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Study on shrinkage behavior of cementitious materials with large addition of nitrite-based accelerator under restraint conditions

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ABSTRACT

Recently, the use of calcium-nitrite ($Ca(NO_2)_2$) and calcium-nitrate ($Ca(NO_3)_2$) as the main component of salt- and alkali-free anti-freezing agents has been increasing for the purpose of promoting concrete hydration in cold weather concreting. As the amount of nitrite-based accelerators increases, the hydration of C_3A, C_3S and βC_2S in the cement is accelerated, thereby improving early strength and effectively preventing the initial frost damage. Meanwhile, as the amount of nitrite-based accelerators increases, it is expected that the expansion and shrinkage of the concrete will increase, and therefore, the crack occurrence could possibility increase.

In this study, various experiments were conducted on shrinkage and crack initiation and development of mortar containing a large amount of a nitrite-based accelerator. As a result, it was confirmed that as the amount of the nitrite-based accelerator was increased, the shrinkage was increased and the cracking in early age were more likely to occur than in cases without the addition of the nitrite-based accelerator.

1. INTRODUCTION

When cold-weather concreting, it is necessary to control the temperature until the concrete strength reaches $5N/mm^2$ of heat curing by using a temporary enclosure and heater in order to prevent initial frost damage. On the other hand, when the temperature is very low or the conditions are bad in situations such as a steep slope, narrow space, or strong wind, anti-freezing agents are used to prevent initial frost damage and secure initial strength by sheet curing. Generally, the allowable range of anti-freezing agents is -4 to -8°C **[1]**. However, when the daily average temperature is below -10°C, it is necessary to increase the amount of anti-freezing agents.

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At present, calcium nitrite and calcium nitrate are used as the main components of a salt- and alkali-free type nitrite-based accelerator (CN) **[2][3]**. It has been proposed that Increasing the amount of nitrite-based accelerator contributes to good initial strength development in low-temperature environments due to the effect of hydration promotion of C_3A in cement as well as hydration promotion due to the increased solubility of C_3S and βC_2S **[4][5]**. In "Japanese Architectural Standard Specification for Reinforced Concrete Work JASS5", it is necessary to reduce shrinkage cracks in order to ensure the durability of concrete. Therefore, it is stipulated that the drying shrinkage rate of concrete is under 8×10^{-4} **[6]**.

Nitrite-based accelerator (CN) accelerates the hydration reaction of C_3A contained in cement and increases the amount of ettringite and monosulfate **[7][8][9]**. The reason for this is that hydrate such as nitrite-nitrate hydrate ($3CaO\cdot Al_2O_3\cdot Ca\ (NO_2/NO_3)_2\cdot xH_2O$) are formed through reactions between C_3A (Al_2O_3) and NO_2^- and NO_3^- ions of the CN **[7][8][9]**. Therefore, the chemical shrinkage potential of the cement matrix increases, and it is expected that there is greater concern about shrinkage cracking. However, few studies have focused on shrinkage cracking.

In this study, we aim to clarify the shrinkage behavior of concrete and the initiation and development of cracks when a large amount of CN is present in the mixture. Therefore, various experiments were conducted to quantitatively evaluate the physical properties and shrinkage cracking properties of mortar containing a large amount of CN. **Figure 1** shows the flow chart for this study.

