

# EVALUATION OF A PENETRATION-REINFORCING AGENT TO PREVENT THE AGING OF CONCRETE

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Concrete has three major properties after a penetration-reinforcing agent is applied on its surface. First, the durability is improved by the sol-gel process of synthesized material from the polycondensation of TEOS (tetra-ethoxyorthosilicate) and acrylate monomer. Second, the capability to absorb impact energy is reinforced through the formation of a soft and flexible layer of organic monomers by Tea (Tetra Ethyl Amin). Third, the capability to prevent deterioration is enhanced by adding isobutyl-orthosilicate and alcohol. The performance and application of an agent developed through the synthesis of organic and inorganic material in an effort to prevent concrete from deterioration and improve the durability of concrete structures were verified in diverse experiments. The results of these experiments showed that the application of the proposed penetration-reinforcing agent has the effect of increasing the compressive strength by filling up the internal pores of concrete with physically and chemically stable compounds after penetrating the concrete. It also improves the durability against the deterioration factors such as salt water damage, carbonation, freezing and thawing, and compound deterioration. Therefore, it is confirmed that the penetration-reinforcing agent is a useful substance for the management and repair of concrete structures.

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**KEYWORDS :** Penetration-reinforcing Agent, Durability, Sol-gel Process, Tetra-ethoxyorthosilicate, Tetra Ethyl Amin, Isobutyl-orthosilicate, Acrylate monomer

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## 1. INTRODUCTION

The deterioration of concrete structures, which progresses as time passes, is caused by external factors such as salt water damage and carbonation. Chloride ions and carbon dioxide, which are main causes of deterioration, penetrate from the surface and then permeate into the concrete. Concrete is a porous material [1] which has numerous pores with a range of diameters such as entrapped air pores, entrained air pores, capillary pores, and gel pores. These pores have a detrimental influence on the strength of concrete and on the durability because they become permeation paths for other deterioration factors. Therefore, the coating or penetrating of a concrete surface [2] with organic or inorganic materials is a common method that has been used to maintain the performance of a concrete structure and to prevent external deterioration factors from penetrating into concrete. However, concrete can be coated with organic materials such as epoxy and urethane to create a simple layer on the surface without chemically bonding to the concrete. Such a layer has excellent waterproof ability but allows no air permeability. Consequently, swelling and peeling of the concrete occur due to moisture

evaporation inside concrete. As a result, long-term durability declines due to discrepancies of the elastic modulus and thermal expansion ratio between the layer and the concrete. Furthermore, in the case of inorganic materials such as sodium silicate or lithium silicate, the concrete strength increases as the pores in concrete are filled after the materials penetrate into the concrete and a gelation reaction occurs. However, these materials cannot penetrate concrete up to a sufficient depth due to their rapid reactions with concrete. Moreover, the bonding body can be destroyed easily by external factors such as temperature changes and can be disassembled by moisture because the gels cannot absorb the impact energy and they are typically hydrophilic. [3-6]

In order to offset the shortcomings of both organic and inorganic materials, a penetration-reinforcing agent was developed by synthesizing inorganic materials of the silicate series with an ethoxy group and organic materials with a hydroxide functional group. This paper aims to discuss the performances of the formulated penetration-reinforcing agent such as the functional mechanism, penetration ability, concrete strengthening effect, and deterioration prevention capability.

## 2. MATERIALS AND MECHANISMS

### 2.1 Characteristics of the Materials and Synthesis

The inorganic material of the silicate series TEOS with the ethoxy functional group, which has effects on concrete strengthening and penetrating, and the organic materials with the hydroxide functional group were polycondensed into the base material of the penetration-reinforcing agent. Isobutyl ortho silicate (ISi) and alcohol were added to the base material in order to improve the penetration ability as well as the deterioration-prevention properties of the agent. The property of each material is shown in Table 1.

On one hand, a penetration-reinforcing agent should have low viscosity of single-molecule materials to penetrate easily into concrete. On the other hand, it should have the flexibility of macromolecule materials to withstand contraction and expansion due to temperature changes. In order to satisfy these requirements, an organic-inorganic complex can be a basic form of the agent. It is predicted that the inorganic

substance will increase the compressive strength of the concrete and that the organic substance of macromolecule materials will diminish the influence of external factors such as temperature changes. As the penetration-reinforcing agent should be converted into a rigid body to increase the concrete strength after penetration, the agent should be composed of stable liquids of low viscosity before application. They should also allow polymerization reactions to convert from single molecule materials to an organic-inorganic complex after application. Tetra-methoxyorthosilicate (TMOS) and tetra-ethoxyorthosilicate (TEOS), which have a methoxy or an ethoxy functional group, are the representative inorganic materials that satisfy these conditions because they react with  $\text{Ca}(\text{OH})_2$ , which is produced from the hydration process in concrete.

