

Article

Study on Physical Properties of Mortar for Section Restoration Using Calcium Nitrite and CO₂ Nanobubble Water

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Abstract: This study investigated the physical properties of section-restoration mortar with calcium nitrite and carbon dioxide (CO₂) nanobubble mixing water to develop materials and methods for the repair and reinforcement of cracks in reinforced concrete (RC) structures. As the calcium nitrite content increased, the generation rate and generated amount of nitrite-based hydration products increased, owing to the rapid reaction between NO₂⁻ ions in calcium nitrite and C₃A(Al₂O₃). Further, the reaction with C₃S and C₂S was accelerated, thereby increasing the generation rates of Ca(OH)₂ and C-S-H. Further, the large amount of Ca²⁺ ions in these hydration products reacted with CO₃²⁻ ions in CO₂ nanobubble water, thereby increasing the generation of calcite-based CaCO₃ in the cement matrix. This appears to have affected the strength development and durability improvement via the densification of the structure. These results suggest that the performance of polymer cement mortar for repairing concrete structures can be improved if calcium nitrite and CO₂ nanobubble water are properly combined and applied.

Keywords: calcium nitrite; CO₂ nanobubble water; section restoration; mortar

1. Introduction

In recent years, global efforts have focused on reducing industrial carbon dioxide (CO₂) emissions. In this light, South Korea, too, has aimed to reduce industrial CO₂ emissions. The construction industry accounts for approximately 40% of total industrial CO₂ emissions [1]. Further, cement production and concrete manufacturing account for approximately 5% of the emissions. Therefore, it is essential to reduce CO₂ emissions in the construction industry. One way of doing so is to properly maintain the existing structures through repair and reinforcement instead of building new structures. For this purpose, repair and reinforcement methods with reduced environmental loads must be developed for extending the service life of concrete structures.

Concrete is widely used in the construction industry. The tensile strength of concrete is significantly lower than its compressive strength. In particular, cracks inevitably occur in buildings owing to various problems in the mix design and construction process [2]. Microcracks in buildings are generally not considered as significant structural problems [3]. Nonetheless, microcracks facilitate

the penetration of chlorides and CO₂ that are highly likely to critically degrade the structural stability of reinforced concrete (RC) structures [4]. Cracks in RC structures also negatively impact the appearance of these structures [5]. Therefore, crack formation must be prevented in concrete. Further, materials and methods for crack repair and reinforcement must be developed to realize high-performance RC structures and sustainable buildings.

A previous study noted that, in a moist environment, concrete containing small cracks showed a self-healing phenomenon in which a part of the crack was filled [6]. This phenomenon occurred due to the rehydration of cement particles and the precipitation of CaCO₃; specifically, CaCO₃ was generated by the reaction between Ca²⁺ in concrete and CO₃²⁻ dissolved in water. Further, a strong self-healing effect was observed when CO₂ nanobubble water was used [7]. Calcium nitrite (Ca(NO₂)₂) is widely used as the main component in antifreeze admixtures. Increasing the calcium nitrite content accelerates the hydration reaction of C₃A and C₃S (both of which are components of cement) and thereby increases the generation of ettringite-based hydrate (Aft). Further, the generation of nitrite-based hydrates in large quantities owing to the reaction between C₃A(Al₂O₃) and NO₂⁻ increases the initial strength of concrete [8].

In this light, the present study investigates the physical properties of section-restoration mortar with calcium nitrite and CO₂ nanobubble mixing water to develop materials and methods for the repair and reinforcement of the cracks that occur in RC structures.

2. Materials and Methods

2.1. Experimental plan

Tables 1 and 2 show the experimental plan and mortar mix proportion of this study, respectively. The design strength was set in accordance with KS F 4042 [9]. Through a preliminary mixing experiment, the water/binder ratio (W/M(B+S)) was determined to be 16%. Experiments were conducted by adding 0%, 1%, 3%, and 5% calcium nitrite relative to the weight of cement. Ordinary tap water and CO₂ nanobubble water were used as mixing water, and eight types of mortar specimens were prepared.

The table flow, compressive strength, flexural strength, length change rate, and carbonation depth were measured. For microstructure analysis, the porosity was analyzed and scanning electron microscopy (SEM) was conducted. The results of these experiments were used to examine whether the polymer cement mortar used for repairing concrete structures satisfied the KS F 4042 quality criteria [9].