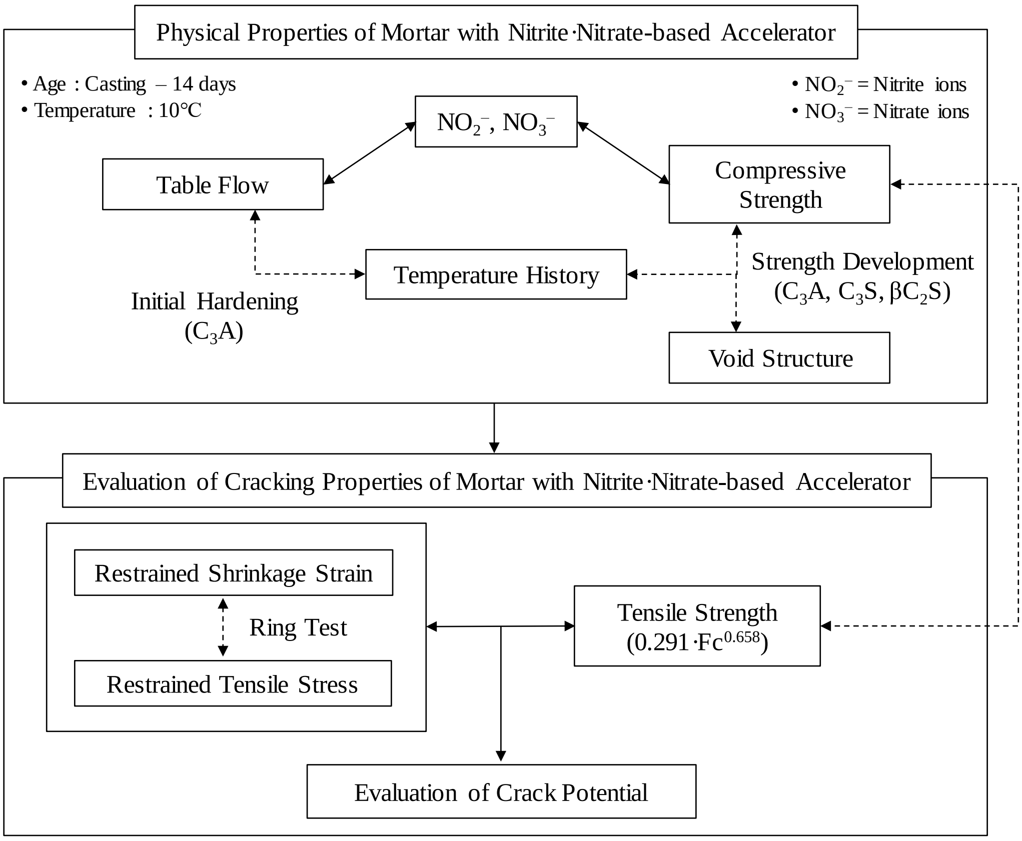


Figure 1. Study flow chart

2. EXPERIMENT

2.1 Materials and procedures

Table 1 presents the materials used and **Table 2** presents the components of CN used in this experiment. The CN is a 45% mixed aqueous solution of calcium nitrite and calcium nitrate. **Table 3** presents the mortar composition used in this experiment. Water-cement ratio was 50% and S/C was 2.5 **[3][4]**. The standard addition amount of accelerator is approximately 4 to 7% of cement mass (3 to 5 L per 100 kg of cement) depending on the ambient temperature **[3]**. Assuming the case where a large amount of CN was added in the severe cold season, the addition amount of CN was set to 4 levels of 0%, 7%, 9%, and 11% when compared to the cement weight. The temperature of concrete at the time of unloading is specified as 10 to 20 °C by the Architectural Institute of Japan in the Recommendation for Practice of Cold Weather Concreting [Practical Guideline for Investigation (2010)]. In this study, the mixing and curing were performed in a temperature- and humidity-controlled testing room (10 ± 1 °C and 85% ± 5% relative humidity) to control the temperature of the mortar.

Table 1. Properties of the materials used

Materials (Code)	Properties
Cement (C)	Normal Portland Cement, Density: 3.16 g/cm^3
Fine aggregate (S)	No.5 silica sand, Absolute dry density: 2.61 g/cm^3
Accelerator (CN45)	Main component: calcium nitrite; calcium nitrate (45% water solution)

Table 2. Properties of the nitrite-based acclerator (CN)

Component	Component ratio	Density of aquarious solution	pH aquarious solution
$Ca(NO_2)_2$	23.02%	1.43 g/cm^3	9.3
$Ca(NO_3)_2$	22.81%		

