finally, this SO₄²⁻ elution resulted in the increase in the amount of ettringite.

Figure 4 shows the reaction ratios of CA₂ in the LHC-CSA-CA₂ and LHC-CSA-CA₂ + CaCl₂ systems. The reaction ratios were almost 80% for 3 days hydration in both systems. Moreover, the reaction ratios were above 90% for 28 days hydration with and without CaCl₂ addition. Therefore, although C₄AF reaction was considerably influenced by CaCl₂ addition, the influence of CaCl₂ addition on CA₂ reaction was small.

3.3 Relationship between SO₃/Al₂O₃ molar ratio and AFm phase generation

Figure 5 shows the molar ratios of reacted SO₃ to reacted Al₂O₃ in the four systems. Incidentally, aluminum is contained in C₄AF, CA₂, C₃A of LHC, and ye'elimite of CSA. However, C₃A and ye'elimite were not detected by XRD for any hydration time, thus the authors assumed that all of C₃A and all of ye'elimite reacted in the first 1 day hydration. This assumption means that reacted Al₂O₃ is the sum of C₃A, ye'elimite, reacted C₄AF, and reacted CA₂. Moreover, the authors assumed that all of SO₃ reacted for any hydration time.

Independently of the hydration time, the SO₃/Al₂O₃ reacted molar ratios were larger than 1 in the LHC-CSA and LHC-CSA + CaCl₂ systems. SO₃/Al₂O₃ = 3 corre-

sponds to the stoichiometric value for ettringite generation, and SO₃/Al₂O₃ = 1 corresponds to the stoichiometric value for monosulfate generation. In short, since LHC contains little aluminum, the SO₃/Al₂O₃ reacted ratio was not suitable for the AFm phase generation in the LHC-CSA system. Incidentally, the SO₃/Al₂O₃ reacted ratio in the LHC-CSA + CaCl₂ system was smaller than that in the LHC-CSA system. This corresponds to the accelerated C₄AF reaction with CaCl₂ addition, as shown in Fig. 3. However, the SO₃/Al₂O₃ reacted ratio in the LHC-CSA + CaCl₂ system was still larger than 1, i.e. the amount of reacted aluminum was not sufficient, too. In contrast, the SO₃/Al₂O₃ reacted ratios were smaller than 1 in the LHC-CSA-CA₂ and LHC-CSA-CA₂ + CaCl₂ systems. The CA₂ addition increased the amount of Al₂O₃ and made the SO₃/Al₂O₃ reacted ratio less than 1, resulting in the AFm phase generation as shown in Figs. 1 and 2.

4. Conclusions

To investigate the possibility of chloride immobilization in concrete containing LHC, this paper discusses the hydration reaction and hydrated products in LHC containing calcium sulfoaluminate (CSA) and CaO·2Al₂O₃ (CA₂). Four systems: LHC-CSA, LHC-CSA + CaCl₂, LHC-CSA-CA₂, and LHC-CSA-CA₂ + CaCl₂ systems were investigated. The following conclusion can be drawn.

(1) In the LHC-CSA system, since ettringite was mainly generated and AFm phases were not generated, immobilization of chloride ions is not expected.

(2) CA₂ addition aided in AFm phase generation. In the LHC-CSA-CA₂ system, monosulfate was generated and the amount of monosulfate increased with increasing hydration time. Especially, Friedel's salt was also generated in the LHC-CSA-CA₂ + CaCl₂ system.

(3) C₄AF hydration was restrained in the LHC-CSA and LHC-CSA-CA₂ systems but not restrained in the LHC-CSA + CaCl₂ and LHC-CSA-CA₂ + CaCl₂ systems. It is supposed that CaCl₂ addition decreased the amount of gel-like coating on C₄AF particles and accelerated the C₄AF hydration.

(4) In the LHC-CSA-CA₂ and LHC-CSA-CA₂ + CaCl₂ systems, the SO₃/Al₂O₃ reacted molar ratios were less than 1 and suitable for AFm phase generation. From these results, although LHC-CSA type materials without CA₂ cannot immobilize chloride ions, LHC-CSA-CA₂ type materials should be able to immobilize chloride ions.

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