

# **Fresh Properties and Strength Development of Cement Mortar Using Nitrite-based Accelerator and Chemical Admixtures**

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## **Abstract**

A nonfreezing agent prevents initial frost damage by simplified curing and also promotes early strength development. In general, a nitrite-based accelerator is used as the main component of this nonfreezing agent. When a large proportion of a conventional accelerator is used, the slump loss increases because the setting and hardening processes are strongly enhanced. In addition, these conventional accelerators may not be sufficiently effective at temperatures of -10 °C or less. Therefore, the fresh properties and strength development of cement mortars when using a nitrite-based accelerator and chemical admixtures in a low-temperature environment are examined. The objective is to develop a high-performance nonfreezing agent. This paper presents the contributions of the nitrite-based accelerator and two types of high-range water-reducing agents, used in combination. From the investigation, it was confirmed that the change in the mortar flow can be suppressed by combining two types of high-range water-reducing agents with a nitrite-based accelerator, even after the passage of 60 min after mixing. Furthermore, the mix was found to contribute to not only the initial strength but also toward maintaining the good strength for a longer time.

**Keywords:** nitrite-based accelerator, high-range water-reducing agent, mortar flow, compressive strength, cold-weather concrete

## **1. Introduction**

In the case of concrete constructions in cold weather, it is necessary to control the temperature of heat curing using a temporary enclosure and heater to prevent initial frost damage. If the installation of the temporary enclosure is difficult, owing to a steep slope, narrow working space, and strong winds, a nonfreezing agent is commonly used. This nonfreezing agent, by simplified curing, prevents initial frost damage and also secures initial strength development. Furthermore, the function of this agent is to reduce the freezing temperature of the water in the concrete. The characteristics of concrete, using a nitrite-based accelerator and chemical admixtures in a low-temperature environment, are investigated in this study with the aim to develop a high-performance nonfreezing agent [1-4]. In general, a nitrite-based accelerator is used as the main component of this nonfreezing agent [5]. Calcium nitrite chiefly accelerates the hydration process by increasing the solubility of C<sub>3</sub>S (alite, 3CaO·SiO<sub>2</sub>) and (belite, 2CaO·SiO<sub>2</sub>). In addition, it also reacts with C<sub>3</sub>A (aluminate phase, 3CaO·Al<sub>2</sub>O<sub>3</sub>) in cement to generate hydronitroaluminate, 3CaO·Al<sub>2</sub>O<sub>3</sub>·Ca(NO<sub>2</sub>)<sub>2</sub>·10H<sub>2</sub>O. Furthermore, calcium nitrite also reacts with calcium hydroxide in concrete to generate calcium hydroxynitrate, CaO·Ca(NO<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O. These cement hydrates lead to refinement in cement hardening, resulting in the improvement of the mechanical properties of concrete in low-temperature environments [6]. It is

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assumed that the early strength development of concrete is promoted by increasing the proportion of the added accelerator. However, conventional nonfreezing agents might not induce the process leading to the early strength development of concrete at temperatures of  $-10\text{ }^{\circ}\text{C}$  or lower. To promote early strength development at these low temperatures, it is necessary to increase the proportion of the accelerator added in the concrete. However, if the accelerator is added in excess, a strong hydration reaction will occur. As a result, the slump loss of fresh concrete after mixing will become too large, and the workability of the fresh concrete is impaired [7].

In this study, the fresh properties and strength development of cement mortar, when using a nitrite-based accelerator and chemical admixtures, in a low-temperature environment are examined. The objective is to develop a high-performance nonfreezing agent. This paper presents the contributions of the nitrite-based accelerator and various high-range water-reducing agents used in combination.

## 2. Evaluation of Fresh Properties

### 2.1. Outline of the experiment

According to previous studies, the initial slump loss can be suppressed by combining a melamine-based water-reducing agent and polycarboxylic acid-based water-reducing agent in a normal temperature environment ( $+20\text{ }^{\circ}\text{C}$ ) [1, 8]. Initially, the fresh properties of cement mortar using a large proportion of a nitrite-based accelerator and two types of high-range water-reducing agents, in a low-temperature environment, are examined. The aim is to clarify the compatibility of the accelerator and chemical admixture.