Table 3. Mix proportions of mortar

Specimen	W/C(%)	S/C	Until content (kg/m^3)			CN (C×%)
			W	C	S	
CN0	50	2.5	281	562	1407	0
CN7						7
CN9						9
CN11						11

Note: W/C; water-cement ratio, (C × %); weight ratio to the cement weight used, CN0; Mixing amount of anti-freezing agent = 0%, CN7; Mixing amount of anti-freezing agent = 7%, CN9; Mixing amount of anti-freezing agent = 9%, CN11; Mixing amount of anti-freezing agent = 11%

2.2 Fresh property

The fresh properties conformed to JIS R 5201 “Flow test”, and a table flow test was performed immediately after mixing.

2.3 Compressive Strength

As for the compressive strength, mortar was placed into a φ10×20cm mold, and was demolded at the age of 1 day to carry out sealing curing. After that, a compressive strength test was performed at each age (1d, 3d, 7d, 14d).

2.4 Internal temperature

For the internal temperature, a thermocouple was installed in the center of the mold with a diameter of 10×20cm, and the time-dependent change in mortar temperature immediately after placement was measured.

2.5 Void structure

The change in the void structure with time was measured using a Mercury Injection Method (MIP) to measure the void volume and void diameter. After the compressive strength test, a sample of about 5mm square was taken from the center of the test piece. The sample was immersed in acetone for 4 hours to stop hydration, and dried in a vacuum chamber for 3 days.

2.6 Restrained shrinkage strain

To determine the restrained shrinkage, restrained shrinkage strain due to the internal steel ring's restraint was measured when the height of the ring specimen was set to 75mm from the 152mm previously proposed by AASHTO (1998) to induce uniform dry shrinkage at the cross-section of the concrete ring, as shown in **Figure 2 [15]**. In this experiment, a teflon sheet was installed between the outer ring and the mortar to minimize the restraint from the outer ring and provided to prevent evaporation of water on the upper part of the test body. At the age of 1 day, the lower wood plate and the upper teflon sheet of the ring specimen were removed so that only the upper and lower surfaces were dried. For restraint shrinkage strain, strain gauges were attached at three locations (h = 37.5mm) in the center of the inner ring, and the change with time of strain was measured immediately after placing.

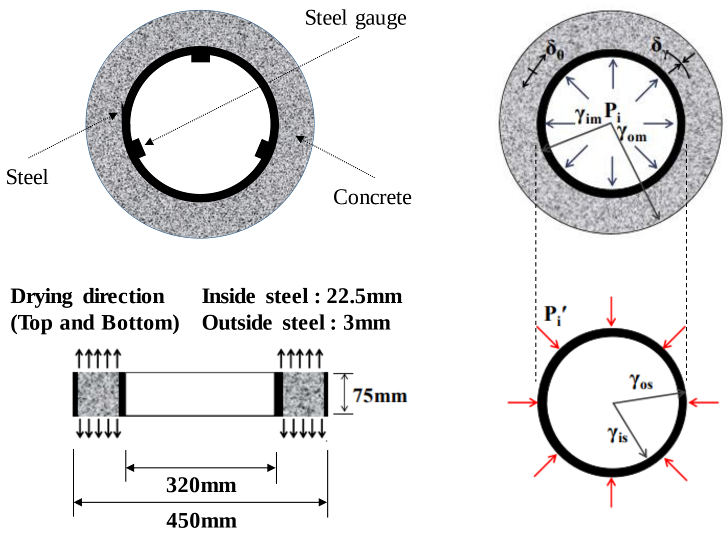


Figure 2. Overview of ring test (Restrained shrinkage strain)