Table 1. Experimental plan

Item	Values	
Experimental variables and level	W/M(%)	16
	Ca(NO ₂) ₂ dosage ¹	CN0*, CN1, CN3, CN5*
	Mixing water type	Tap water (TW), Nanobubble water (NW)
Evaluation items	- Flow	
	- Compressive strength (3, 7, 28 days)	
	- Flexural strength (3, 7, 28 days)	
	- Length change	
	- Carbonation depth (4, 8, 12 days)	
	- Porosity*	
- Scanning electron microscopy micrograph*		

¹ CNx: x = Amount of Ca(NO₂)₂ (Binder × wt%)

Table 2. Mix proportion of mortar

W/M ¹ (%)	B:S ²	Binder (wt%)
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		Cement	CSA	Resin	Anhydrous gypsum	PVA fiber	Others
16	1:1.45	89.5	6.6	1.5	1.2	0.6	0.6

¹ M: =B + S, ² B: Binder, S: Sand

2.2. Materials and CO₂ nanobubble water

2.2.1. Materials

Polymer cement mortar in which an expansive admixture and polyvinyl alcohol (PVA) fibers were premixed as repair/reinforcement materials was used in the experiments. Ordinary tap water (temperature: 20°C, no impurities) and CO₂ nanobubble water (particle diameter: ~50 nm, pH adjusted to ~4.5 (slightly acidic)) produced using a nanobubble device (HACK FB11, JAPAN) were used as mixing water.

2.2.2. Equipment and process to generate CO₂ nanobubble water

Figure 1 shows the equipment and process used to generate CO₂ nanobubble water. A nanobubble generator connected to a CO₂ source was operated in a water tank filled with tap water. The gas pump generated a negative pressure to pressurize the mixing header. CO₂ nanobubbles (particle diameter: ~50 nm) generated by cavitation were then discharged through the foam nozzle into the water tank to produce CO₂ nanobubble water [10-11]. These nanobubbles generally have small buoyancy and negative surface charges of the order of tens of microvolts; therefore, they repel and do not easily stick to each other, consequently lasting for longer durations in water than microbubbles [12].

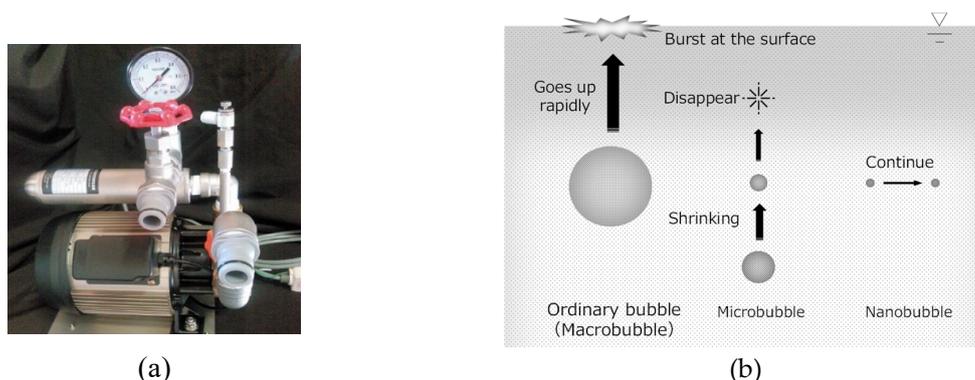


Figure 1. Equipment and process used to generate CO₂ nanobubbles. (a) is a depiction of the nanobubble device; (b) shows the behavior of nanobubbles in water

2.3. Experimental parameters

2.3.1. Flow

For the flow of mortar, a non-hardening property, the experimental flow table of KS L 5111 [13] was used. The flow was measured immediately as well as 30 and 60 min after mixing in proportion with KS F 2476 [14].

2.3.2. Compressive and flexural strength

Prismatic mortar specimens with a size of (40 × 40 × 160 mm) were fabricated for the strength test. They were demolded at two days of age and subjected to standard water curing at 20 °C. Their flexural strength was measured at 3, 7, and 28 days of age by using the central loading method and a

universal testing machine (UH-F1000 kNX, Shimadzu) in accordance with KS F 2408 [15]. To test the compressive strength, the specimens fractured after measuring the flexural strength were used. The compressive strength was measured at 3, 7, and 28 days of age in accordance with KS F 2405 [16] after mounting the specimens in a compression mold ($40 \times 40 \times 40$ mm). Figure 2 shows the setup for measuring the compressive and flexural strengths.