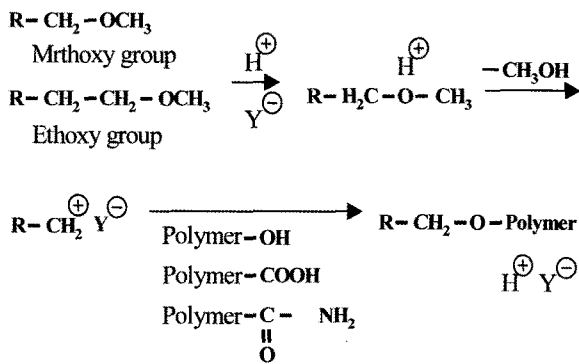


Fig. 1. Synthetic Mechanism of Organic Substances and Inorganic Substances with the Methoxy and Ethoxy Group [7]

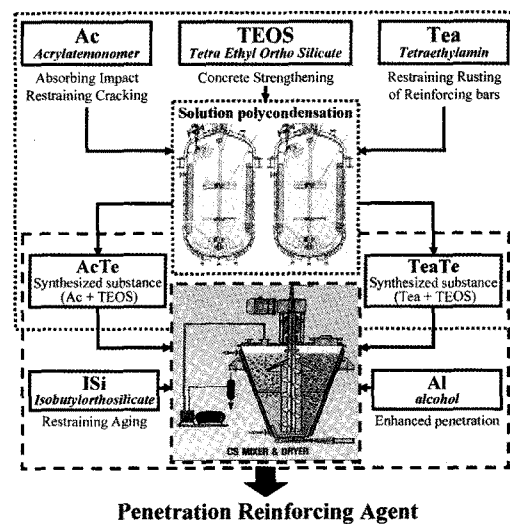


Fig. 2. Manufacturing Process of the Penetration-reinforcing Agent

Table 1. The Property of the Materials Used in the Penetration-reinforcing Agent

	Role	Property
Basic materials	Concrete strengthening	Tetra Ethyl Ortho Silicate (TEOS, inorganic material) Basic structure: $\text{Si}(\text{OH})_4, \text{R}_4\text{Si}(\text{OR})_{4-n}, \text{YRSi}(\text{OR})_3$
	Absorbing impact and restraining cracking	Acrylate Monomer (Ac, organic material) Basic structure: $\text{CH}_2=\text{C}(\text{CN})$
	Restraining rusting of reinforcing bars	Tetra Ethyl Amin (Tea, organic material) Basic structure: $\text{R}-\text{C}_n\text{H}_{2n+1}$
Additional materials	Restraining material aging	Isobutyl Ortho Silicate (ISi, synthesized material) Basic structure: Isobutyl-Si <sub>n</sub>
	Enhancing the penetration ability	Alcohol (Al, organic material)

TMOS and TEOS are polymerized through the synthesis mechanisms as shown in Fig. 1. They transform into an electronically unstable state with a positive or negative charge because CH<sub>3</sub>OH (methanol) or CH<sub>3</sub>CH<sub>2</sub>OH (ethanol) are produced when they are mixed with ionic matters such as Ca(OH)<sub>2</sub>. The transformed substances with positive or negative charges easily react with other substances having the functional group OH / COOH / -C(=O)-NH<sub>2</sub>. Consequently, Ca(OH)<sub>2</sub> is reproduced and substances having the functional group OH / COOH / -C(=O)-NH<sub>2</sub> bond with the methoxy or ethoxy functional group. Through this mechanism, organic-inorganic synthesized substances can be produced by polycondensing nano-particle silicates (about 5 nm) and organic monomers in a high temperature and high pressure environment.

The penetration-reinforcing agent was manufactured through the solution polycondensation of the basic materials shown in Table 1 in a high temperature and high pressure environment. The synthetic mechanism and manufacturing process is shown in Fig. 1 and Fig. 2, respectively. In Fig. 2, AcTe signifies the synthesized substance of acrylate monomer (Ac) and TEOS, and TeaTe signifies the synthesized substance of tetraethylamin (Tea) and TEOS. Isobutylorthosilicate (ISi) is added in order to prevent the concrete from deteriorating, and alcohol (Al) is added in order to decrease the viscosity and surface tension and increase the penetration depth.