3. EVALUATION OF PHYSICAL PROPERTIES

3.1 Fresh property

Figure 3 shows the results of the table flow test in each case. The flow value was 186 mm for CN0, and based on the flow value of CN0, CN7 decreased by 6.5%, CN9 decreased by 9.2%, and CN11 decreased by 25.9%. AS the amount of the CN increased, flow value tended to decrease. **Figure 4** shows the history of the internal temperature of the mortar (~ 2h). The temperature peaks are 15.2°C for CN0, 17.1°C for CN7, 18.6°C for CN9 and 22.0°C for CN11. As the amount of CN increased, the temperature tended to rise. When CN is added, in addition to that produced by normal hydration reaction, NO_2^- and NO_3^- react rapidly with C_3A in cement to produce nitrite/nitrate hydrate **[5][7][9][10]**. From these results, it is considered that when a large amount of CN is added, hydration is promoted, the mortar temperature rises, and the flow value decreases.

3.2 Compressive Strength

Figure 5 shows the compressive strength from 1 to 14 days in each case. The day 1 compressive strength is 4.38N/mm^2 for CN0, 5.15N/mm^2 for CN7, 6.51N/mm^2 for CN9 and 7.03N/mm^2 for CN11, the strength tended to increase as the amount of CN increase. **Figure 6** shows the mortar internal temperature history (~ 24h). Especially, the temperature peaks of 0 to 4 hours and 6 to 18 hours has risen **[8]**, and the time to reach the peak became shorter. As the amount of CN increased, the temperature tended to rise. When the amount of CN increases, the amount of NO_2^-, NO_3^- increases and reacts rapidly with C_3A in the cement, which promotes hydration, raises the mortar temperature, and increases the amount of nitrite/nitrate hydrate. Therefore, it is considered that the strength of day 1 increased. However, the compressive strength at 3 days tends to decrease as the amount of CN increases. Furthermore, this tendency became remarkable after 7 days, and the case of adding CN was below the strength of CN0. As the amount of CN increases, the amount of ettringite and nitrite/nitric hydrate produced increases. Therefore, it is considered that the structure became dense and the strength increased at day 1. After 3 days, when CN was added, a large amount of H_2O was consumed as the amount of nitrite/nitrate hydrate increased **[7][9][10]**. From this, the amount of C-S-H and $Ca(OH)_2$ produced by the reaction of ordinary cement is relatively reduced, and the structure without CN is denser than with CN. Therefore, it is considered that the strength increased.

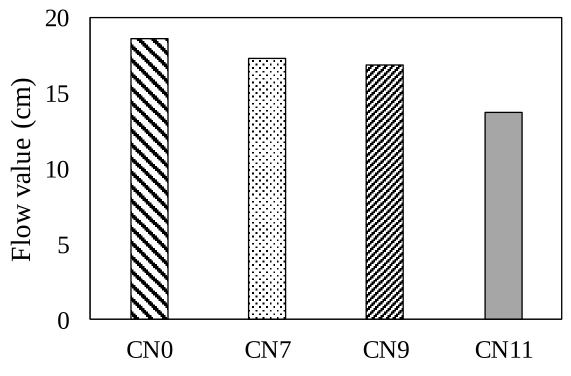


Figure 3. Flow value

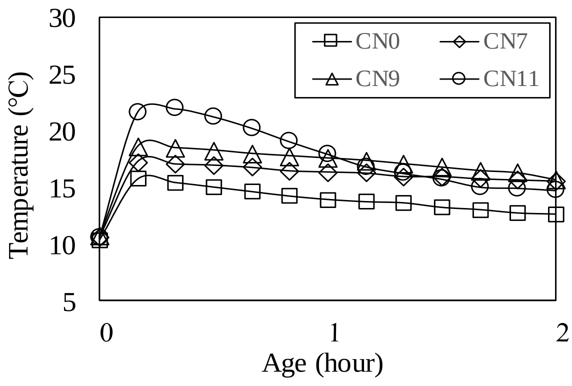


Figure 4. Temperature history (up to 2 hours)

