The fundamental study on the expansion and shrinkage behaviors of concrete using nitrite-based accelerator

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ABSTRACT

In the preparation of concrete that can withstand cold weather conditions, a non-freezing agent is added to prevent initial frost damage by simplified curing and promote strength development at an early stage. In general, a nitrite-based accelerator is used as the main component of this non-freezing agent. When a large proportion of accelerator is used, expansion and shrinkage of the concrete are increased as hydration of C\textsubscript{3}S (alite, 3CaO·SiO\textsubscript{2}) and C\textsubscript{2}S (belite, 2CaO·SiO\textsubscript{2}) is promoted from the beginning. If the transformation of the concrete becomes big, it will affect the durability for crack propagation in the long term.

In this study, we conducted fundamental research to clarify the effect of a large amount of nitrite-based accelerator on the expansion and shrinkage characteristics and strength development of concrete. As the addition amount of nitrite-based accelerator was increased, the hydration of the cement was rapidly promoted, and the expansion increased from over a long period, even after curing in an environment with temperature at -10 °C environment; the amount of C–S–H gel produced by the hydration eventually exceeded the amount of Ca(OH)\textsubscript{2}. Moreover, the void structure ratio gradually decreased. These changes were found to greatly affect the strength development of concrete.

1. INTRODUCTION

When constructing cold-weather concrete, it is necessary to prevent initial frost damage by controlling the temperature of heat curing through the use of a temporary enclosure and heater. When it is difficult to install the temporary enclosure owing to a steep slope at the construction site, narrow working space, or strong wind, a non-
freezing agent is commonly used to prevent initial frost damage and secure initial strength development through simplified curing [1]. Furthermore, the function of the agent is to reduce the freezing temperature of water in the concrete. We have been studying the characteristics of concrete that was prepared using a nitrite-based accelerator and chemical admixtures in a low-temperature environment to develop a high-performance non-freezing agent [1, 2]. In general, a nitrite-based accelerator is used as the main component of this non-freezing agent. In particular, calcium nitrite (Ca(NO\textsubscript{2})\textsubscript{2}) chiefly accelerates the hydration process by increasing the solubility of C\textsubscript{3}S (alite, 3CaO·SiO\textsubscript{2}) and C\textsubscript{2}S (belite, 2CaO·SiO\textsubscript{2}) and reacts with C\textsubscript{3}A (aluminate phase, 3CaO·Al\textsubscript{2}O\textsubscript{3}) in cement to generate hydronitroaluminate, 3CaO·Al\textsubscript{2}O\textsubscript{3}·Ca(NO\textsubscript{2})\textsubscript{2}·10H\textsubscript{2}O. Furthermore, calcium nitrite (Ca(NO\textsubscript{2})\textsubscript{2}) also reacts with calcium hydroxide in concrete to generate calcium hydroxynitrate, CaO·Ca(NO\textsubscript{2})\textsubscript{2}·3H\textsubscript{2}O. These cement hydrates lead to a refinement in cement hardening; hence, they improve the mechanical properties of concrete in low-temperature environments [3].

A considerable number of studies have been conducted on the effects of a non-freezing agent on the properties of concrete at the initial stage after production. However, very few attempts have been made study the expansion and shrinkage characteristics of concrete consisting of a non-freezing agent after casting. In a low-temperature environment of -10 °C or less, it is necessary to add a larger amount of the non-freezing agent; with this increase, however, the hydration reaction of the C\textsubscript{3}SC\textsubscript{2}S phases progresses from the initial stage. In addition, the reaction of C\textsubscript{3}A generates a large amount of ettringite [3]. As a result, the expansion of concrete increases from the initial stage, and there is concern about the occurrence of cracks in the structure and adverse effects on durability in the long term.

The purpose of this study is to clarify the effect of a large proportion of a nitrite-based accelerator on the deformation characteristics and strength development of cement materials at -10 °C. The compressive strength and the expansion and shrinkage strain of the hardened cement materials were measured when the proportion of the nitrite-based accelerator was changed. Furthermore, the amount of hydration product and the void volume ratio were measured at each stage, and the correlation between each item on a checklist were examined.

2. OUTLINE OF THE EXPERIMENTS

2.1 Materials used

In this study, experiments were conducted using cement paste to clarify the promotion of hydration of cement materials by a nitrite-based accelerator. Normal Portland cement (hereafter abbreviated as C; density: 3.16 g/cm\textsuperscript{3}) was used, and a 45% water solution composed primarily of calcium nitrite (CN45; density: 1.42–1.44 g/cm\textsuperscript{3}) was used as the accelerator.