### 2.2 Reaction Mechanism

Various types of inorganic networks are produced from silicon or metal alkoxide monomer precursor in a sol-gel reaction of silicate compounds. This is the basic reaction mechanism of the penetration-reinforcing agent within the concrete.

The sol-gel reaction mechanism of the penetration-reinforcing agent within concrete is shown in Fig. 3. The sol-gel reaction can be divided into the two stages of hydrolysis and condensation. In the hydrolysis stage, the silicate compound reacts with H<sub>2</sub>O due to the catalytic action of Ca(OH)<sub>2</sub>, which exists in concrete, to form a colloidal sol. In the condensation stage, the liquid gel that is gelatinized from the sol combines with cement hydrate to produce inorganic networks. As a silicate precursor that forms a colloidal sol, metal alkoxide, which has metal or metalloid elements and various reactive ligands, is used. The penetration-reinforcing agent was manufactured using TEOS, a type of commonly used alkoxy silane.

The penetration-reinforcing agent, which is composed of silicate with alkoxy functional groups and macromolecular organic substances, goes through a de-alcohol process due to the catalytic reaction of calcium hydroxide in concrete, and silicate with alkoxy functional groups transforms into an electronically unstable material with a positive or negative charge. The electronically unstable material is easily reacted with concrete hydrates through the mechanism shown in Fig. 4.

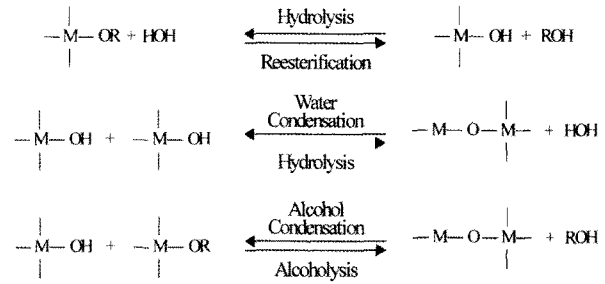


Fig. 3. The Sol-gel Reaction Mechanism (M=Silicate)

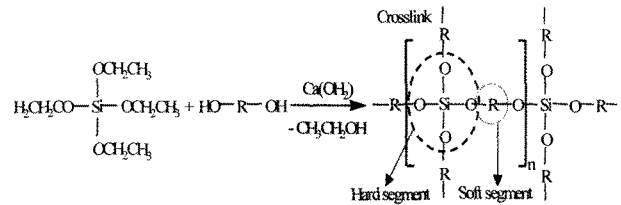


Fig. 4. Reaction Mechanism of the Penetration-reinforcing Agent

As shown in Fig. 4, TEOS reacts with calcium hydroxide and fills the internal pores of the concrete with the hard segment of O-Si-O, while the organic macromolecules with the alkoxy functional groups lead to cross-link and form a soft segment of O-R-O.

## 3. EVALUATION OF CAPACITY

### 3.1 Penetration Depth

The penetration-reinforcing agent can easily penetrate into the concrete by sufficient capillary suction after the agent is applied to the concrete surface because the particles of the penetration-reinforcing agent are nano-sized and are therefore smaller than the capillary pores in concrete. Furthermore, the penetration depth can be a basic factor in the evaluation of the performance of the penetration-reinforcing agent, as the strengthening of the concrete and the prevention of deterioration by filling capillary pores are restricted within the penetrated depth. As the penetration depth of the agent is mainly influenced by the concrete strength,  $\Phi 100 \times 100$ mm concrete specimens at water-cement ratios of 35%, 40%, 50%, and 60% were fabricated and then cured under the conditions of a relative humidity of 50% and a temperature  $20 \text{ }^\circ\text{C} \pm 3 \text{ }^\circ\text{C}$  for 120 days. The upper surface had the penetration-reinforcing agent applied after curing, and the penetration depth was subsequently measured 14 days after the curing process. As the penetration depth, the length from the surface to