Figure 2. Pictures of the strength tests, with (a) the compressive strength test and (b) the flexural strength test

2.3.3. Length change rate

Prismatic mortar specimens ($40 \times 40 \times 160$ mm) were used to test the length change rate. The specimens were demolded at two days of age and subjected to water curing at $(20 \pm 3)^\circ\text{C}$ for five days. They were then cured in a constant temperature and humidity chamber at $(20 \pm 3)^\circ\text{C}$ and $(60 \pm 5)\%$ RH. The length change rate was measured for predetermined ages by using the dial gauge method of KS F 2424 [17].

2.3.4. Carbonation depth

The carbonation depth was measured by the accelerated carbonation test of KS F 2596 [18]. The acceleration conditions were a temperature of $(20 \pm 2)^\circ\text{C}$, a humidity of $(60 \pm 5)\%$, and a CO_2 concentration of $(5 \pm 0.2)\%$. The specimens were sealed with aluminum tape except at the top surface to block the infiltration of CO_2 . A solution of 1% phenolphthalein was sprayed on the split specimens, and the depth of the part that turned red was measured at 10 mm intervals by using a Vernier caliper.

2.3.5. Porosity and SEM analysis

Porosity measurements and SEM analysis were conducted only for specimens with 0% and 5% calcium nitrite to investigate the properties of tap water and CO_2 nanobubble water according to the calcium nitrite content.

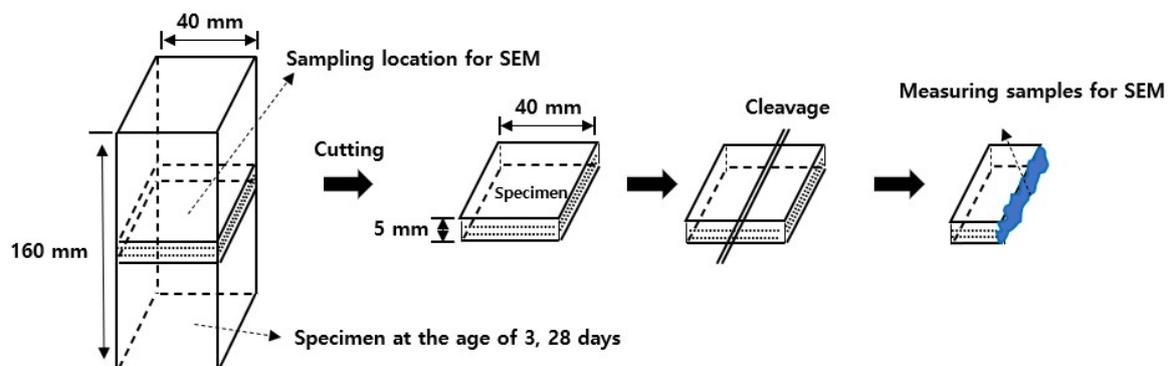


Figure 3. Specimen sampling for SEM

As shown in Figure 3, samples were collected from the specimens fractured after measuring the strength at 3 and 28 days of age. The collected samples were used in the experiment after being immersed in acetone for more than four hours to stop the hydration reaction.

The samples used for porosity measurements were oven-dried at 60 °C. Mercury was then pressurized at 0–60,000 psi by using a porosity analyzer (AutoPore IV 9520), and the pore size and cumulative pore volume of each specimen were measured from the amount of penetration. SEM analysis was conducted using the SNE-3200M (NanoImages) device, and the collected powder-type samples were coated with platinum. They were then observed at 3,000× magnification at an acceleration voltage of 15 kV.

3. Results and Discussion

3.1. Flow

Figure 4 shows the flow test results. Regardless of whether tap water or CO₂ nanobubble water was used, specimens with calcium nitrite tended to show high flow values. The flow did not seem to show any relation to the type of mixing water or the calcium nitrite content.