2.2 Mixing proportions and experimental conditions

The mixing proportions and curing temperatures used to prepare the cement materials are listed in Table 1. The water-to-cement (W/C) ratio was 50%. The standard replacement ratio of conventional accelerators is approximately 4–7% of the unit content of cement (3–5 L per 100 kg of cement). In this study, the replacement ratios of
CN45 were 0%, 11% (7.6 L per 100 kg of cement), 14% (17 L per 100 kg of cement), as recommended by our previous studies of high-performance of non-freezing agent [1, 2]. The temperature of concrete at the time of unloading is specified as 10–20 °C by the Architectural Institute of Japan in “Recommendation for Practice of Cold Weather Concreting” [4]. In this study, the material management and mixing of cement paste were performed in the testing room with control of temperature and humidity (temperature: 10 ± 1 °C, relative humidity: 85 ± 5%) to control the temperature of the fresh cement paste.

The temperature settings of the experiments are shown in Figure 1. After mixing, cement paste samples were cast, and the test surfaces of the specimens were covered with a thin vinyl sheet to protect the concrete by sealed curing. The specimens were cured at 10 ± 1 °C for one day, and then at -10 ± 2 °C for the next 13 days. Furthermore, the specimens were cured at 20.0 ± 1 °C from day 14 to day 28 days to ensure strength recovery. And some specimens were cured at a constant temperature of -10.0 ± 2 °C from day 14 to day 28. In addition, the material management and mixing of cement paste were performed at 20.0 ± 1 °C and 85 ± 5% relative humidity. After casting under the same conditions, the sealed specimen was cured at 20.0 ± 1 °C for 28 days.

Table 1. Mixing proportions and curing temperatures for the preparation various samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>W/C (%)</th>
<th>Unit content (kg/m³)</th>
<th>Admixture (C×%)</th>
<th>Curing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN0_-10</td>
<td>50</td>
<td>617</td>
<td>0</td>
<td>+10 → -10 → +20</td>
</tr>
<tr>
<td>CN11_-10</td>
<td>50</td>
<td>617</td>
<td>11</td>
<td>+10 → -10 → +20</td>
</tr>
<tr>
<td>CN14_-10</td>
<td>50</td>
<td>617</td>
<td>14</td>
<td>+10 → -10 → +20</td>
</tr>
<tr>
<td>CN0_20</td>
<td>50</td>
<td>617</td>
<td>0</td>
<td>+20</td>
</tr>
</tbody>
</table>

2.3 Test method

The compressive strength (φ50 × 100 mm) was measured after 1, 3, 7, 14, and 28 days of curing under the different conditions, as shown in Figure 1.

In the unrestrained deformation test, the cement paste was cast in the mold (10 × 10 × 40 cm). A polytetrafluoroethylene sheet and a styrene board were installed on the inside of the mold to prevent restraint of cement on the surface and water dispersion of
hardened cement paste. An embedded gauge was also installed in the center position of the mold. After that, the sealed specimens were cured under the different conditions shown in Figure 1. The expansion and shrinkage strain of the test specimen for each case was measured immediately after casting.

An X-ray computed tomography (CT) scan was conducted at 1, 3, 7, and 28 days of age to observe any change in the void structure of the specimen. The size of the specimen was φ50 × 100 mm, and an X-ray beam (180 kV, 40 μA) irradiated the specimen. In addition, as Figure 2 shows, the void structure was compared by setting an image analysis area and analyzing the three-dimensional (3D) image [5]. Meanwhile, in the histogram of luminance and frequency of the 3D image, normal distribution of each peak shows a clear the boundary luminance between luminance of the void and the cement matrix. After that, the void volume was calculated, and the void structure ratio was analyzed using the difference between the void density and the cement matrix density.

The hydration product and the hydration ratio were measured using thermogravimetric–differential thermal analysis (TG–DTA) at the predetermined test age. The decomposition temperature ranges of calcium hydroxide (Ca(OH)\(_2\)) and calcium silicate hydrate (C–S–H) gel in TG–DTA are 420–500 °C and 650–750 °C, respectively; endothermic peaks are generated by decomposition in these ranges, and the weight of the sample is decreased by the endothermic reaction [6]. The mass change of Ca(OH)\(_2\) and C–S–H gel in these temperature ranges were measured at days 7, 14, and 28 of curing, and the hydration ratio in each case was calculated from the mass change before and after the TG–DTA measurement [7].
3. RESULTS AND DISCUSSION