### 2.2. Materials used

The properties of the materials used in this study are listed in Table 1. Normal Portland cement was used, and number 5 grade silica sand was used as a fine aggregate. A 45% water solution, primarily composed of calcium nitrite (CN) was used as the accelerator. A melamine-based high-range water-reducing agent (Me) and a polycarboxylic acid-based high-range water-reducing agent (Pc) were also used.

Table 1 Properties of the materials used

| Material(Code)                                      | Properties  |
|---|---|
| Cement (C)  | Normal Portland cement, Density: $3.16\text{ g/cm}^3$ , Specific surface area: $3280\text{ cm}^2/\text{g}$                      |
| Fine aggregate (S)                                  | No.5 silica sand, Absolute dry density: $2.61\text{ g/cm}^3$ , Water absorption: $0.26\%$ , Fineness modulus: 2.16              |
| Accelerator (CN)                                    | Main component: calcium nitrite; other accelerating components (45% water solution), Density: $1.42\text{--}1.44\text{ g/cm}^3$ |
| Melamine-based water reducing agent (Me)            | Main component: amidosulfonic-acid-modified melamine condensate, Density: $1.17\text{--}1.19\text{ g/cm}^3$                     |
| Polycarboxylic acid-based water reducing agent (Pc) | Main component: polycarboxylic acid ether compound, Density: $1.03\text{--}1.07\text{ g/cm}^3$                                  |

### 2.3. Mix proportions

The mix proportions of the cement mortar used in the experiment are listed in Table 2. The water-to-cement ratio used was 50%. The mass ratio of the aggregate (S) to the cement (C) used was 2.50. In general, the processes leading to the early strength development of concrete increases with an increase in the amount of added accelerator. The standard replacement ratio of conventional accelerators is approximately 4% to 7% of the unit content of cement (3-5 L per 100 kg of cement). In this study, the replacement ratios of CN used were 0%, 7%, 11%, and 15% as recommended by previous studies on high-performance non-freezing agents [1-4]. In addition, the replacement ratios of the melamine-based water-reducing agent (Me) to the polycarboxylic acid-based high-range water-reducing agent (Pc) used were 1:0, 0:1, 1:2, and 2:1. The total amounts

of Me and Pc were determined to satisfy the target value of mortar flow. The target value of the mortar flow was  $200 \pm 20$  mm immediately after mixing.

2.4. Test method

Table 2 Mix proportions of cement mortar

| Symbol | W/C (%) | S/C | Unit content (kg/m <sup>3</sup> ) |     |      | Admixture (C×%) |      |      |
|--------|---------|-----|-----------------------------------|-----|------|-----------------|------|------|
|        |         |     | W                                 | C   | S    | CN              | Me   | Pc   |
| CN0    | 50      | 2.5 | 282                               | 564 | 1409 | 0               | 0    | 0    |
| CN7    |         |     |                                   |     |      | 7               |      |      |
| CN11   |         |     |                                   |     |      | 11              |      |      |
| CN15   |         |     |                                   |     |      | 15              |      |      |
| CN7-d  |         |     |                                   |     |      | 7               | 0.4  | 0.2  |
| CN11-a |         |     |                                   |     |      | 11              | 1    | 0    |
| CN11-b |         |     |                                   |     |      |                 | 0    | 1    |
| CN11-c |         |     |                                   |     |      |                 | 0.33 | 0.67 |
| CN11-d |         |     |                                   |     |      |                 | 0.67 | 0.33 |
| CN15-a |         |     |                                   |     |      | 15              | 3    | 0    |
| CN15-b |         |     |                                   |     |      |                 | 3    | 0    |
| CN15-c |         |     |                                   |     |      |                 | 1    | 2    |
| CN15-d |         |     |                                   |     |      |                 | 2    | 1    |