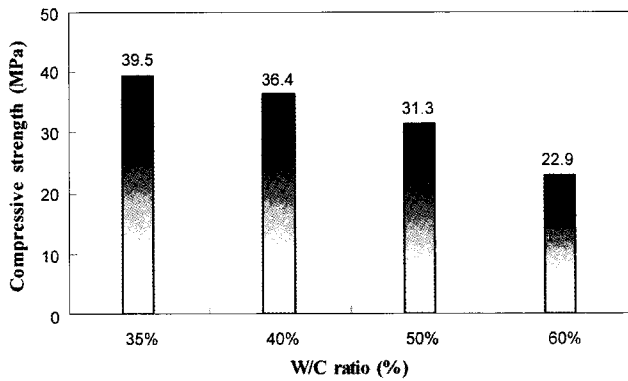


Fig. 5. Compressive Strength of Specimens with Respect to the w/c Ratio

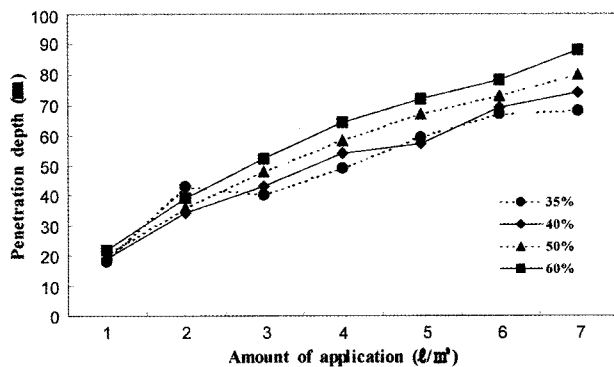


Fig. 6. Penetration Depth with Respect to the w/c Ratio and the Amount of Application

the position where the waterproof ability was apparent after splitting the specimen in half was measured according to the Korean Industrial Standards KS F4930 (Penetrating water repellency of liquid type for concrete surface application) [9]. The compressive strength of the specimen with respect to the w/c ratio is shown in Fig. 5, and the penetration depth with respect to the w/c ratio and the amount of application is shown in Fig. 6. The result shows that the agent penetrates to more than 30 mm at a low w/c ratio of 60% to a high w/c ratio of 35% when more than 2 l/m<sup>2</sup> of the agent is applied.

### 3.2 Microstructure Characteristics

X-ray diffraction analysis and SEM (scanning electron microscope) observations were carried out in order to analyze the change of hydrated products and microstructure inside the concrete after applying the agent onto the surface of the concrete.

From the x-ray diffraction analysis shown in Fig. 7 and Fig. 8, Torbermorite ( $5CaO \cdot 6SiO_2 \cdot 5H_2O$ : C-S-H

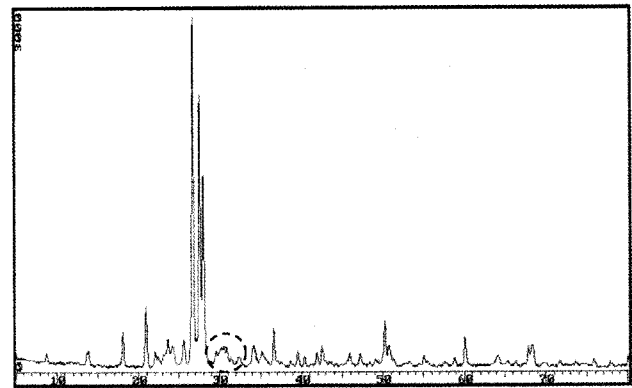


Fig. 7. XRD Spectrum without Application

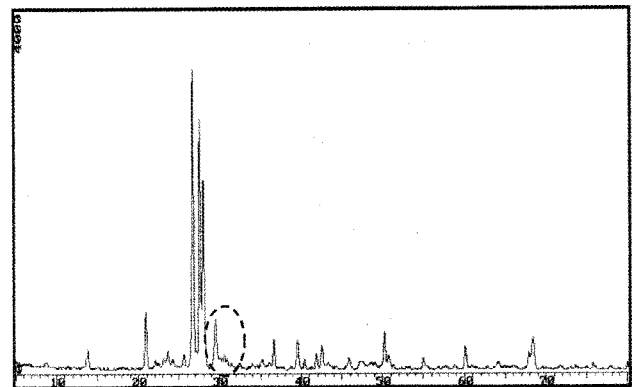


Fig. 8. XRD Spectrum with Application

gel) and Orthoclase ( $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ ), which are the bonding products between the concrete and the agent, were observed more in the concrete with the application than in that without the application. Therefore, it was confirmed that strong and stable chemical bonds are built up in the pores of concrete after the agent penetrates into the concrete.