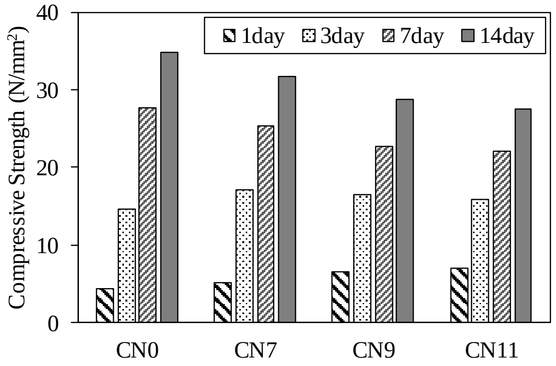


Figure 5. Compressive strength

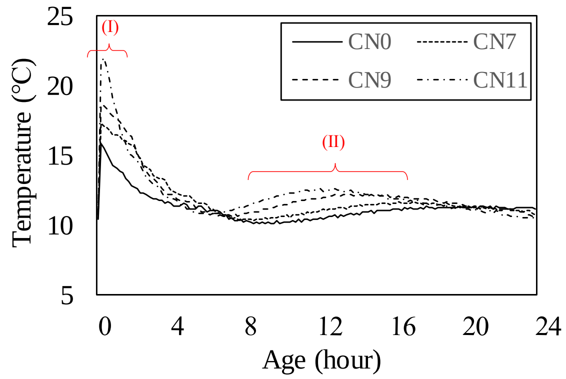


Figure 6. Temperature history (up to 24 hours)

3.3 Void structure

Figure 7 shows the void distribution at day 1. CN1 had a void distribution in the range of 0.5 to 5μm, CN7 from 0.1 to 3μm, CN9 from 0.05 to 0.5μm, and CN11 from 0.03 to 0.1μm. From these results, the void diameter and the void volume tended to decrease as the amount of CN added increased. In particular, in the case of a large amount of CN was added (CN9, CN11), there were many voids within the range of 0.05μm or less, which is considered to greatly affect dry shrinkage **[8]**. **Figure 8** shows the void distribution at 14 days. In all cases, the void volume tended to be smaller than the void volume on day 1. From these results, it is considered that the addition of CN increases the amount of nitrite/nitrate hydrate produced immediately after mixing and promotes hydration, and the voids are filled, resulting in good strength at day 1. On the other hand, at 14 days, there was no clear relationship between the void structure and the fact that the case of adding CN had lower compressive strength than the case of adding no CN.

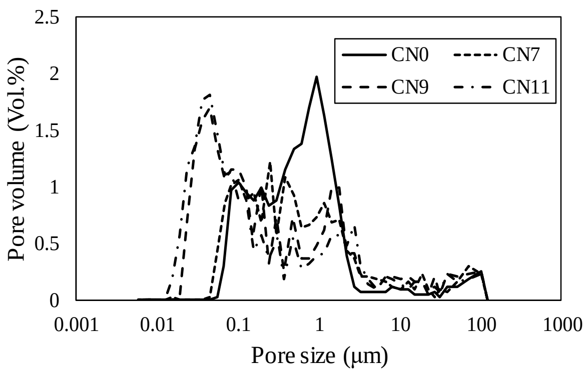


Figure 7. Void distribution (1d)

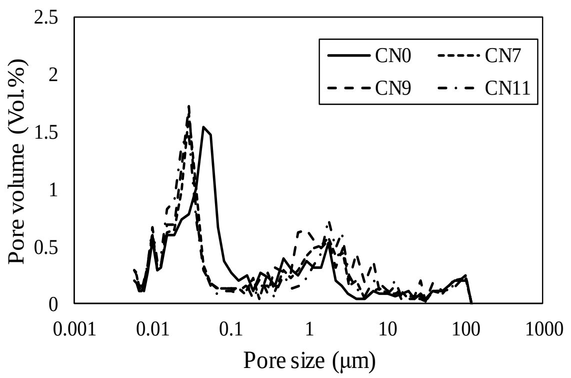


Figure 8. Void distribution (14d)

