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Influence of a $C_{12}A_7$ mineral-based accelerator on the strength and durability of shotcrete

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Abstract

This study analyzed the long-term strength and durability of shotcrete when a $C_{12}A_7$-based accelerator is added to the mixture. Since an accelerator with a high alkali content causes a remarkable decrease in the long-term strength of shotcrete and is toxic to humans, this study evaluated the setting time, compressive strength, and resistance to permeability and repeated freeze–thaw cycles of an amorphous $C_{12}A_7$-based accelerator. The results showed that the $C_{12}A_7$ accelerator set quickly by forming a web structure from its initial setting state due to the presence of ettringite. In addition, the ettringite, with its characteristic acicular crystals, proved resistant to permeability and repeated freeze–thaw cycles. Ettringite has a structure that encouraged a smooth hydration reaction, maintaining the voids at the surface of the cement particles and resulting in the observed initial strength and decrease in the reduction of the long-term strength.

Keywords: $C_{12}A_7$ mineral-based accelerator; Durability; Long-term strength

1. Introduction

When using shotcrete to construct tunnels or underground structures, the poured mixture must set quickly in order to stabilize the structure [1–3]. The important basic requirements of shotcrete are good adhesiveness, a low amount of rebounding, good shooting, and the quick formation of initial strength [4–6]. To meet these requirements, accelerators have become an important additive in shotcrete [7–9]. With the recent development of mineral-based accelerators, demand for shotcrete is growing due to its good mechanical properties, workability, safety, reduced environmental impact, and ease of maintenance. Mineral-based accelerators, derived from materials with quick setting characteristics such as calcium aluminate (a cement mineral), are manufactured in the form of powder by crushing the mixed minerals. They provide excellent quick setting and stable strength formation properties.

Although numerous minerals, such as calcium aluminate and calcium sulfoaluminate, are widely used for quick setting [1], amorphous mineral-based accelerators such as $C_{12}A_7$, $C_{11}A_7$, CaF_2, and C_4A_3S are the most popular. $C_{12}A_7$, $C_{11}A_7$, and CaF_2 are often adopted for general use due to their excellent setting characteristics. C_4A_3S is often added to shotcrete to increase the long-term strength despite its disadvantages, such as a slow setting time and the large quantity that must be added (more than 10% of the mixture). The most important properties of mineral-based accelerators are their low decrease in long-term strength and their ability to stop water leaks. With these characteristics, mineral-based accelerators confer various benefits, such as a decreased rebound volume, increased long-term strength without an increase in the volume of cement, and improved safety of the structure. They also contribute to reduce environmental pollution and harmful effects on workers.

The performance of shotcrete is greatly affected by the material, mix proportion, shotcreting equipment, and skill of the operator. Therefore, shotcrete should be evaluated considering these factors. The $C_{12}A_7$-based accelerator is a powder and can be used for dry mixing with shotcrete using standard equipment,

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but cannot be used for wet mix shotcrete using standard wet mix shotcrete equipment. Unlike a liquid accelerator, it is difficult to measure a fixed quantity using a simple transfer system. Therefore, the input quantity of $C_{12}A_7$-based accelerator and its combination with concrete is controlled by it floating on compressed air. This method has been applied for tunnel construction after it was developed by companies specializing in shotcrete equipment, for example, Denka Japan. Generally, to apply the $C_{12}A_7$-based accelerator, a compressed-air transfer method is used; this has the shortcoming of a slow construction speed, with a shotcreting capacity of 7 to 10 m^3/h. In this study, we increased the shotcreting capacity to between 15 and 20 m^3/h using a pump compression method with two piston pumps.

This study evaluated the long-term strength and durability of shotcreting using our shotcrete equipment. In order to simplify the test variables, laboratory tests were conducted to determine the quantity of $C_{12}A_7$-based accelerator that gave a satisfactory setting time and the amount of admixture that gave a satisfactory slump and air contents. Standard quantities of aluminate- and silicate-based accelerators were added to the shotcrete mix, as controls.

