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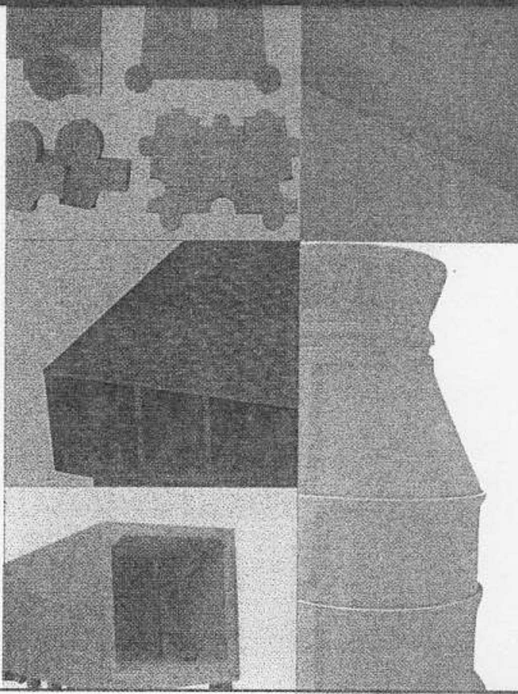

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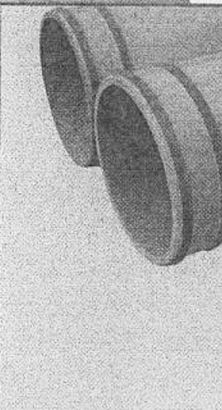

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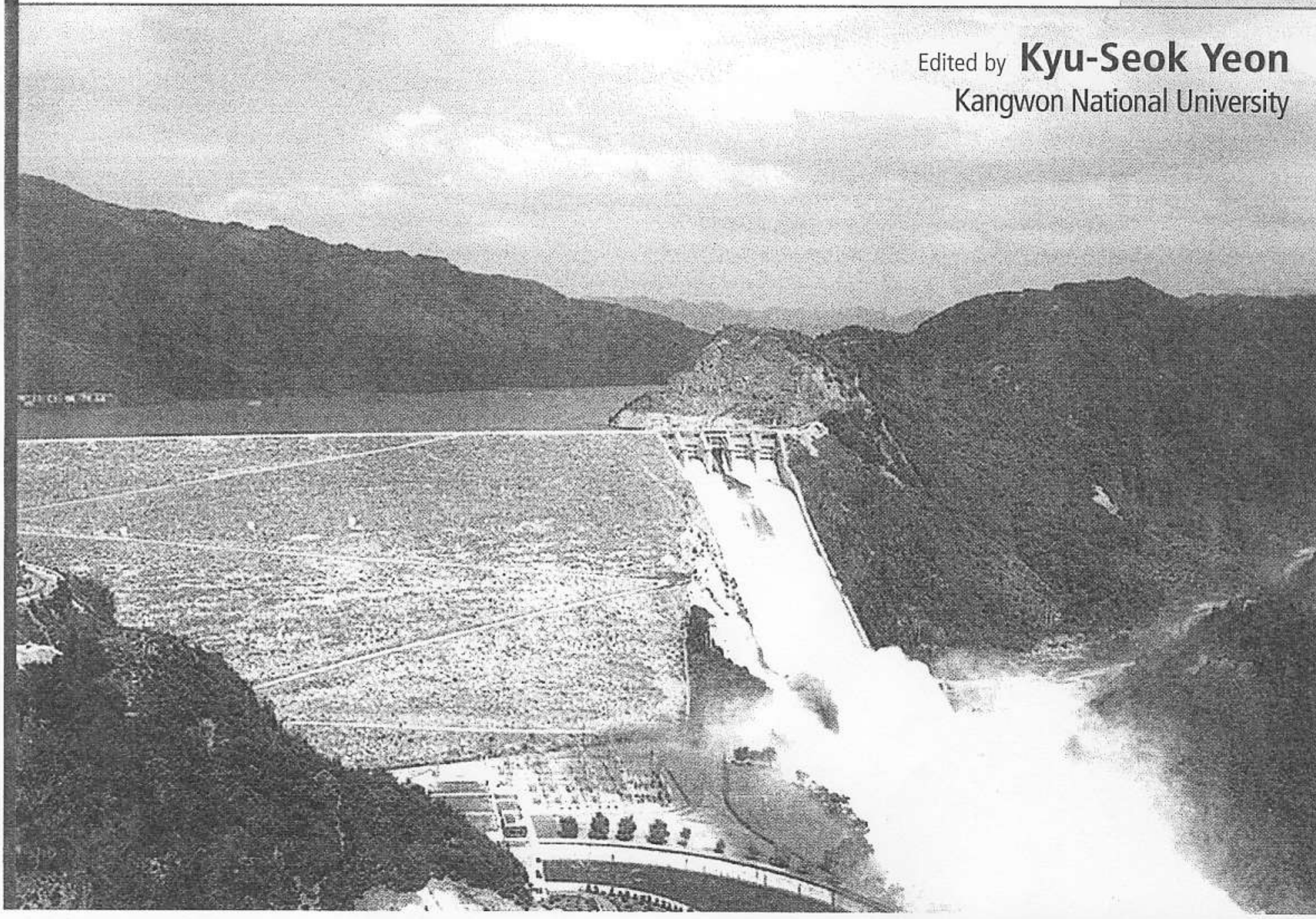