4. SHRINKAGE CRACKING CHARACTERIZATION

4.1 Restrained shrinkage

Figure 9 shows the restrained shrinkage strain results for the ring test. **Table 4** shows the occurrence of cracks in each test piece and the number of days until the occurrence of cracks. First, the shrinkage was started after casting, about 10 hours for CN11, 11 hours for CN9, after 12 hours for CN11, and after 36 hours for CN0. In particular, in the case of adding CN, shrinkage gradually occurred about 6 hours after casting. After that, cracks occurred in the process of increasing shrinkage. The cracking dates were 2.8 days for CN11, 3.6 days for CN9, and 4.4 days for CN7. Cracks tended to occur faster as the amount of CN increased. The restrained shrinkage strain at the time of cracking were 25μ for CN11, 27μ for CN9, 30μ for CN7. On the other hand, in the case of CN0, no cracks occurred during the measurement period of this experiment.

4.2 Restraint tensile stress and crack potential

The restraint tensile stress can be calculated by **Eq. (1)** using the radiuses of the concrete and steel ring, restrained shrinkage strain, and the elastic modulus of the steel ring assuming that the concrete poured into the ring specimen had uniform shrinkage in the shear plane with linear behavior **[11][12][13]**.

$$\sigma_{\theta imax} = \frac{({\gamma_{os}}^2 - {\gamma_{is}}^2)}{2{\gamma_{os}}^2} \cdot \frac{({\gamma_{im}}^2 + {\gamma_{is}}^2)}{({\gamma_{om}}^2 - {\gamma_{im}}^2)} \cdot E_{st} \cdot \varepsilon_{st} \quad (1)$$

Here, $\sigma_{\theta imax}$ refers to the restraint tensile stress, γ_{is} and γ_{os} refer to internal and external radii of the steel ring, γ_{im} and γ_{om} refer to the internal and external radii of the concrete, E_{st} refers to the elastic modulus, and ε_{st} refers to the restrained shrinkage strain.

Figure 10 shows the restraint tensile stress calculated by **Eq. (1)**. The restraint tensile stress tended to increase as the restraint shrinkage strain increased. The maximum restrained tensile stress was 1.8N/mm^2 for CN11, 1.9N/mm^2 for CN9, and 2.1N/mm^2 for CN7, and cracks occurred after reaching maximum tensile stress. The restrained tensile stress increased as the amount of CN added increased due to the increase in pressure generated in the inner steel ring. It was confirmed that this accelerates the occurrence of cracks in the mortar. It is considered that the stress relaxation was reduced by the tensile creep. On the other hand, the cracking potential was calculated by the ratio of restraint tensile stress/tensile strength. **Figure 11** shows the change in tensile strength over time, and **Figure 12** shows the crack potential in each case. The tensile strength was calculated by **Eq. (2)** using the result of the compressive strength **[14][15]**.

$$\sigma_B = 0.291 \cdot Fc^{0.658} \quad (2)$$

Here, σ_B refers to the tensile strength and Fc refers to the compressive strength.

In the case of adding CN, the cracking potential increased between the age of 1 day and 2 days. The possibility of the occurrence of cracking became very high at an early age, compared with the case of not adding CN. From this result, in the restraint conditions in this test, as the amount of CN increased, the shrinkage increased and the crack occurrence possibility increased.