2. Experimental procedure

2.1. Materials

Ordinary ASTM type I standard Portland cement, crushed coarse aggregate with a maximum size of 13 mm, and fine aggregate with a specific gravity of 2.65 were used in this study. The $C_{12}A_7$-based accelerator was compared to silicate- and aluminate-based accelerators. Table 1 shows the characteristics and required amounts of each accelerator.

Table 1
Properties and amounts of the accelerators used

Accelerator	Component	Type	Amount (%)[a]
Silicate	Inorganic silicate based	Liquid	10
Aluminate	Inorganic aluminate based	Liquid	5
$C_{12}A_7$	$C_{12}A_7$	Powder	4

[a] Weight of accelerator/weight of cement × 100(%).

The $C_{12}A_7$-based accelerator used in this study can set and harden in 1 to 3 min using a water reaction and has the quickest hydration reaction of all calcium aluminate minerals (Table 2). Crystalline $C_{12}A_7$ is likely to produce C_2AH_8 in the case of sole hydration, and if properly mixed with cement, sets very quickly. However, the $C_{12}A_7$-based accelerator is not suitable as a setting agent in tunnels due to its inferior performance, since the calcium hydrate $Ca(OH)_2$ arising from the hydrated cement prevents hydration by coating the surface of the $C_{12}A_7$ particles, delaying the setting time by several minutes during the initial stage. When mixed with Portland cement, $C_{12}A_7$ in its amorphous, separate state reacts promptly and solidifies within tenths of a second without hampering the hydration process. Amorphous $C_{12}A_7$ is a commercial product manufactured by adding a small amount of SiO_2 to a $C_{12}A_7$ composite. The composite is melted and refrozen quickly, transforming it into an amorphous state that sets quickly. Amorphous $C_{12}A_7$ is the best quick-setting agent known and can result in a mixture of C_2AH_8 and C_4AH_X (X=13 or 19) when it reacts with water. This mixture, with a structure similar to that of a card house, has a high initial strength because it forms a large amount of acicular $C_3A\cdot 3CaSO_4\cdot 32H_2O$ (ettringite) crystals due to its coexistence with $Ca(OH)_2$ and $CaSO_4$ during the reaction with Portland cement. The $C_{12}A_7$-based accelerator used in this study was ground to a specific surface area exceeding 5000 cm^2/g and its reactivity was increased in order to increase the initial strength to allow fast setting. The actual reaction starts within seconds after this powder is mixed with cement and water. Therefore, the slaked lime, which raises the creation speed of calcium aluminate hydrate, and the initial calcium aluminate hydrate respond together by increasing the concentration of $Ca(OH)_2$ in the initial hydrate reaction, creating needle-shaped crystals called ettringite, which contain anhydrous plaster that has the effect of increasing the hardening speed and compressive strength, and includes sodium carbonate for increasing bond strength by strengthening the combination of the hydrate structure as it grows.

Table 2
Chemical composition of the $C_{12}A_7$-based accelerator

$C_{12}A_7$	NaCO	$CaSO_4$	$NaAlO_2$	$Ca(OH)_2$
50–90	4–30	0.1–20	0.1–10	0.1–20

2.2. Mix proportions

The mixtures gave a slump of 12 ± 2.5 cm and an air content of 4 ± 1%, as shown in Table 3, both of which were fixed to analyze the mechanical characteristics and durability of shotcrete with the $C_{12}A_7$-based accelerator.