The temperature of concrete at the time of unloading is specified as 10 °C to 20 °C by the Architectural Institute of Japan in the Recommendation for Practice of Cold Weather Concreting [9]. In this study, the mixing and all tests of the mortar were performed in a temperature and humidity controlled testing room ( $10 \pm 1$  °C and  $85\% \pm 5\%$  relative humidity) to obtain the desired temperature of the mortar. The mortar flow was measured immediately after mixing the mortar and also after mixing with a shovel for 30 min and 60 min, assuming that cast-in-place concrete is placed in a construction field within 60 min. The initial and final setting times were measured according to JIS A 1147 (Method of testing for the time of setting of concrete mixtures by penetration resistance). The inside temperature of the mortar ( $\phi 50 \times 100$ mm) was measured immediately after casting using a thermocouple.

2.5. Results and discussion

(1) Mortar flow

The results of the flow test of mortar are presented in Fig. 1. When the accelerator (CN) was only used, the change in mortar flow of mix CN0 (without CN) was hardly observed after mixing to after 60 min. The change in the mortar flow of mix CN7 (with CN 7%) was relatively small over the same period. However, the changes in the mortar flow of mixes CN11 and CN15, which contained a large proportion of CN became was large during the first 30 min and then almost constant for the rest of the time. This is because the hydration reaction of fresh mortar proceeded rapidly owing to the presence of large proportions of the accelerator. From these initial results, more mortar flow tests of mixes, which combined two types of high-range water-reducing agents, were conducted to control the changes in the mortar flow of mixes CN11 and CN15.

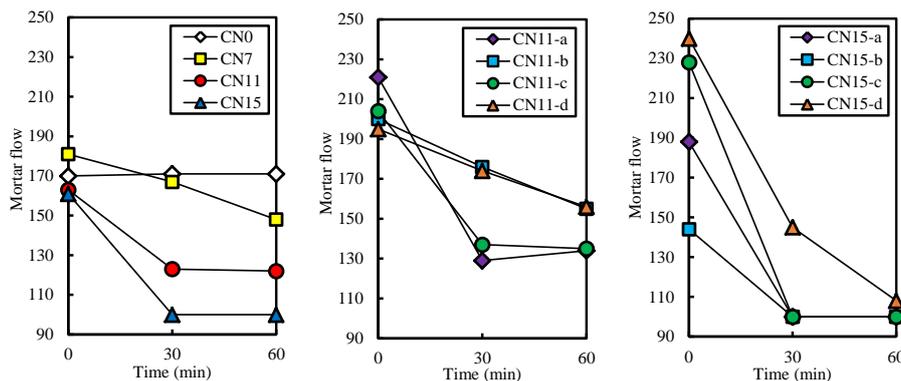


Fig. 1 Mortar flow

When the accelerator and high-range water-reducing agents were used, the changes in mortar flows of mixes CN11-a (with only Me) and CN11-c (with Me:Pc=1:2) were larger after mixing, when compared with those of the other mixes. However, the changes in mortar flows of mixes CN11-b (with the only Pc) and CN11-d (with Me:Pc=2:1) became smaller, and these mixes had good fluidity even after the passage of 60 min after mixing. On the other hand, mixes CN15-a, CN15-b, and CN15c had no fluidity after the passage of 30 min after mixing. However, the change in the mortar flow of mix CN15-d (with Me:Pc=1:2) was relatively small but had no the fluidity, after the passage of 60 min after mixing. It can be concluded from these results that it is difficult to secure fresh properties of mix CN15 at real site, even if the high-range water-reducing agents were to be used.

(2) Setting time

The results of the setting tests are presented in Fig. 2. When the accelerator (CN) was only used, the initial and final setting times decreased with an increase in the amount of accelerator. However, when the accelerator and different high-range water-reducing agents were used, there was no significant difference in the set times of these mixes. On the other hand, the set time of these mixes when using CN11 and high-range water-reducing agents was slightly longer when compared with that of mix CN11. However, there were no significant differences in the set times. Therefore, it can be concluded that the effect of high-range water-reducing agents on setting and hardening times is relatively small.