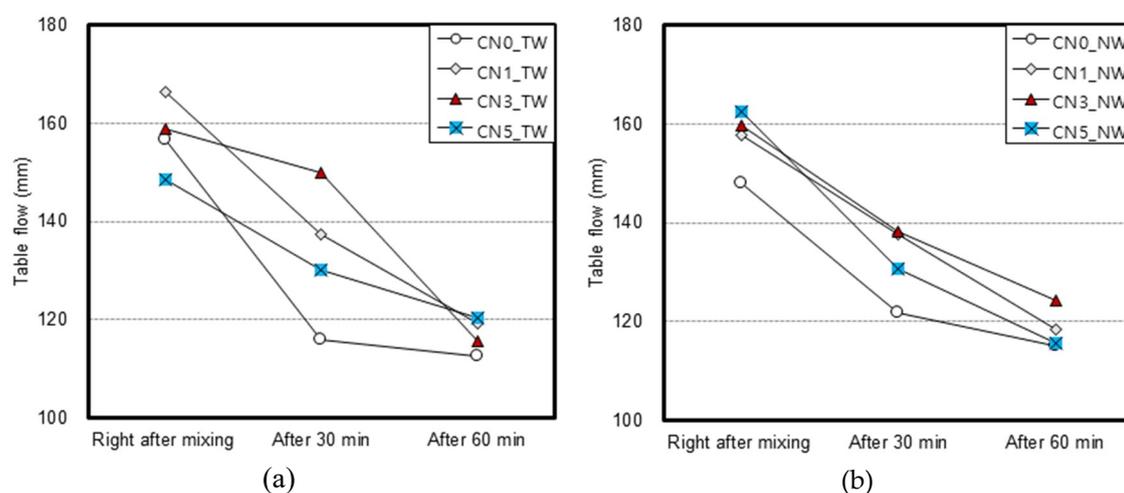


Figure 4. Flow test results. (a) presents the result with tap water; (b) presents the result with nanobubble water

3.2. Compressive and flexural strength

Figures 5 and 6 show the compressive and flexural strength results of the specimens when using tap water and CO₂ nanobubble water according to the calcium nitrite content and age. For both types of mixing water, the compressive and flexural strengths increased with an increase in the calcium nitrite content, because NO₂⁻ ions in calcium nitrite rapidly reacted with C₃A(Al₂O₃), a component of cement, to increase the generation rate and amount of nitrite-based hydration products [19]. The CN0 specimen with CO₂ nanobubble water showed somewhat higher compressive and flexural strengths because this water was initially produced at 30 °C, which was higher than the temperature for other specimens.

A comparison of the compressive and flexural strength results with the use of tap water and CO₂ nanobubble water revealed a larger strength improvement effect with the latter. This result is similar to a previously reported result on the compressive strength of cement mortar using CO₂ nanobubble water [20]. It seems attributable to the increased generation of calcite-based CaCO₃ in the cement matrix, as a large amount of Ca²⁺ ions generated through the aforementioned accelerated the reaction between calcium nitrite, and cement react with the CO₃²⁻ ions in the CO₂ nanobubble water; this leads to strength improvement via the densification of the structure [21].

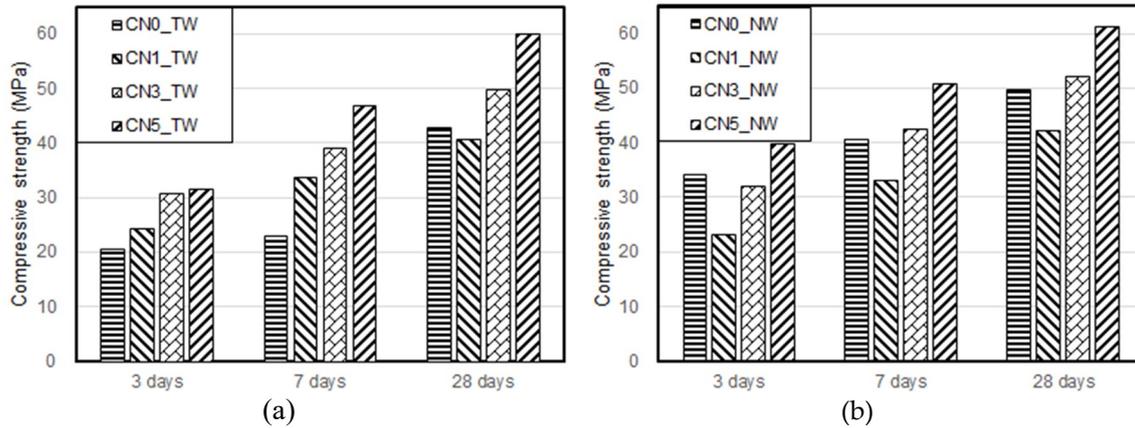


Figure 5. Compressive strength test results; (a) result with tap water; (b) result with nanobubble water