2.3. Shotcreting equipment

For this study, we modified the piston-type liquid accelerator input equipment made by Putzmeister in order to input the accelerator by installing a device to supply powder on the wet mix shotcreting equipment. As mentioned in the Introduction, the equipment generally used to apply the $C_{12}A_7$-based accelerator has the disadvantage of a low shotcreting capacity of 7 to 10 m^3/h. Our modification increased the shotcreting capacity to between 15 and 20 m^3/h. The shotcreting equipment used is shown in Fig. 1, in which the $C_{12}A_7$-based accelerator was provided in a fixed quantity from the power supply device, and mixed with the concrete by forcing it through the Y pipe with compressed air. Since it is difficult for compressed air to enter a hose filled with concrete, our shotcreting equipment allows the concrete to float; this is achieved by installing an injection ring that enables compressed air to be input between the concrete pump and Y pipe and another between the Y pipe and the nozzle. This facilitates the addition of the accelerator by decreasing the pressure in the Y

Table 3
Mix proportions of shotcrete

Type of mixture	G_{max} (mm)	Slump (m)	W/C (%)	S/a (%)	Air (%)	W	C	S	G	Accelerator	Plasticizer (g/m^3)
						(kg/m^3)					
P [a]	13	12±2.5	45.5	65	4±1	209.3	460	1047	581	–	2300
AL [b]										23	
SI [c]										46	
CM [d]										18.4	

[a] Plain.
[b] Aluminate.
[c] Silicate.
[d] $C_{12}A_7$-based.

pipe and accelerating the movement of the mixed concrete. The air pressure at the first injection ring is 3.4–4.9 m^3/min and that at the second injection ring is 5.9–7.7 m^3/min, while that at the Y pipe is 4.7–5.4 m^3/min. The compressor used can produce the air flow by 23.4–25.5 m^3/min, which is more that (14–18 m^3/min) required for the shotcreting equipment. A Q-gun produced by Plibrico Japan was used to supply the powder, and can supply 2.27–7.08 kg/min.

2.4. Test methods

In order to evaluate the performance of the $C_{12}A_7$-based accelerator, the setting time, compressive strength, and durability, including the chloride ion permeability and repeated freeze–thaw cycles, were evaluated.

The setting time was measured using the method described in the ASTM C 403 standard. The initial and final setting times were defined as the times at which the penetration resistance was 3.5 and 28.0 MPa, respectively. The test specimens were produced by carrying out the shotcreting at a speed of 15 m^3/h after installing the Φ 150 mm × 150-mm test specimen.

The penetration resistance was measured once per minute for the initial 5 min of the test, and then once every 5 min until the final setting time. The compressive strength was measured in accordance with the ASTM C 39 standard. The shotcrete equipment was used to make Φ 800 mm × 400 mm × 400-mm panels. Then, cylindrical test specimens measuring Φ 100 mm × 200 mm were obtained and tested after curing for 1, 3, 7, 28, and 91 days. Fig. 2 shows the setup used to produce the test panels. Every three specimen was tested twice to verify the repeatability of the tests. The specimens were cured in water at a constant temperature of 23 ± 2 °C after curing for 1 day initially in a curing room at 50% relative humidity. The chloride ion permeability of the shotcrete was measured using the method described in the ASTM C 1202 standard. Again, Φ 800 mm × 400 mm × 400-mm test panels were produced, and cylindrical test specimens measuring Φ 100 mm × 50 mm were obtained and tested after curing for 7, 14, 28, and 91 days. Repeated freeze–thaw tests were performed in accordance with the ASTM C 666-B standard, in which the dynamic modulus of elasticity was measured every 30 cycles for 300 cycles. The shotcrete equipment was used to produce 100 × 100 × 400-mm specimens, and the repeated freezing and thawing test was performed after curing them for 14 days in water at 23 °C.