From the SEM (scanning electron microscope) observations shown in Fig. 9 and Fig. 10, many pores exist among the hydrates in the concrete without the application whereas a compact microstructure is formed with O-Si-O bonds in the concrete with the application. In the specimen without the application, the size of the pores formed by concrete hydration was observed to be in the range of 10 nm~100 μm, while that of the capillary pores was in the range of 3 nm~2 μm. Here, the observed hydrates were ettringite, calcium silicate hydrate, and calcium hydroxide. The concrete with the agent applied not only had a compact microstructure with O-Si-O bonds but also had good ventilation with micro capillary pores due to the reaction of the agent, as shown in Fig.10; hence,

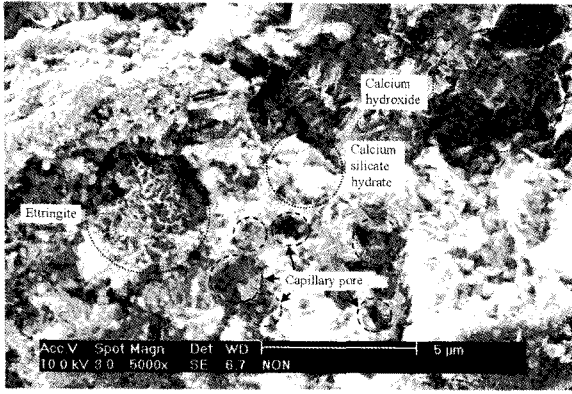


Fig. 9. SEM without Application (× 5000)

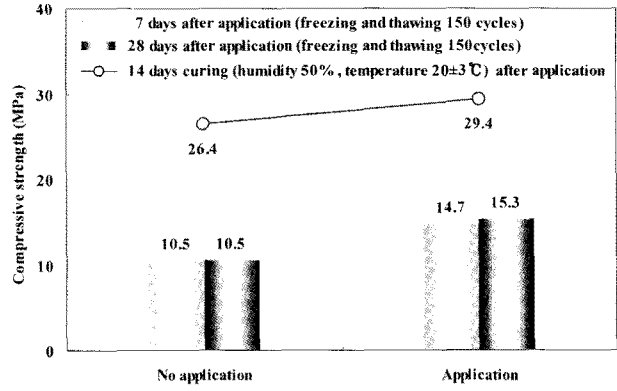


Fig. 11. Compressive Strength

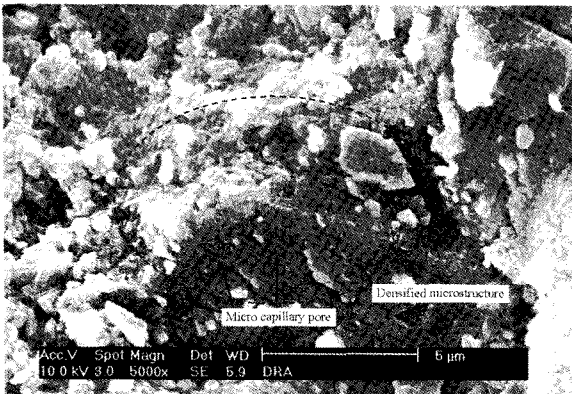


Fig. 10. SEM with Application (× 5000)

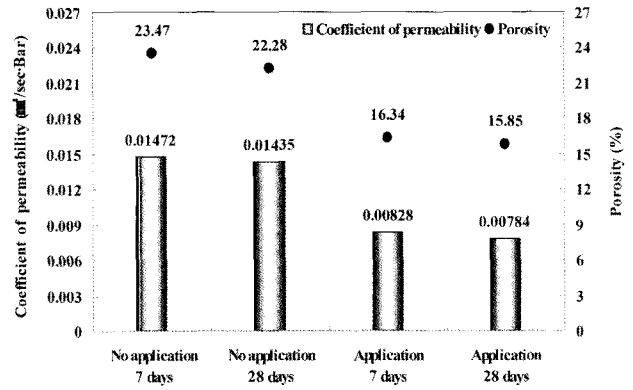


Fig. 12. Coefficient of Permeability and Porosity after 150 Cycles of Freezing and Thawing

Table 2. Mixing Proportion of a Concrete Specimen

Target compressive strength at 28 days	w/c ratio (%)	Unit content (kg/m <sup>3</sup> )			
		Water	Water	Water	Water
24MPa	48	178	370	771	891

deterioration such as swelling and peeling due to moisture evaporation can be prevented in applied concrete.

### 3.3 Concrete Strengthening

To evaluate the concrete strengthening ability of the penetration-reinforcing agent,  $\Phi 100 \times 200$  mm specimens with mixed proportions, as shown in Table 2, were fabricated. The penetration-reinforcing agent was applied to half of the specimens after 28 days of curing at a relative humidity

of 50% and a temperature of  $20 \text{ }^\circ\text{C} \pm 3 \text{ }^\circ\text{C}$ . The compressive strength of all specimens was measured 14 days after the agent was applied. The compressive strength of the treated specimens was 11% higher compared to the untreated specimens. As shown in Fig. 11, the compressive strength of the untreated specimens was 26.4MPa whereas that of the treated specimens was 29.4MPa.