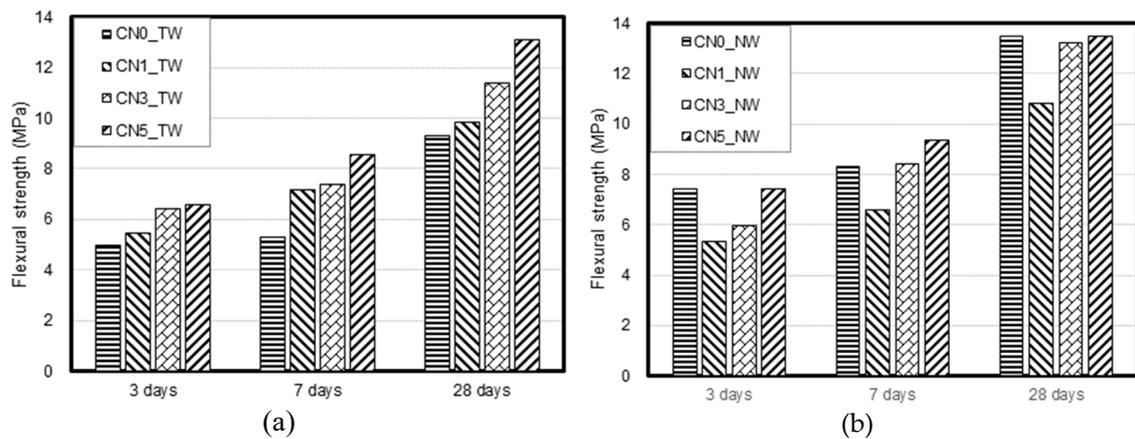


Figure 6. Flexural strength test results; (a) result with tap water; (b) result with nanobubble water

For calcium nitrite content of 3% or higher, both the compressive and the flexural strengths satisfied the quality criteria of 20 and 6 MPa, respectively, specified in KS F 4042 [9] for the compressive and flexural strengths of polymer cement mortar required to repair concrete structures.

This indicates that a certain strength improvement effect can be expected if the CO₂ nanobubble water and calcium nitrite contents are properly adjusted in consideration of the site conditions at the time of the section restoration.

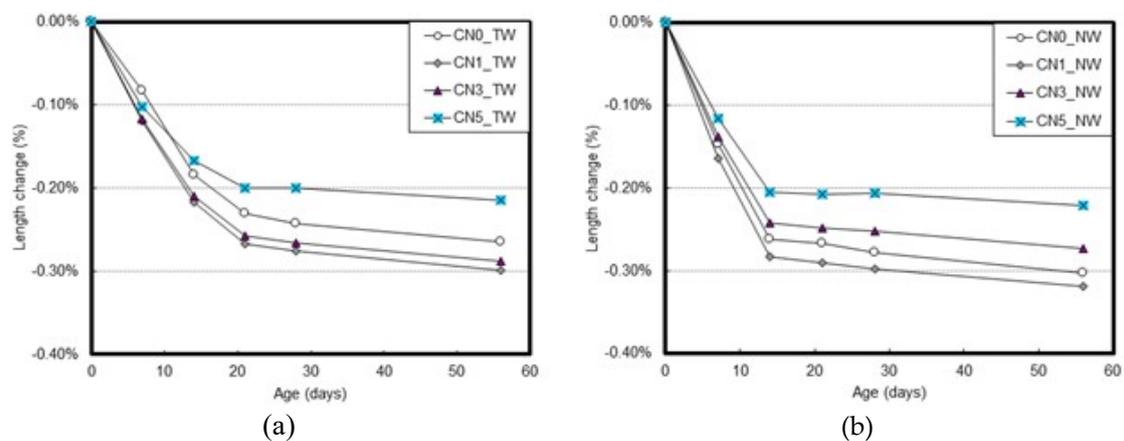


Figure 7. Length change rate of mortar; (a) result with tap water; (b) result with nanobubble water

3.3. Length change rate

Figure 7 shows the length change rate measurement results of specimens that used tap water and CO₂ nanobubble water according to the calcium nitrite content and age. As the age increased, the shrinkage increased, owing to drying and the rapid hydration reaction at early ages.

For tap water, the length change rate was higher with calcium nitrite contents of 1% or 3% than with contents of 0% or 5%. For CO₂ nanobubble water, the length change rate decreased with calcium nitrite contents of 3% or higher. In particular, for calcium nitrite contents of 5% or higher, the length change rate decreased sharply regardless of the type of mixing water used. A shrinkage reduction effect of 0.05%–0.08% was confirmed at 56 days of age compared to the specimen without calcium nitrite.