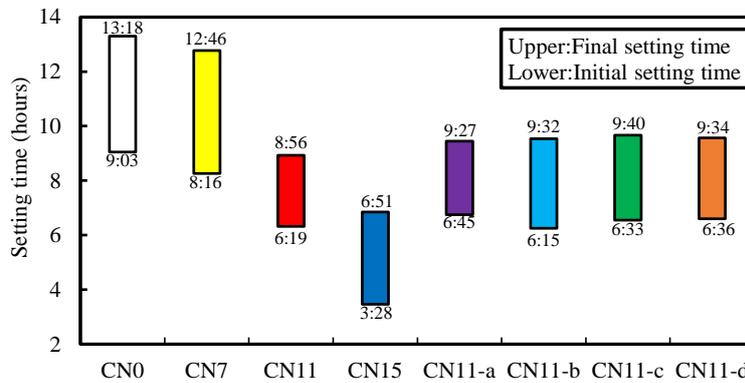


Fig. 2 Setting time

(3) Inside temperature of mortar

The changes in the inside temperature of the mortar are presented in Fig. 3. The temperature changes in mixes CN11 and CN15, which contained a large proportion of accelerator (CN), are larger when compared with the temperature changes of mix CN0. The time to reach a temperature peak for mixes CN11 and CN15 were 15 min and 20 min, respectively. After these respective periods, the temperature of these mixes decreased rapidly. This is because the hydration reaction proceeded rapidly after mixing with a high proportion of accelerator. Therefore, it can be concluded that the changes in mortar flow become very large remarkably because of mixing with a high proportion of accelerator.

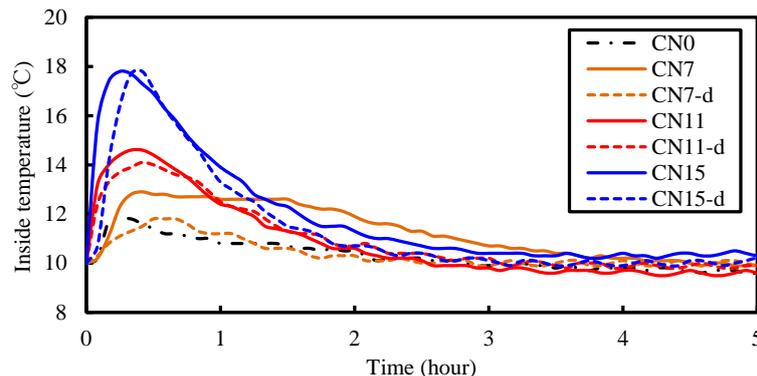


Fig. 3 Changes in the inside temperature of mortar

On the other hand, the temperature changes of mixes CN7-d, CN11-d, and CN15-d, which contained the accelerator and high-range water-reducing agents (with Me:Pc=1:2), were smaller when compared with those of mixes CN7, CN11, and CN15, which contained only the accelerator. Furthermore, the time required to reach a temperature peak for mixes CN11-d and CN15-d was shorter when compared with that required for mixes CN11 and CN15. In particular, the peak temperature for mix CN11-d was smaller when compared with that of CN11. This is because the hydration reaction of mix CN11-d was suppressed as a result of using two high-range water-reducing agents from the time of initial mixing up until 60 min after mixing.

### 3. Evaluation of Strength Development

#### 3.1. Outline of the experiment

In this study, experiments were conducted using cement mortar to study the influence of a nitrite-based accelerator and various high-range water-reducing agents, used in various combinations, on the strength development process of the cement mortar. The compressive strength, expansion strain, and change in pore structure were determined.

#### 3.2. Materials used and mix proportions

The same materials and mix proportions were used, as mentioned in section 2. The replacement ratios of the accelerator (CN) were 0%, 7%, 11%, and 15%. The replacement ratio of the melamine-based water-reducing agent (Me) to the polycarboxylic acid-based high-range water-reducing agent (Pc) was 2:1, which had a controlling effect on the mortar flow, as mentioned earlier in section 2.