To evaluate the damage restoration performance of the penetration-reinforcing agent, the penetration-reinforcing

agent was applied to the specimens after they were pretreated with 150 cycles of freezing and thawing at temperatures of  $-18\text{ }^{\circ}\text{C} \sim +4.5\text{ }^{\circ}\text{C}$ . The compressive strength, coefficient of permeability, and porosity were measured 7 and 28 days after the application. The results show that the compressive strength of the treated specimens was 46% higher than compared to the untreated specimens 28 days after the application, as shown in Fig. 12. This shows that the concrete strength can be recovered after the penetration-reinforcing agent is applied to concrete in which the internal microstructure was previously destroyed due to freezing and thawing.

The coefficient of permeability and porosity as measured 28 days after the application are consistent with the increase in the compressive strength. As shown in Fig. 12, the coefficient of permeability of the treated specimens is 45% less than the untreated specimens. Moreover, the porosity of the former is 29% less than that of the latter.

### 3.4 Preventing and Recovering Deterioration

The performance of the agent in terms of preventing and recovering deterioration due to salt water, carbonation, freezing and thawing, and compound aging was verified on the specimens with the mixing proportions shown Table 2.

To evaluate the capability of the agent to prevent damage by salt water, the chloride ion concentration was measured from extracted portions that were 0~15mm and 15~30mm from the top of a  $\Phi 100 \times 100\text{mm}$  specimen. This specimen was coated with epoxy on all sides except the top in order to derive the chloride ion penetration in one direction and was then deposited in NaCl solution (3.6%) for 28 days. The chloride ion concentration of a specimen treated in this manner was 97% less compared to an untreated specimen, as shown in Fig. 13.

To evaluate the capability of the agent to recover from a chloride attack, the amount of chloride which is

immobilized by the penetration-reinforcing agent was measured from the samples extracted from each depth after fabricating mortar specimens with a w/c ratio of 54% using NaCl solutions of 0.01, 0.03, 0.1, and 0.2% mixed with water and applying the agent to half of the mortar specimens. The results in Fig. 14 show that the immobilized chloride amounts to approximately 70% of the entire amount of chloride in the untreated specimens.

To evaluate the capability of the agent to prevent carbonation, the colored depth from the surface after spreading a phenolphthalein solution onto a split section of a concrete specimen was measured. The specimens were exposed to an accelerating condition characterized by a carbon dioxide concentration of 10%, a temperature of  $30 \pm 3\text{ }^{\circ}\text{C}$ , and a relative humidity of  $60 \pm 5\%$  for 91 days after the  $\Phi 100 \times 100\text{mm}$  specimens were coated with

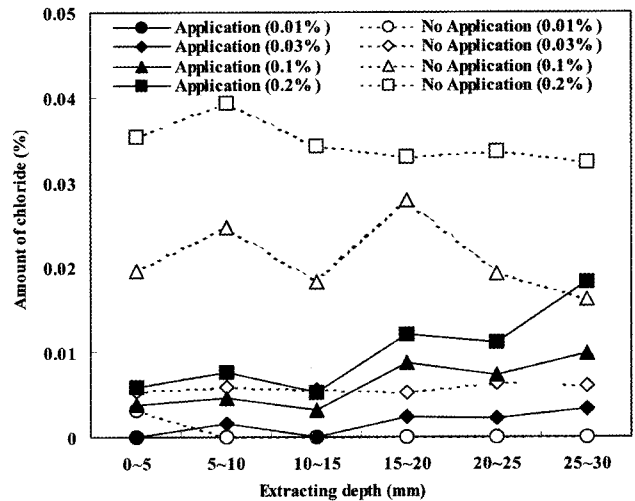


Fig. 14. Immobilization of Chloride Ions

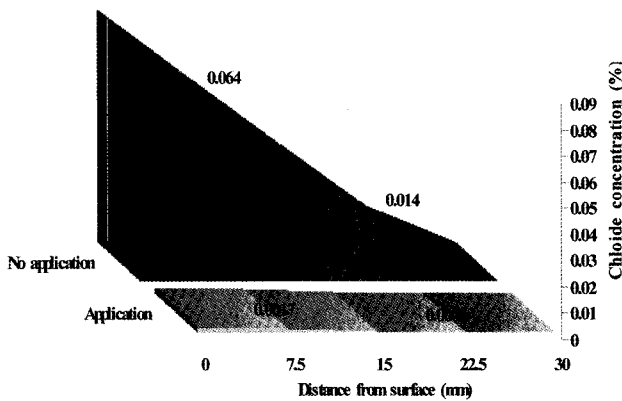


Fig. 13. Concentration of Chloride Ions According to the Distance from the Surface