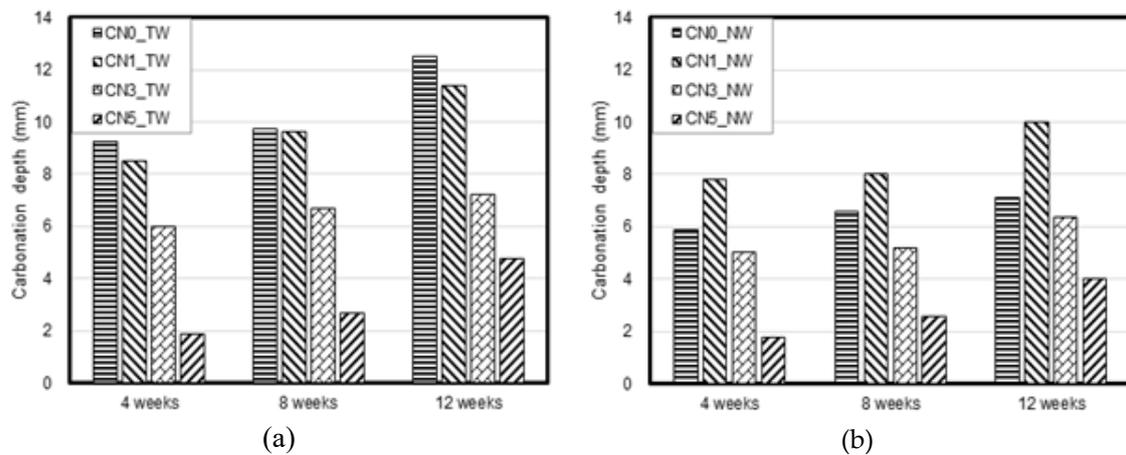


Figure 8. Carbonation depth; (a) result with tap water; (b) result with nanobubble water

3.4. Carbonation depth

Figure 8 shows the carbonation depth measurement results of specimens that used tap water and CO₂ nanobubble water according to the calcium nitrite content. With both types of mixing water, the carbonation depth decreased as the calcium nitrite content increased.

As mentioned in Section 3.2, this appears to be because the internal structure became denser with increasing calcium nitrite content as nitrite-based hydration products increased and, in particular, a large amount of ettringite was generated owing to the accelerated reaction between C₃A(Al₂O₃) in cement and the NO₂⁻ ions in calcium nitrite. In particular, when CO₂ nanobubble water was used, an accelerated reaction occurred between the CO₃²⁻ ions in CO₂ nanobubble water and the Ca⁺ ions in cement. Therefore, the supply of CO₃²⁻ ions alone caused the carbonation reaction, thereby increasing the generation of CaCO₃ in the specimen. As a result, CO₂ nanobubble water has a higher carbonation suppression effect owing to the densification of the structure [21]. In particular, when 5% calcium nitrite was added, the quality criterion of KS F 4042 [9] for the carbonation depth of polymer cement mortar for repairing concrete structures (less than 2 mm carbonation depth at four weeks of age) could be met.

This indicates that carbonation can be suppressed through the proper use of CO₂ nanobubble water and calcium nitrite. They are judged to be helpful in improving the performance of the section-restoration mortar via the densification of the structure of the cement matrix.