#### 3.3. Test method

The mixing was performed in a temperature and humidity controlled testing room ( $10 \pm 1$  °C and  $85\% \pm 5\%$  relative humidity) to obtain the required temperature of the mortar. The compressive strength ( $\phi 50 \times 100$  mm) was measured after 1, 3, 7, 14, and 28 d of curing in the testing room ( $10 \pm 1$  °C and  $85\% \pm 5\%$  relative humidity). In the unrestrained deformation test, the cement mortar was cast in a mold ( $100 \times 100 \times 400$  mm). A polytetrafluoroethylene sheet and styrene board were installed on the inside of the mold to prevent restraint of volume change of mortar and water dispersion of mortar. An embedded gauge was also installed in the center position of the mold. The sealed specimens were then cured in the temperature and humidity controlled testing room ( $10 \pm 1$  °C and  $85\% \pm 5\%$  relative humidity). The expansion and shrinkage strains of the test specimen for each case were measured immediately after casting. The change in pore structure was measured using mercury porosimetry. Initially, the mortar specimens were immersed for 4 h in acetone to stop the hydration of the mortar. Later, the specimens were dried in a drying oven of 105 °C for 24 h.

#### 3.4. Results and discussion

##### (1) Compressive strength

The results of the compressive strength test of mortar are presented in Fig. 4. When the only accelerator was used, the compressive strength measured at 1 day of curing, became larger with an increase in the amount of added accelerator. Mixes CN11 and CN15 showed compressive strengths 6.6 MPa and 8.0 MPa, respectively, which exceeded the 5.0 MPa value of the compressive strength required for preventing the initial frost damage. However, after 3, 7, 14, and 28 d of curing, the compressive strength decreased with an increase in the amount of added accelerator. This is because the hydration reaction was sufficiently enhanced during the curing process, at a temperature of +10 °C. In addition, when a large proportion of the nitrite-based accelerator is used, calcium nitrite chiefly accelerates the hydration process by increasing the solubility of  $C_3S$  and  $C_2S$ , and it also reacts with  $C_3A$ . In particular, the reaction of  $C_3A$  generates a large amount of ettringite, and this reaction also helps in the expansion of concrete, from the initial stage [6, 10]. It is assumed that the formation of these rough hydrated phases by the generation of ettringite affected the strength development process of the cement mortar.

When the accelerator and two types of high-range water-reducing agents (Me:Pc=2:1) were used, mixes CN11-d and CN15-d showed compressive strengths 6.0 MPa and 7.5 MPa, respectively, which exceeded the critical value of 5.0 MPa. After 3 and 7 d of curing, the compressive strengths became larger with an increase in the amount of added accelerator. Even after 14 and 28 d, mixes CN11-d and CN15-d showed good strength development. Therefore, it can be concluded that a large proportion of the added accelerator not only helps in obtaining the initial strength for preventing the initial frost damage but also maintains good strength for a long time.