3. Test results

3.1. Setting time

The setting time of shotcrete with the different accelerators is shown in Fig. 3. The initial setting times of the $C_{12}A_7$- and

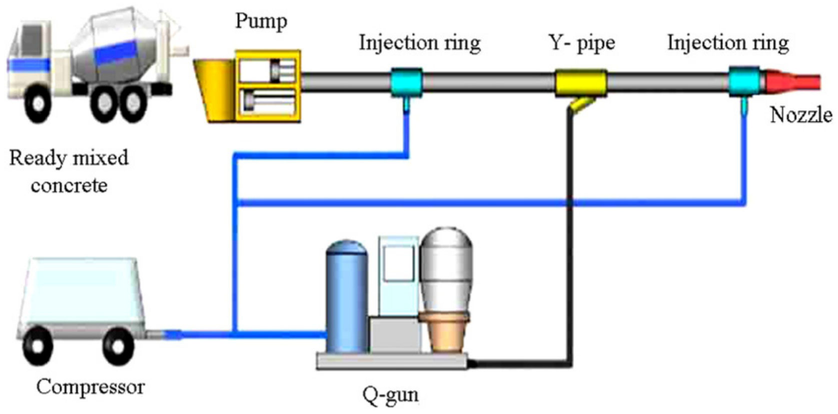


Fig. 1. Shotcreting setup used in this study.

Fig. 2. Manufacturing the test specimens.

silicate-based accelerators were less than 5 min, while the aluminate-based accelerator reached the initial setting stage after 9 min. The final setting time of the $C_{12}A_7$ mixture was approximately 15 min; the mixtures with other accelerators were slower. The silicate-based accelerator had a quick initial setting time and the slowest final setting time irrespective of the characteristics of the cement, and was attributed to a glue effect that influenced the setting phenomenon through the formation of a gel state. The initial setting time of the aluminate-based accelerator was slightly longer than that of the silicate-based accelerator, but the final setting time was only 30 min due to the accelerated hydration reaction of C_3 S and β-C_2S in the cement and the quick setting effects of hydrolysis sodium hydrate (NaOH) in water, similar to the silicate-based accelerator.

The $C_{12}A_7$-based accelerator had the shortest initial and final setting times compared to the silicate- and aluminate-based accelerators, and appeared to be the most effective for fast setting, which is an important property for an accelerator. When the $C_{12}A_7$-based accelerator reacts with water, it creates a mixture of C_2AH_8 and C_4AH_X (X=19 or 13) and forms a structure like a card house. By contrast, when it reacts with Portland cement, it creates many needle-shaped crystals of $C_3A\cdot 3CaSO_4\cdot 32H_2O$ (ettringite) by coexisting with $Ca(OH)_2$ and $CaSO_4$, so that its initial strength is acquired. In addition, the $C_{12}A_7$-based accelerator used in this study had a specific surface area exceeding 5000 cm^2/g, which accelerated the creation of calcium aluminate hydrate by increasing the concentration of $Ca(OH)_2$ in the hydrate reaction after adding slaked lime. Adding anhydrous plaster caused it to react with the calcium aluminate hydrate in the initial hydrate, which resulted in the needle-shaped ettringite crystals and increased the hardening speed and compressive strength by strengthening the combined hydrate structure as it grew.

3.2. Compressive strength

Fig. 4 shows the compressive strength of the shotcrete. After curing for 1 day, the compressive strength of the mixture with the $C_{12}A_7$-based accelerator was slightly greater than that of the other mixtures because when the accelerator was mixed with the cement, it formed a large amount of acicular ettringite. By contrast, the aluminate- and silicate-based accelerators were relatively slow at reaching their initial strengths. As the curing age increased, the compressive strengths of the mixtures with accelerators were less than that of the control case in which no accelerator was used. On curing for 28 days, the rate of strength reduction of the

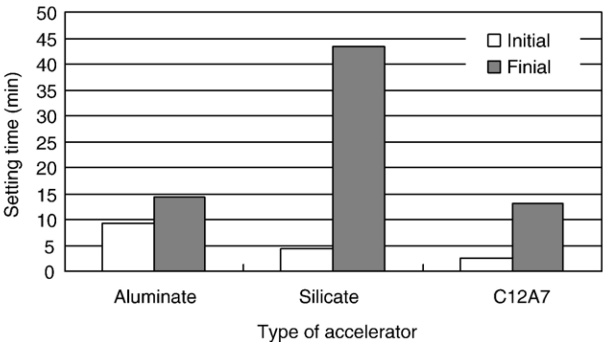


Fig. 3. Setting time for the shotcrete with different accelerators.