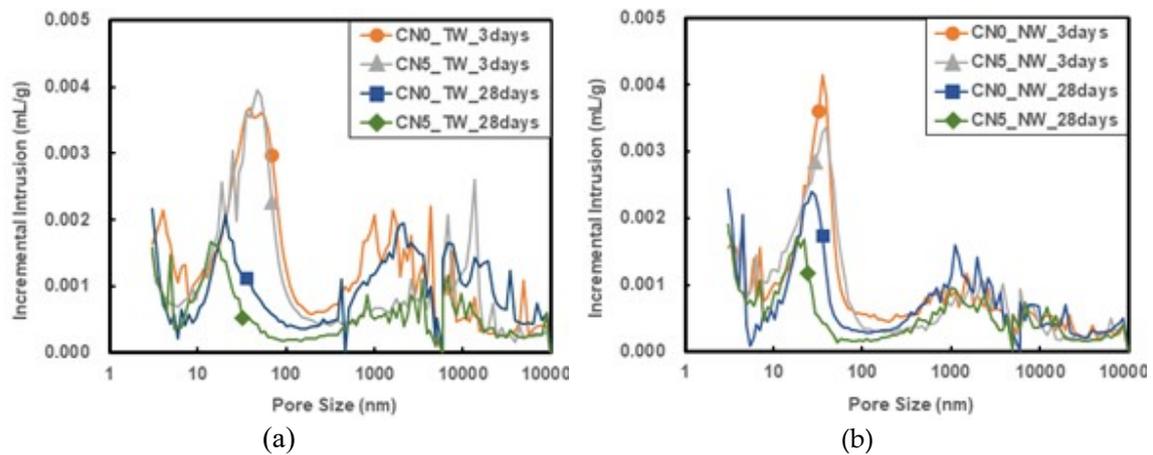


Figure 9. Incremental intrusion results; (a) result with tap water; (b) result with nanobubble water

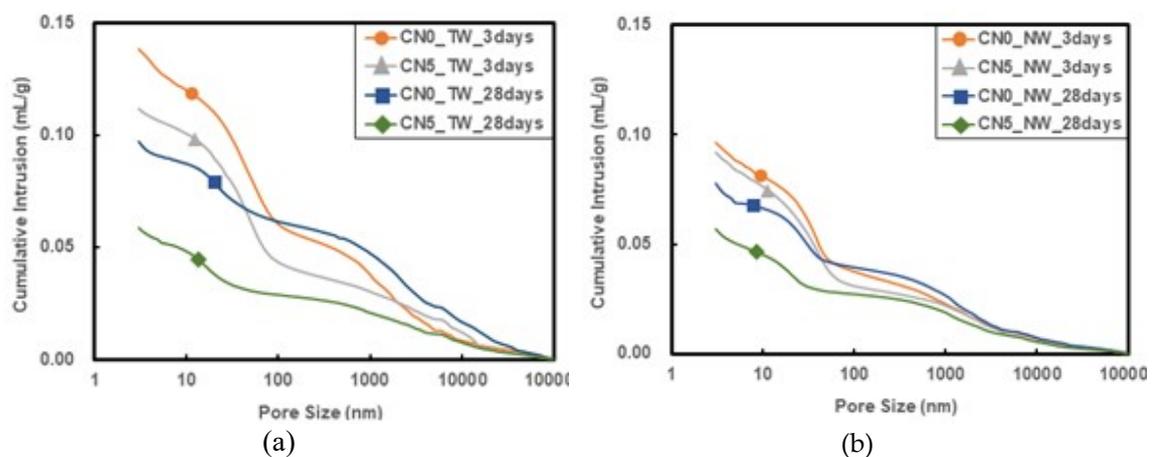


Figure 10. Cumulative intrusion results; (a) result with tap water; (b) result with nanobubble water

3.5. Porosity

Figures 9 and 10 show the pore size distribution and cumulative pore volume results of specimens that used tap water and CO₂ nanobubble water according to the calcium nitrite content and age. As the age increased, the cumulative pore volume decreased, indicating that the specimen structure became denser, thereby affecting the strength development. Overall, the addition of calcium nitrite slightly reduced the pore size and significantly reduced the cumulative pore volume.

In particular, when CO₂ nanobubble water was used, the cumulative pore volume was smaller than when tap water was used. This effect increased when calcium nitrite was used. As with strength development, this appears to be because the structure became denser through the accelerated reaction between C₃A(Al₂O₃) in cement and the NO₂⁻ ions in calcium nitrite and the reaction between the CO₃²⁻ ions in CO₂ nanobubble water and the Ca⁺ ions in cement.

3.6. SEM

Figure 11 shows the SEM observation results of specimens that used tap water and CO₂ nanobubble water according to the calcium nitrite content. Each hydration product was estimated by comparing the crystal structures obtained in this study with the crystal forms and sizes of hydration products confirmed in previous studies.