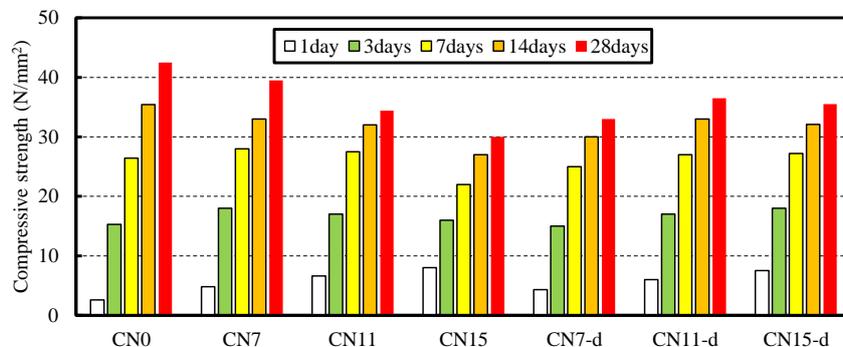


Fig. 4 Compressive strength

### (2) Unrestrained expansion and shrinkage strain

The expansion and shrinkage strain behavior of each specimen under unrestrained deformation from the onset of casting to 4 h after casting is presented in Fig. 5. When only the accelerator (CN) was used, the expansion strain immediately after casting increased with an increase in the amount of added accelerator. It is assumed that mixes CN11 and CN15 showed a large expansion strain because the reaction rate of  $C_3A$  was very high from the initial stage of casting and also because of the enhanced hydration of  $C_3S$  and  $C_2S$  [6, 10]. However, the expansion strain of mixes using the accelerator and high-range water-reducing agents was smaller than that of mixes using only the added accelerator. Furthermore, the time to reach the peak temperature peak was longer by approximately 40 min. These results support the argument that the strength development of mixes is increased by using high-range water-reducing agents.

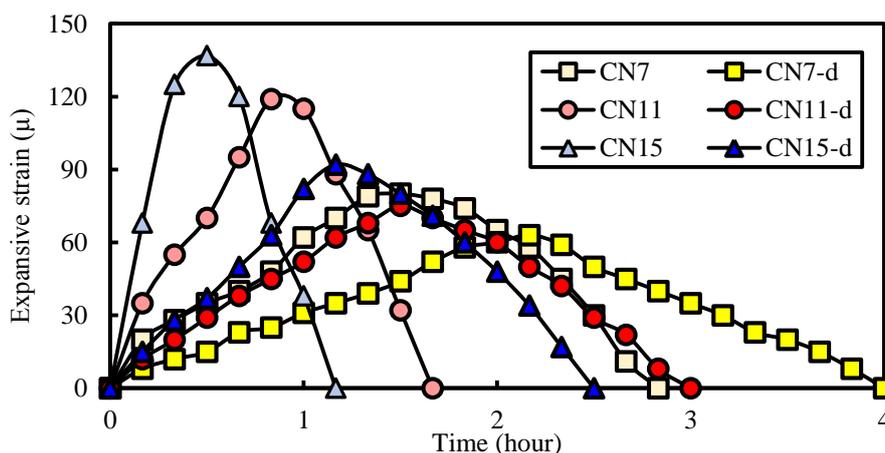


Fig. 5 Changes of expansive strain

### (3) Changes in the pore structure

The pore volume distributions of mixes CN0, CN11, and CN-d are presented in Fig. 6, and the cumulative pore volume distributions of each case are presented in Fig. 7. When the specimens were cured for 1 d, the pore volume of mixes CN11 and CN11-d became larger when compared with that of mix CN0 without the accelerator, and the total pore volume became smaller when compared with that of mix CN0. This is because the hydration reaction was sufficiently enhanced because of using a large proportion of the nitrite-based accelerator. On the other hand, when the specimens were cured for 7 and 28 d,

there were no significant differences in the pore distributions between mixes CN11 and CN11-d. However, the total pore volume of mix CN11-d became smaller when compared with that of mix CN11 without the high-range water-reducing agents. When a large proportion of the accelerator only was used, it was assumed that the total pore volume increased owing to the formation of the rough hydrated phases during the initial hydration process.