3.1 Compressive strength

The results of the compressive strength test are presented in Figure 4. When the specimens were cured at +10 °C immediately after mixing for one day, mix CN0_-10 showed a compressive strength of 2.7 MPa. However, mixes CN11_-10 and CN14_-10 showed compressive strengths 5.1 and 5.8 MPa, respectively, which exceeded 5.0 MPa. When the specimens were further cured at -10 °C until day 14, the compressive strength of mix CN0_-10 was 4.1 MPa, but 9.4 and 13.5 MPa for mixes CN11_-10 and CN14_-10, respectively. When the specimens were cured at -10 °C from day 14 day to day 28, the compressive strengths of mixes CN0_-10, CN11_-10, and CN14_-10 were 4.9, 13.3, and 18.5 MPa, respectively. On the other hand, when the specimens were cured at 20 °C from day 14 day to day 28 days, the compressive strengths of mixes CN0_-10, CN11_-10, and CN14_-10 were 20.6, 30.1, and 41.7 MPa, respectively. In particular, the compressive strength of mix CN14_-10, which contained a large amount of CN45, was almost the same as that of mix CN0_20 (45.2 MPa), which was cured at 20 °C for 28 days. Based on the strength recovery at 20 °C from day 14 days to day 28 observed for mixes CN11_-10 and CN14_-10, it is thought that further strength recovery was possible with passing time.

Figure 5 shows the compressive strength ratio and the regression equation at -10 °C from day 1 to day 14. The compressive strength ratio is a value obtained by setting the compressive strength at day 1 as 100%. On day 14, the compressive strength of mix CN0_-10 showed a tendency to increase by about 150%, mix CN11_-10 by about 195%, and mix CN14_-10 by about 230%. In addition, from the regression equation, the compressive strength of mix CN11_-10 was about twice that of mix CN0_-10, and the compressive strength of mix CN14_-10 was about 2.5 times that of mix CN0_-10. As a result, it can be confirmed that when the outside air temperature was -10 °C, the compressive strength increased by increasing the amount of added calcium nitrite (Ca(NO\(_2\))\(_2\)).
3.2 Unrestrained expansion and shrinkage strain

The expansion and shrinkage strain behavior of each sample under unrestrained deformation is presented in Figure 6. Since the experimental data for mix CN14_-10 were not available owing to failure, this sample was excluded from our examinations. When the specimens were cured at +10 °C immediately after mixing for one day, the maximum expansion strain during this time was 223 μ in mix CN0_-10 after about 10 h. 734 μ in mix CN11_-10 after about 13 h, and 260 μ in mix CN0_20 after about 9 h. It is thought that mix CN11_-10 showed a large expansion strain because the reaction rate of C₃A was very high from the initial stage of casting, the hydration of C₃S and C₂S was promoted to some extent, and the setting was accelerated immediately after the mixing of the cement paste [3, 8]. Then, when the specimens were cured at -10 °C until day 14, mix CN0_-10 showed continuous shrinkage, with a strain of about 260 μ on day 14. Mix CN0_-10 showed an expansion strain of about 50 μ about 10 h after the beginning of curing at -10 °C and remained constant until day 14. In contrast, mix CN11_-10 expanded and showed a strain of about 400 μ about 12 h after curing at -10 °C began; it then shrank and the strain reached about 160 μ, after which expansion progressed gradually, showing an expansion strain of about 270 μ on day 14. Mix CN11_-10 experienced the second expansion because calcium nitrite (Ca(NO₃)₂), which did not react in the 10 °C environment for up to 1 day, eventually reacted with the cement particles, thus promoting the hydration of C₃A and C₃S [3, 8]. In addition, of the small increase in strain resulted from the gradual contribution of a large amount of calcium hydroxide and C₂S to hydration. When the specimens were cured at 20 °C from day 14 to day 28, mix CN0_-10 showed slight expansion and shrinkage. However, mix CN11_-10 expanded and showed a strain of 640 μ after about 10 h, after which it shrank gradually. This is considered to represent the hydration reaction between unreacted Ca(NO₃)₂ remaining in the cement matrix and the unhydrated cement particles, as well as the behavior of the cement paste as the temperature was varied from -10 °C to 20 °C; these changes are presumed to have resulted in the strength of the cement paste.
3.3 Changes in void structure

The changes in the void structure ratio of each sample are listed in Table 2. The void structure ratio decreased as the material age advanced. In particular, there was no significant difference on day 1 in the ratios of the samples without and without added CN45. However, in the subsequent period of curing at -10 °C, the void structure ratio decreased significantly from day 3 to day 7, indicating that the densification of the tissue progressed with hydration even in the low-temperature environment. In addition, after curing at 20 °C from day 14 to day 28, the void structure ratio of mix CN0_-10 was 0.13%, but 0.06% and 0.05% for mixes CN11_-10 and CN14_-10 was, indicating that the ratio decreased greatly when a large amount of CN 45 was added.

Changes in the void structure of each sample are presented in Figure 7 as 3D images. The color of each image changes in accordance with the density. Therefore, the lower the density, the thicker the displayed color, whereas the higher the density, the thinner the color. During observation of the 3D analysis images of samples containing CN45, calcium nitrite (Ca(NO$_2$)$_2$) reacted with cement particles to promote the hydration of C$_3$A and C$_3$S in the initial hydration process. After that, calcium hydroxide and C$_2$S gradually contributed to hydration, which suggests that the void structure ratio decreased even in a low-temperature environment and at normal temperatures.
Table 2. Changes in the void structure ratio (%) of each sample.