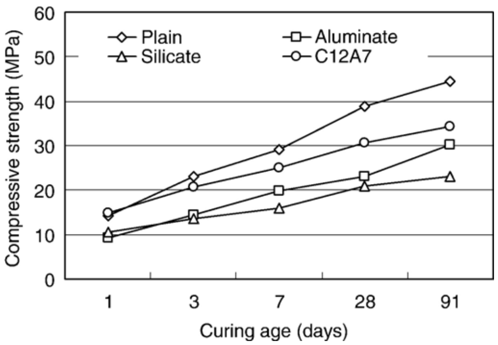
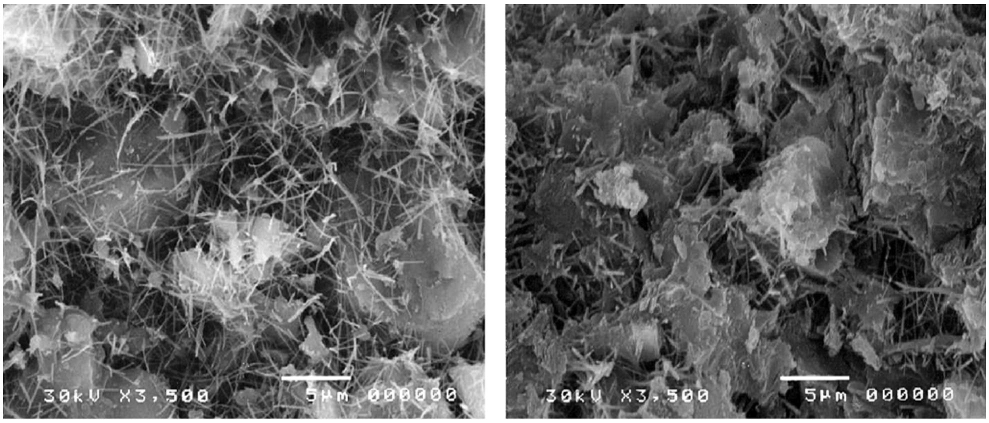


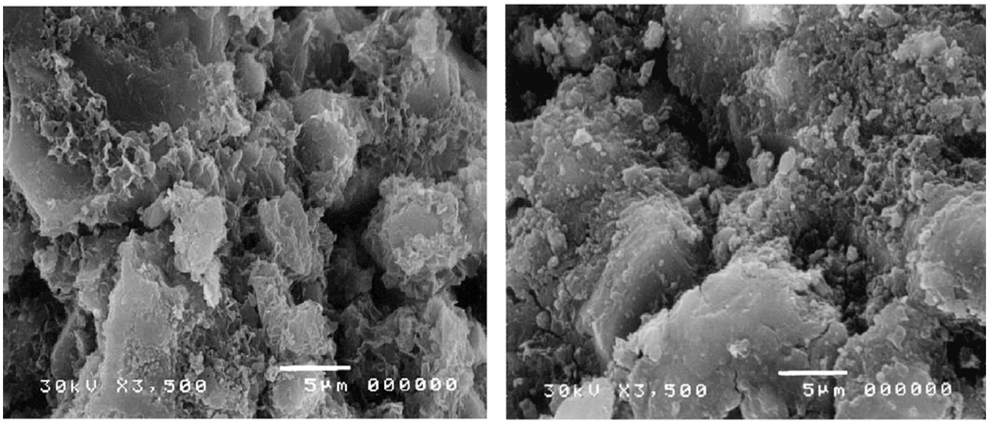
Fig. 4. Compressive strength of shotcrete with different accelerators.

shotcrete with the silicate-, aluminate-, and $C_{12}A_7$-based accelerators compared to plain shotcrete was 46.2, 40.6, and 20.9%, respectively. On curing for 91 days, the respective values were 48.2, 32.0, and 22.7%. All the accelerators decreased the strength of the shotcrete, but the $C_{12}A_7$-based accelerator decreased the strength the least and provided an excellent initial strength.