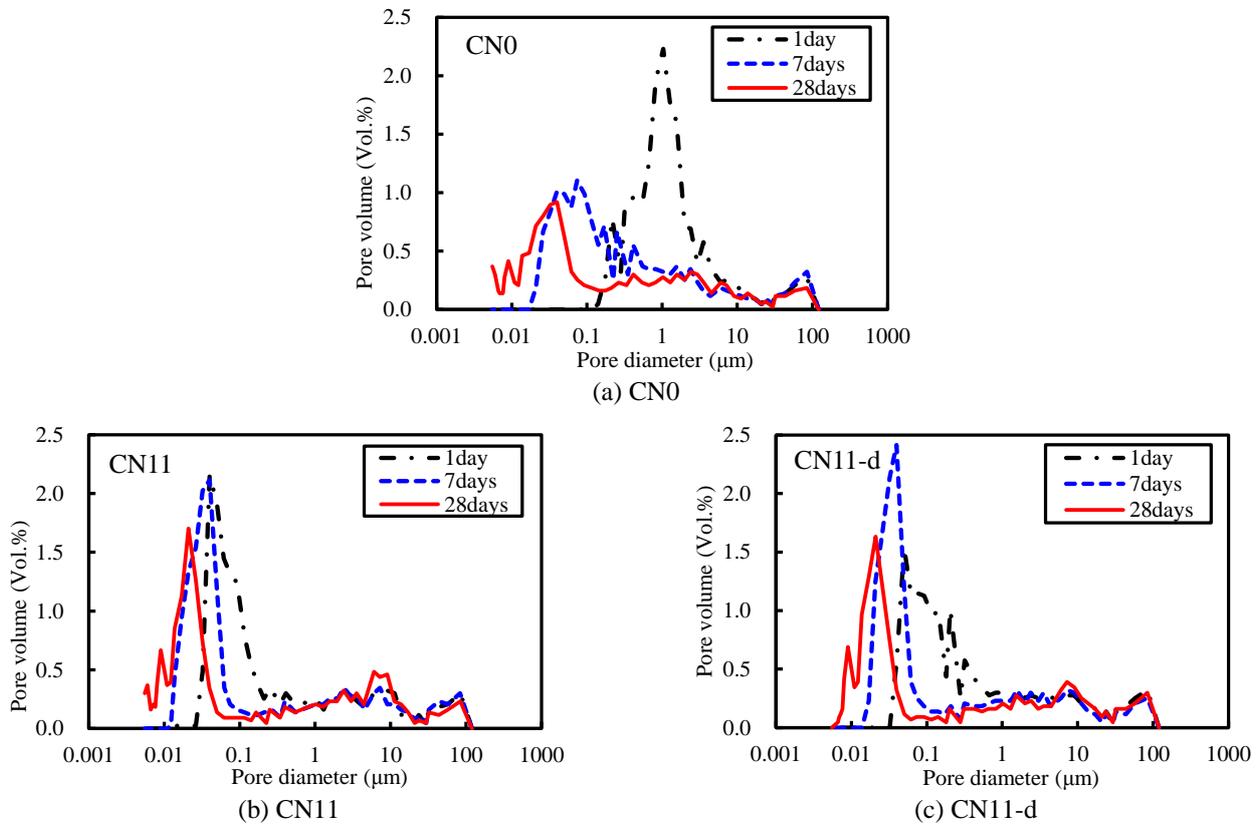


Fig. 6 Pore volume distribution

#### 4. Conclusions

The aim of this study was to develop a high-performance nonfreezing agent for use in the construction of cold-weather concrete. Tests to determine the fresh properties and strength development processes of mortar specimens containing a nonfreezing agent were performed, and the contributions of a nitrite-based accelerator and high-range water-reducing agents used in combination were examined. The following conclusions were obtained from the investigation.

- (1) The changes in the mortar flow of mix CN11-d, which contained a large proportion of accelerator and two types of high-range water-reducing agents, became smaller, and this mix had good fluidity even after the passage of 60 min after the completion of mixing.
- (2) When a large proportion of the accelerator only was used, the compressive strength at 1 d increased with an increase in the amount of added accelerator. However, after 3, 7, 14, and 28 d of curing, the compressive strength decreased with an increase in the amount of added accelerator.
- (3) Mix CN11-d (with Me:Pc=2:1) showed not only the initial strength for preventing initial frost damage but also maintained good strength for a long time.
- (4) The expansion strain of mix CN11-d was smaller than that of mix CN11 without high-range water-reducing agents. Furthermore, the total pore volume of mix CN11-d after 28 d of curing was smaller when compared with that of mix CN11.

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