Edited by **Kyu-Seok Yeon**
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Kangwon National University

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6 CONCLUSIONS

1. The developed mix proportion for M20 grade to M40 grade Geo Polymer concrete is attaining the target strength
2. Geo Polymer Concrete is achieving higher strength at early stage when compare to normal concrete.
3. Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of fly ash-based geopolymer concrete.
4. Higher the ratio of sodium silicate-to-sodium hydroxide ratio by mass, higher is the compressive strength of fly ash-based geopolymer concrete.
5. Curing time, in the range of 2 days, produces higher compressive strength of fly ash-based geopolymer concrete however; the increase in strength beyond 7 days is not significant.
6. The slump value of the fresh fly-ash-based geopolymer concrete increases with the increase of extra water added to the mixture.
7. The Rest Period, defined as the time taken between casting of specimens and the commencement of curing, of up to 5 days increases the compressive strength of hardened fly ash-based geopolymer concrete. The increase in strength is substantial in the first 3 days of Rest Period.
8. The fresh fly ash-based geopolymer concrete is easily handled up to 120 minutes without any sign of setting and without any degradation in the compressive strength.
9. As the H_2O-to-Na_2O molar ratio increases, the compressive strength of fly ash-based geopolymer concrete decreases.
10. As the ratio of water-to-geopolymer solids by mass increases, the Compressive strength of fly ash-based geopolymer concrete decreases.
11. The average density of fly ash-based geopolymer concrete is similar to that of OPC concrete.

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Evaluation of Inorganic Polymer as Adhesive Material for Repair of Reinforced Concrete

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ABSTRACT

A new development in the repair and strengthening of reinforced concrete systems is the use of carbon fiber reinforced polymers (CFRP) strips bonded to concrete substrate with epoxy resins. It has been reported that epoxy adhesive used are extremely sensitive to high temperatures. Some authors conclude that the epoxy temperature should not exceed 70 ° C in order to safeguard the adhesiveness of the epoxy and, thus, the integrity and adequate functioning of CFRP. It is noted that frequently exposure to direct sunlight causes temperatures higher than 70 °C. Inorganic polymers are often referred to as geopolymers or alkali-activated cements and are known to possess high stability at high temperature. Tungsten mine waste inorganic polymer (TMWIP) is a new cementitious material, obtained from dehydroxylated mine waste powder mixed with minor quantities of calcium hydroxide and activated by NaOH and waterglass solutions. This paper reports some results on the bonding capacity of this inorganic polymer, i.e. TMWIP, and concrete. Results show that given the proper mix the new binder demonstrates high adhesion to concrete substrate.

KEYWORDS: reinforced concrete, inorganic polymers, repair material, elasticity, mine waste

1 INTRODUCTION

A new development in the repair and strengthening of reinforced concrete systems is the use of carbon fiber reinforced polymers (CFRP) strips bonded to concrete substrate with epoxy resins. This method is a relatively new retrofitting method, developed first in Japan [1,2]. Epoxy adhesive being used in the construction industry is very sensitive to temperature variations. Both experimental and finite element results show that the epoxy temperature should not exceed 70 °C in order to maintain the integrity between the CFRP and concrete [3]. It is noted that frequently exposure to direct sunlight causes temperatures higher than 70 °C which causes malfunction CFRP. This means that adhesive materials that remain stable with higher temperatures are needed. Inorganic polymers are often referred to as geopolymers or alkali-activated cements and are known to possess high stability at high temperature. Studies of alkali-activated cements have a long history in the former Soviet Union, Scandinavia, and Eastern Europe [4]. In 1978, Davidovits created the term "geopolymer", to characterise new materials with the ability to transform, polycondense and adopt a shape rapidly at low temperatures like "polymers" [5]. The polymerisation process involves a chemical reaction under higly alkaline conditions on Al-Si minerals yelding polymeric Si-O-Al-O bonds with empirical formula Mn [- (Si - O_2)z – Al - O]n. wH2O, where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium [6]. Davidovits reported several advantages of geopolymeric cementitious systems over Portland cement mainly environmental, due to the fact that geopolymeric based concrete has a much longer service life than Portland cement based ones, to the metals waste encapsulation capacity and to lower CO_2 emissions [7]. The geopolymerization requires a precursor that contains significant quantities of silicon and aluminium held in an amorphous phase such as ashes from power stations or mining and quarrying wastes.