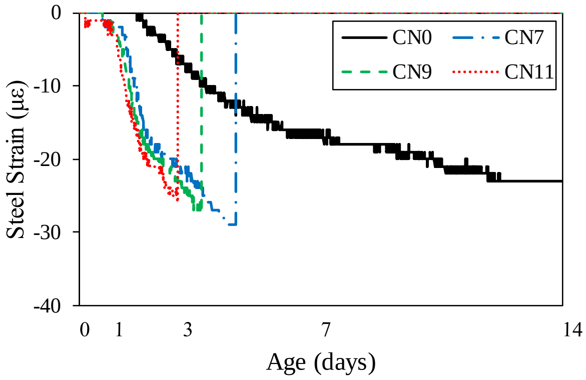


Figure 9. Restraint shrinkage

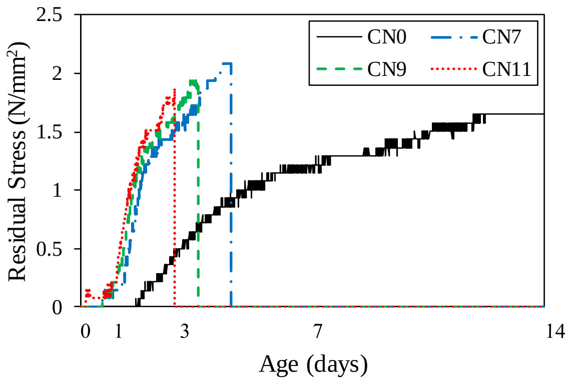


Figure 10. Restraint tensile stress

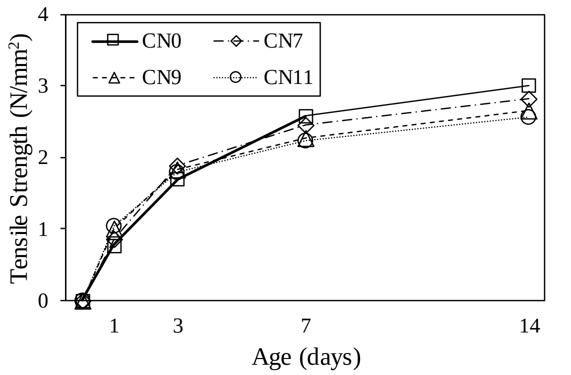


Figure 11. Tensile strength

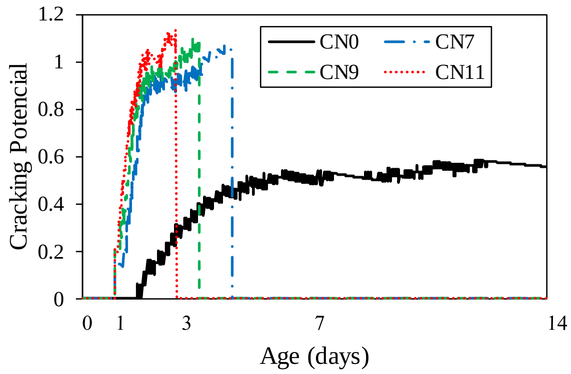
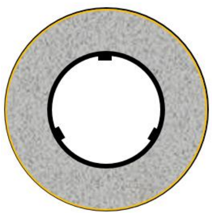
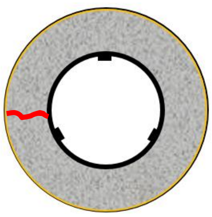
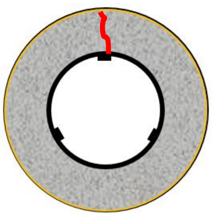
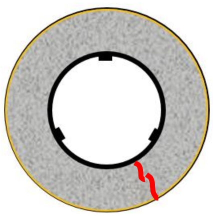


Figure 12. Cracking potential

Table 4. Crack configuration and cracking days

Cracking				
Case	CN0	CN7	CN9	CN11
Days of cracking	-	4.4 day	3.6 day	2.8 day

5. CONCLUSION

This study investigated the shrinkage and the cracking of concrete using a large amount of nitrite-based accelerator. The study results obtained the following conclusions.

1) When the amount of CN increased, hydration was accelerated, the mortar temperature increased immediately after casting, and the fluidity decreased.
2) At day 1, the addition of a large amount of CN promoted hydration and formed a large amount of nitrite/nitrite hydrate, resulting in dense voids and increased strength.
3) As the amount of CN increased, shrinkage increased and the start time of shrinkage became earlier.
4) In the restraint conditions in this study, from the results of the restraint shrinkage strain and the cracking potential, as the amount of CN increased, the shrinkage and the crack occurrence possibility increased.

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