<table>
<thead>
<tr>
<th>Curing temperature</th>
<th>+10 °C</th>
<th>-10 °C</th>
<th>+20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>1 day</td>
<td>3 days</td>
<td>7 days</td>
</tr>
<tr>
<td>CN0_-10</td>
<td>0.23</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>CN11_-10</td>
<td>0.21</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>CN14_-10</td>
<td>0.21</td>
<td>0.13</td>
<td>0.08</td>
</tr>
<tr>
<td>CN0_20</td>
<td>0.24</td>
<td>0.21</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 7. 3D images showing changes in the void structure of each sample.

3.4 Changes in the hydration product and hydration ratio

The hydration ratio determined based on the relationship between the extent of decomposition of calcium hydroxide \((\text{Ca(OH)}_2)\) and calcium silicate hydrate \((\text{C–S–H})\) gel is listed in Table 3 for various samples. In the curing period from the immediately after mixing until the day 7 day (+10°C → 10°C), the ratio of hydration was about 20% higher for mix CN11_-10 than mix CN0_-10, and about 30% higher for mix CN14_-10 than mix CN0_-10. In particular, mix CN14_-10 reached the same hydration rate as mix
CN0_20. When comparing the hydration ratio after curing at -10 °C from day 14 to day 28, compared with mix CN0_-10, the hydration rate of mix CN11_-10 increased about 30% and the hydration rate of mix CN14_-10 increased by about 35% to 40%, however the hydration rate was lower than that of mix CN0_20. When the curing temperature was increased from -10 to 20 °C, mixes CN11_-10 and CN14_-10, to which CN45 was added, showed the same degree of hydration as mix CN0_20.

On the other hand, changes in the amount of Ca(OH)2 and C–S–H gel produced in each sample are presented in Figure 8. The amount of hydrated product produced increased during curing in a -10 °C environment. From this, understand that it gradually expanded in low-temperature environment. When the samples were prepared with the addition of CN45, hydration was promoted by the effect and that the amount of C–S–H gel produced was larger than in the sample prepared without CN45. After that, when the curing temperature was changed from -10 to 20 °C on day 28, and the amount of C–S–H gel formed was significantly higher than that in the sample cured at -10 °C for 28 days. In particular, the amount of C–S–H gel formed after 28 days in mix CN14_-10 cured at -10 to 20 °C showed a tendency to exceed the amount formed in mix CN0_20 that was cured at 20 °C. As a result, it is considered that the hydration reaction of Ca(NO2)2 was likely to affect not only the hydration promotion immediately after the setting, but also in the long term.

Table 3. Changes in the hydration ratio (%) of each sample.

<table>
<thead>
<tr>
<th>Curing temperature</th>
<th>-10 °C</th>
<th>-10 → +20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>7 days</td>
<td>14 days</td>
</tr>
<tr>
<td>CN0_-10</td>
<td>10.99</td>
<td>9.75</td>
</tr>
<tr>
<td>CN11_-10</td>
<td>13.96</td>
<td>14.04</td>
</tr>
<tr>
<td>CN14_-10</td>
<td>15.77</td>
<td>16.09</td>
</tr>
<tr>
<td>CN0_20</td>
<td>16.00</td>
<td>17.85</td>
</tr>
</tbody>
</table>

Figure 8. Changes in the amount of Ca(OH)2 and C–S–H gel produced in each sample.
The aim of this study is to clarify the effect of expansion and shrinkage characteristics of concrete in the winter season when the outside temperature is -10 °C and its effect on strength development when a large amount of nitrite-based accelerator was added during its preparation. The compressive strength and the expansion and shrinkage behavior of the hardened cement were measured by changing the amount of added nitrite-based accelerator (CN45). Furthermore, the amount of hydration product and the void structure ratio were measured at each material age, and the correlations between each item were examined. The following conclusions can be drawn from the investigation:

1) After curing in the environment with temperature of -10 °C, strength was recovered by curing by changing the temperature to 20 °C. Furthermore, increasing the amount of addition CN45 increased the strength increase ratio.

2) By adding a large amount of CN45 immediately after mixing, the hydration of specimens during curing at +10 °C was abruptly promoted and expansion increased. Even during subsequent curing at -10 °C, the hydration of cement was accelerated in the long term as a result of the addition of CN45, contributing to the development of strength.

3) When curing was performed in the environment with temperature of -10 °C, hydration proceed as a result of the addition of CN45. More calcium silicate hydrate (C–S–H) gel was produced than Ca(OH)₂, and the void structure ratio gradually decreased. In addition, as the amount of added CN45 was increased, the hydration ratio after 28 days became higher. The accelerated hydration led to the development of strength.

REFERENCES