Over the last years several authors have reported research in a large number of aspects related to geopolymeric based binders such as: dependence of the nature on source materials (geopolymers synthesised from calcined sources show a higher compressive strength than from raw materials) [8,9], immobilization of toxic metals [10-12], reaction mechanisms and hydration products [13-17], the role of calcium in geopolymerization [18-21], manufacture operations [22,23] and even the development of lightweight building materials [24]. Tungsten mine waste inorganic polymer (TMWIP) is a new cementitious material, obtained from dehydroxylated mine waste powder mixed with minor quantities of calcium hydroxide and activated by NaOH and waterglass solutions. This paper reports some results on the bonding capacity of this inorganic polymer, i.e. TMWIP, and concrete.

2 EXPERIMENTAL PROGRAM

2.1 Materials

2.1.1 TMWIP geopolymeric binder

The TMWIP geopolymeric binder used in this investigation as repair product was made using tungsten mine waste mud previously subject to a thermal treatment at 950° C during 2 hours, in order to achieve the dehydroxylated state. Mineralogical composition and thermal conditions have been described elsewhere [27]. The chemical composition of the mine waste mud is shown in Table 1.

Table 1. Gradation and physical characteristics of aggregates

	Cumulative percentage retained	
	Fine aggregate	Coarse aggregate
9,5mm	0	0
4,76mm	0	35,4
2,38mm	0	91,5
1,19mm	13,9	97,2
590µm	61,6	98,5
297µm	97,3	99,2
149µm	99,7	99,4
74µm	99,9	99,6
Dust content (< 74µm)	0	0,4
Fineness modulus	2,72	5,2
Max. dimension (mm)	2,38	9,52
Water absorption (%)	0,	0,4
Density (Kg/m^3)	2624	2689

2.1.2 OPC concrete substrate

The properties of the aggregates used to make the concrete substrates are shown in table 2. Using the Faury concrete mix design method [25], a C30/37 strength class concrete was designed. The concrete mixes and their main properties are described in Table 3. The concrete specimens were cured immersed in water during 3 months. This curing period provides an almost as complete concrete hydration as old concretes in field practice and has been used by other authors [26].

Table 2. Mix proportions and main properties of the concrete substrates

Components	C30/37
Cement II 32,5 (Kg/m^3)	504
Fine river sand	417
Coarse aggregate	1154
W/C ratio	0,43
fc_{28d}^{a} (MPa)	37,8
ft_{28d}^{b} (Mpa)	8,7

[Note] ^{a}Average value of three specimens (150×150×150mm^3), ^{b}Average value of six specimens (40×40×160mm^3

Table 1. Chemical composition of TMWIP (%)

SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	MgO	SO_4	TiO_2	As	Other minor oxides
53,48	16,66	12,33	7,65	0,62	1,27	3,10	1,39	1,28	2,22

The SiO_2/Al_2O_3 atomic ratio is 5,5 higher than the one suggested by Davidovits of about 2 for making cement and concrete, however the final SiO_2/Al_2O_3 atomic ratio in the hardened binder depends mainly on the reactivity of Al-Si because not all the silica and alumina are reactive so even despite the fact Al and Si have synchro-dissolution behaviour in alkaline solution, meaning they dissolve from the mineral in some linked form one cannot expect the same Si/Al ratio in the final hydration product as the one present in the original precursor material. Indeed most of the Al-Si materials cannot even supply sufficient Si in alkaline solution to start geopolymerization, this explains why they need extra silica provided in solution by waterglass, which influences the Si/Al ratio of the hardened binder.