As the age increased, a wider distribution of hydration products, such as C-S-H gel and Ca(OH)₂, was observed. In the case of the specimens without calcium nitrite, ettringite that exhibits acicular

brittle fracture behavior was distributed with monosulfate at an early age. In the case of the specimens with calcium nitrite, monosulfate was partially observed along with sulfuric acid (SO_4^{2-})-based ettringite on the C_3A surface of cement. Meanwhile, calcite was partially observed in the specimens that used CO_2 nanobubble water containing CO_3^{2-} ions. It appears that CaCO_3 (mainly calcite) was observed because the addition of calcium nitrite increased the generation rate of C-S-H gel and $\text{Ca}(\text{OH})_2$, and the CO_3^{2-} ions in CO_2 nanobubble water were adsorbed on the Ca^{2+} ions in the generated hydration products. In particular, nitrite-based hydration products and calcite-based CaCO_3 were generated in large quantities in the specimens that used calcium nitrite and CO_2 nanobubble water, indicating that the physical performance was improved through the densification of the structure.

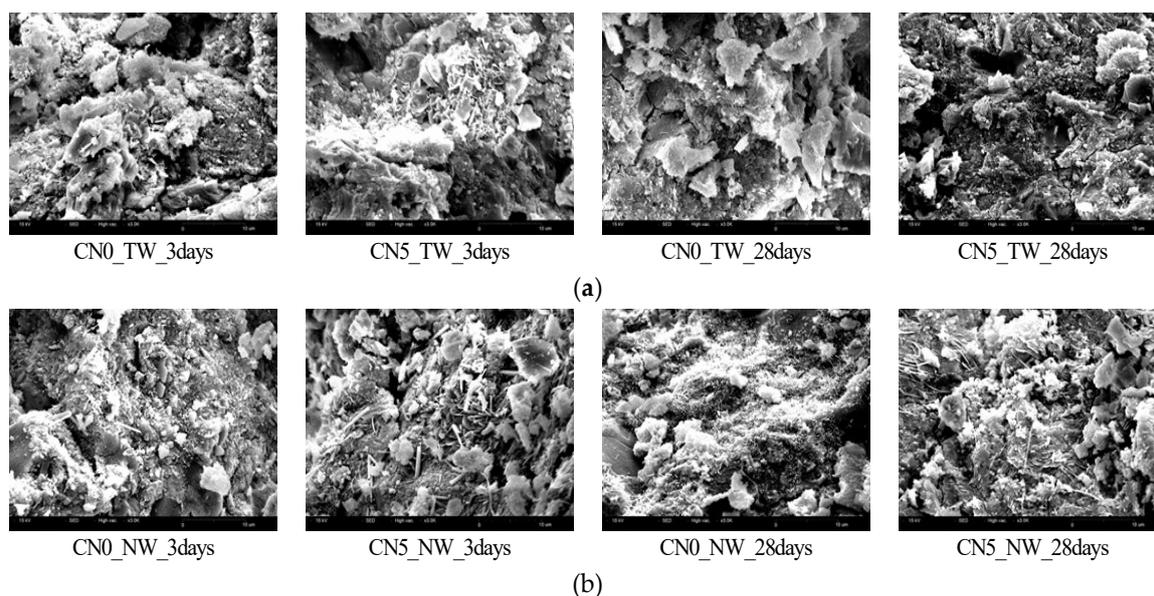


Figure 11. SEM (3000× magnification); (a) Result with tap water; (b) Result with nanobubble water

4. Conclusion

In this study, the physical properties of section-restoration mortar that used calcium nitrite and CO_2 nanobubble water as mixing water were investigated. The following conclusions were derived from this study.

1. The flow values of the specimens with calcium nitrite tended to be high. No special tendency according to the type of mixing water and the calcium nitrite content was seen. When 5% calcium nitrite was added, the length change rate sharply decreased.
2. As the calcium nitrite content increased, the strength and durability increased. In particular, the use of CO_2 nanobubble water effectively increased the strength and reduced the carbonation depth and porosity.
3. As the calcium nitrite content increased, the generation rate and generated amount of nitrite-based hydration products increased owing to the rapid reaction between the NO_2^- ions in calcium nitrite and the $\text{C}_3\text{A}(\text{Al}_2\text{O}_3)$ in cement.
4. A large amount of Ca^{2+} ions from $\text{Ca}(\text{OH})_2$ and C-S-H gel, which were generated through the accelerated reaction between calcium nitrite and cement, reacted with the CO_3^{2-} ions in the CO_2 nanobubble water, thereby increasing the generation of calcite-based CaCO_3 in the cement matrix. This appears to have affected the strength development and durability improvement via the densification of the structure. The densification of the matrix appears to reduce the pore volume and affect the strength development as well as durability improvement.

These results suggest that the performance of polymer cement mortar for repairing concrete structures can be improved if calcium nitrite and CO₂ nanobubble water are properly combined and applied.

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