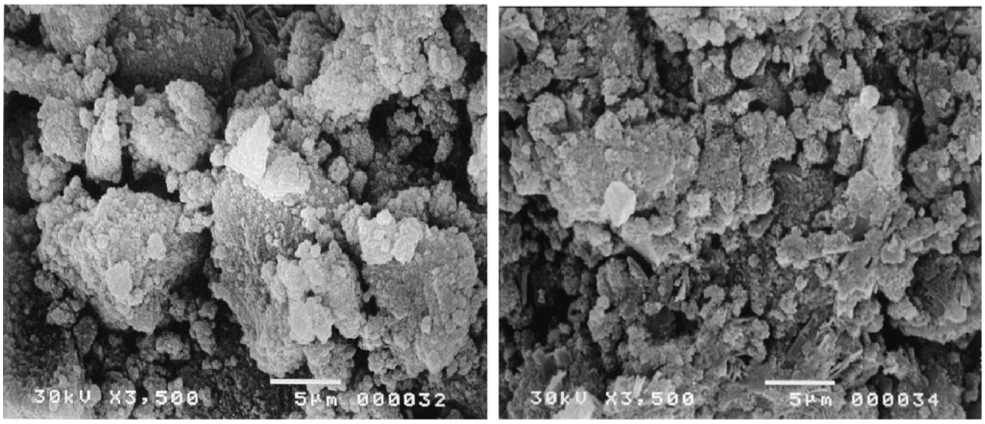
Fig. 5 shows scanning electron microscopic images of the different shotcrete mixtures. Acicular ettringite was already visible in the form of a spider web in the $C_{12}A_7$ mixture after curing for 1 h. After curing for 1 day, an intricate C–S–H gel state had formed as a result of the hydration of cement particles. In the initial image of the aluminate mixture, only the substance mixed with C_3AH_6 from the reaction with Ca



(a) $C_{12}A_7$-based (after 1 h) (b) $C_{12}A_7$-based (after 1 day)



(c) Aluminate-based (after 1 h) (d) Aluminate-based (after 1 day)



(e) Silicate-based (after 1 h) (f) Silicate-based (after 1 day)

Fig. 5. Scanning electron microscope images of shotcrete made with different accelerators. a) $C_{12}A_7$-based (after 1 h). (b) $C_{12}A_7$-based (after 1 day). c) Aluminate based (after 1 h). (d) Aluminate based (after 1 day). (e) Silicate based (after 1 h). (f) Silicate based (after 1 day).

$(OH)_2$ and the C–S–H gel, which covered the cement particles, was visible. The gel was caused by the effects of $Al(OH)_3$ and NaOH, both of which were formed via hydrolysis. After curing for 1 day, the reacting substance was invisible; it was completely covered by the C–S–H gel. For the silicate mixture, neither cement particles nor hydration minerals appeared in the initial image. Only the cement particles coated with the gel material formed by the gluing effect were visible in the image. On curing for 1 day, the substance had developed to the C–S–H gel state and no other hydration substance was observed. The 1-day structure of the aluminate- and silicate-based accelerators, in which there was a C–S–H gel coating the cement particles, not only affects the long-term hydration by preventing contact between water and the cement particles, but also decreases the long-term strength of the mixtures. By contrast, the structure with the $C_{12}A_7$-based accelerator encourages a smooth hydration reaction due to the characteristics of the acicular crystals, which maintain voids on the particle surfaces. As seen in the compressive strength results, this explains why the $C_{12}A_7$-based accelerator minimizes the decrease in strength with aging better than the silicate- and aluminate-based accelerators.