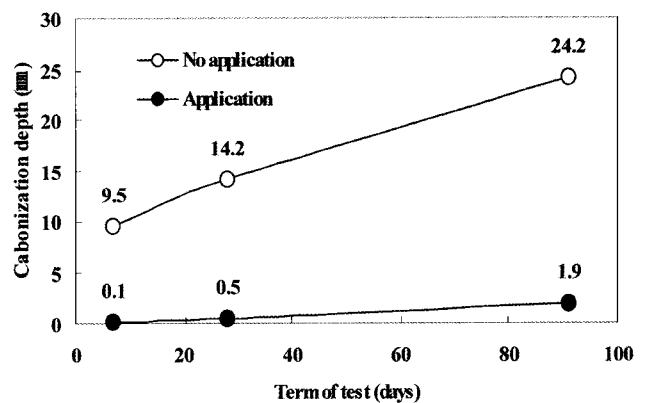


Fig. 15. Carbonization Depth in Terms of the Exposure Time

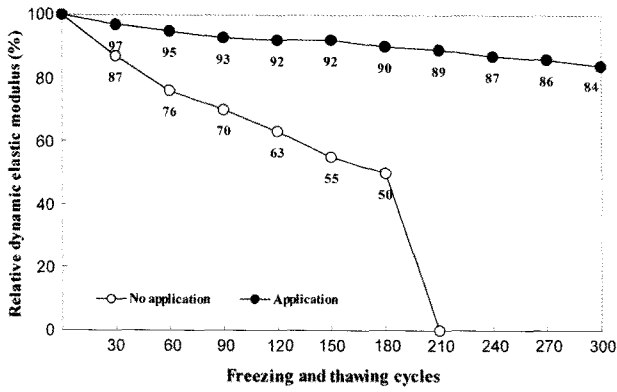


Fig. 16. Relative Dynamic Elastic Modulus in Terms of Freezing and Thawing Cycles