3.3. Permeability

Fig. 6 summarizes the chloride ion permeability results. Although all of the mixtures showed decreased chloride ion penetration due to the increase in strength with curing, the chloride ion penetration was high (more than 4000 C) for all curing ages. The trend for the $C_{12}A_7$ mixture was similar to that of plain shotcrete for all curing ages, and the permeability was less than that of the aluminate and silicate mixtures. This was due to the internal structure, which became relatively packed due to the quick setting characteristics of the mixture because it was able to generate a large amount of ettringite in its initial state.

3.4. Repeated freeze–thaw cycles

Fig. 7 shows the relative dynamic modulus of elasticity as a function of the number of freeze–thaw cycles for shotcrete with and without accelerators. The freeze–thaw resistance was observed for 300 cycles, at which point the dynamic modulus of elasticity exceed 80% for all of the specimens.

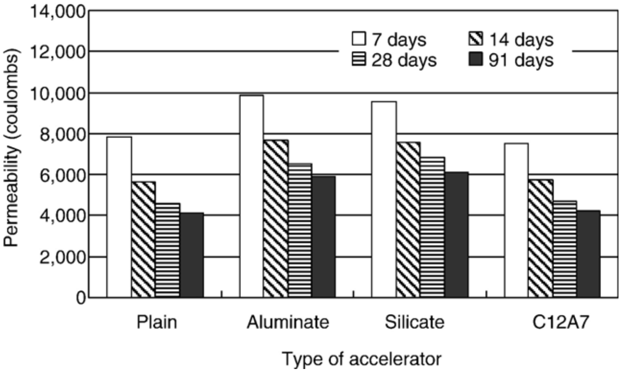


Fig. 6. Results of the chloride ion permeability tests.

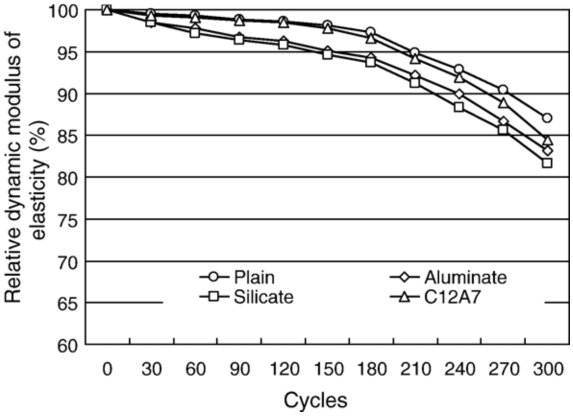


Fig. 7. Results after repeated freeze–thaw cycles.

The trend for the $C_{12}A_7$ mixture was similar to that of plain shotcrete, and the final elasticity was slightly greater than that of the aluminate and silicate mixtures. This was because the $C_{12}A_7$-based accelerator provided excellent strength and, as demonstrated in Section 3.3, its internal structure was sufficiently packed to protected it from humidity, a major cause of frost damage.

4. Conclusions

This study evaluated the performance of shotcrete using a $C_{12}A_7$-based accelerator by examining the setting time, compressive strength, and resistance to chloride ion permeability and repeated freeze–thaw cycles. This study evaluated the long-term strength and durability after manufacturing specimens using shotcreting equipment. The following conclusions were drawn.

1. The $C_{12}A_7$-based accelerator had excellent quick setting characteristics. The $C_{12}A_7$-based accelerator reacts with water and cement to create needle-shaped crystals of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ (ettringite) and to acquire initial strength. In order to increase the initial strength, the specific surface area of the $C_{12}A_7$-based accelerator was increased, and it had a much greater effect on the increase in strength when mixed with slaked lime and anhydrous plaster.
2. The $C_{12}A_7$-based accelerator reduced the strength of the shotcrete less than the silicate- and aluminate-based accelerators did because the $C_{12}A_7$ mixture had a structure that enabled a smooth hydration reaction over the long-term by maintaining the voids on the surface of cement particles due to the crystal characteristics of the acicular ettringite.
3. The $C_{12}A_7$-based accelerator improved the durability of the shotcrete due to its excellent permeability and freeze–thaw cycle resistance compared to other alkali-based accelerators.

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