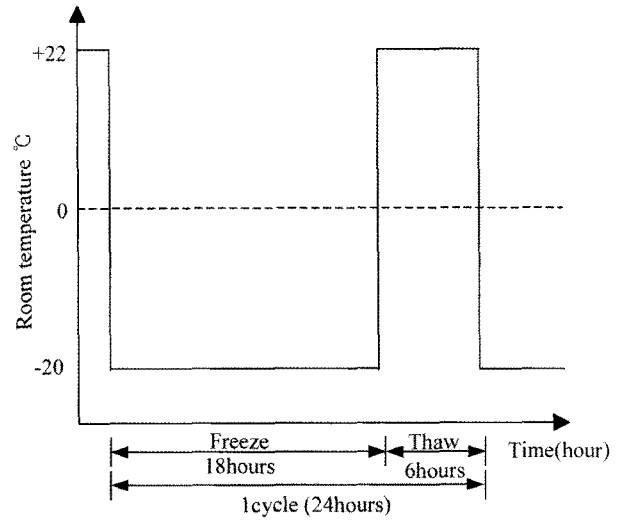


Fig. 18. Temperature Conditions for Compound Deterioration

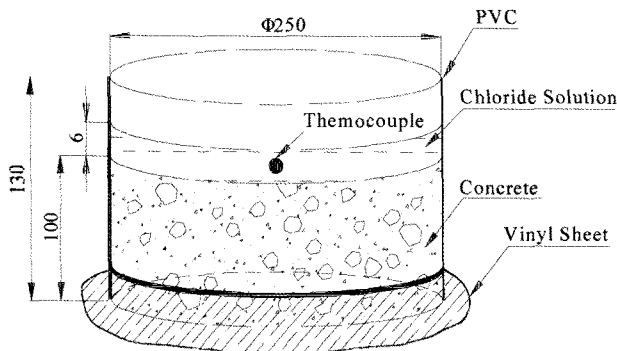


Fig. 17. Specimen for Compound Deterioration

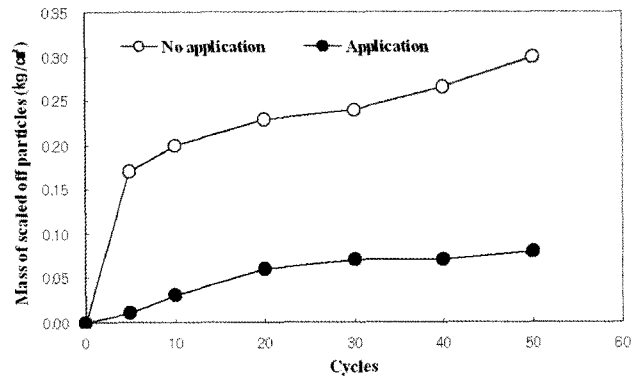


Fig. 19. Scaling Resistance of a Concrete Surface Exposed to Compound Deterioration

epoxy on all sides except the bottom in order to derive the carbon dioxide penetration in one direction. The result in Fig. 15 shows that applying the agent decreased the carbonation depth of the specimens.

To evaluate the capability of the agent to resist freezing-and-thawing cycles, the relative dynamic elastic moduli of the 100 × 100 × 400mm specimens were measured every 30 cycles up to 300 cycles of freezing and thawing. This operation was carried out by freezing in air of -18°C and thawing in water of +4.5°C. According to the results in Fig. 16, the relative dynamic elastic modulus of the specimens treated thus after 300 cycles was 84% of the initial modulus. In contrast, the modulus of the untreated specimens after 150 cycles was 55% of the initial modulus. Moreover, it could not be measured after 210 cycles. This result confirms that the application of the agent decreases the amount of internal moisture by making the concrete microstructure dense. It also thwarts external moisture penetration through the formation of a waterproof layer.

Lastly, in order to evaluate the degree to which the concrete is protected from compound deterioration, including

freezing-and-thawing cycles and salt water damage, the mass of scaled-off particles from the specimen shown in Fig. 17 was weighed up to 50 cycles of the temperature conditions. This is shown in Fig. 18.

The results in Fig. 19 show that the mass of the scaled-off particles from the specimens that received no treatment is greater than that from the treated specimens. After 50 cycles, the mass of scaled-off particles from the treated specimens is only 26% of that from those to which no treatment was applied. In a visual rating of the surface according to ASTM C672 (Scaling resistance of concrete surface exposed to deicing chemicals), specimens that received no treatment were given a rating of 3 (moderate scaling), whereas those that received the treatment were given a rating of 0 (no scaling).

#### 4. CONCLUSION

In this paper, the reaction mechanism and performance of an organic-inorganic synthesized penetration-reinforcing agent which was developed to prevent concrete structures from deterioration and recover damage were proved experimentally. The principal results are given below.

- 1) The penetration-reinforcing agent in this paper was developed by mixing additives, which help the agent to penetrate easily into concrete and prevent the concrete from deterioration, to a synthesized material of TEOS, an inorganic substance of the silicate series, and organic substances with a hydroxide functional group.
- 2) The penetration-reinforcing agent is able to penetrate into concrete only by capillary suction without any external load because the agent is composed molecules of a smaller size compared to the capillary pores of the concrete. Moreover, the penetration depth into the specimens of a w/c ratio of 35% ~ 60% is more than 30mm when 2 l/m<sup>2</sup> of the agent is applied to the surface. This implies that the developed agent increases the penetration depth by controlling the initial rapid reaction of the existing surface-protecting materials.
- 3) From the analysis of the microstructure characteristics using XRD and SEM, it was affirmed that strong and stable chemical bonds are formed within the concrete as the penetration-reinforcing agent reacts with the hydrates and forms C-S-H gel after penetrating.
- 4) With regard to the concrete strengthening effect, the compressive strength of concrete after an application of the proposed agent is 11.4% higher compared to that in untreated samples. In the case of concrete damaged by 150 cycles of freezing and thawing, the compressive strength of concrete increases by 46% and the coefficient of permeability and porosity decrease by 45% after the application of the agent.
- 5) After the agent is applied to concrete, the performance of the concrete in terms of recovering from damage as well as preventing deterioration events such as salt attack, carbonation, freezing and thawing, and compound aging is enhanced.

The penetration-reinforcing agent permeates further and deeper than existing surface protecting materials and forms a physically and chemically stable microstructure as its shortcomings, specifically the rapid reaction with concrete, is improved. It is concluded that the agent can improve the durability of structures in use and that it can protect new concrete structures from deterioration.

#### ACKNOWLEDGEMENT

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