The XRD patterns indicated that mine waste mud consists mainly of muscovite and quartz which were identified by their characteristic patterns as follows: muscovite (card 46 - 1409) and quartz (card 46 - 1045). For those thermal conditions XRD patterns indicated that dehydroxylation did not result in a complete collapse of muscovite structure. Calcination leads to formation of an amorphous phase, causing an increase in the general background (BG) of XRD patterns and dominantly taking place in the calcinations interval from 850 to 950° C, with a thermal behaviour similar to other phyllosilicate clay minerals. The main muscovite peak (2θ=8,8°) persisted even after the sample had been heated at 950° C although it decreased considerably. Peak area measurements revealed that about 12% of muscovite survived calcination at 950°C. Molecular changes during dehydroxylation were also examined with infrared emission spectra (FTIR), confirming decrease in the absorption peaks at 3600-3700 (OH stretch), however the main muscovite peak did not disappear totally indicating only a partial transformation.

The geopolymeric binder used was a mixture of coarse aggregates, mine waste mud, calcium hydroxide, alkaline silicate solution and water. The coarse aggregates were the same used in the design of concrete substrate. The mass ratio of coarse aggregates, waste mud: and alkaline activator was 1,5:1:1. Calcium hydroxide was used to replace mine waste mud with a percentage substitution of 10%, because this percentage has been found to lead to the highest compressive strengths [28]. An activator with sodium hydroxide (24M) and sodium silicate solution (Na_2O=8,6%, SiO_2=27,8%, Al_2O_3=0,4% and water=63,2%) was used with a mass ratio of 1:2,5. Previous investigations have show that these conditions lead to the highest long term compressive strength results in alkali-activated TMWM binders [29]. Distilled water was used to dissolve the sodium hydroxide flakes to avoid the effect of unknown contaminants in the mixing water. The alkaline activator was prepared prior to use. The sand, mine waste mud and calcium hydroxide were dry mixed before being added to the activator. The compressive and tensile strength of geopolymeric based binder was as follow:

Fc_{1d} = 47MPa, fc_{7d} = 60,3MPa, fc_{14d} = 71MPa, fc_{28d} = 78,3MPa

ft_{1d} = 7Mpa, ft_{7d} = 11,5Mpa, ft_{14d} = 13,6Mpa, ft_{28d} = 10,7Mpa

2.2 Specimen preparation, bond strength testing and microanalysis

Bond strength was assessed from a slant shear test. The slant shear test uses square prisms made of two halves, one of the concrete substrate and one of the repair material, tested under axial compression. The adopted geometry for the slant shear specimens was a 50×50×125mm^3 prism with an interface line at 30° to the vertical (Figure 1). Bond strength was calculated by dividing the maximum load at failure by the bond area and was obtained from an average of 4 specimens determined at the ages of 1, 3, 7, and 28 days of curing.

In order to increase the specific surface of the concrete substrate an etching procedure was carried out. The concrete surface was immersed in a 5% hydrochloric acid solution for 5 minutes and then carefully washed to ensure the removal of $CaCl_2$ which results from the reaction between HCl and $Ca(OH)_2$. According to some researchers this procedure leads to an increase of micro and fine roughness of the concrete substrate [30].

The specimens were named after the repair materials and concrete substrate surface treatments. Specimens using concrete substrate repaired TMWIP geopolymer with and with no surface treatment were named respectively, GP - ES (Etched surface) and GP - NTS (No treatment surface). Slant specimens with substrate surface treatment as cast against metallic formwork, and as cast against wood formwork were also used repaired with TMWM geopolymeric binder and were named, GP-MF and GP-WF respectively. For examination by scanning electron microscopy (SEM), the specimens were embedded into a low viscosity epoxy resin, cut and polished. After the lapping stage an additional epoxy impregnation was performed, and the samples were relapped in order to ensure full resin impregnation and a good quality polish. The samples were then carbon-coated. A Hitachi S2700 scanning electron microscope was used equipped with a solid backscattered detector.

3 RESULTS AND DISCUSSION

The results of the effect of the several repair solutions on average bond strength are shown in Figure 3. The failure modes were characterized by the location of the failure in the slant specimens. An adhesive failure occurs when the plane of failure is along the interface surface (Figure 4a). Figure 4b shows a slant specimen failed in a monolithic failure mode. The values of bond strength in slant specimens with a monolithic failure mode are a lower estimate. It can be seen that the specimens repaired with the TMIP geopolymeric binder present the high bond strength´s even at early ages. Specimens repaired with geopolymer binder with 1 day curing have higher bond strength than specimens repaired with current commercial products after 28 days curing. Specimens repaired with the TMIP geopolymeric binder appear to be influenced not by the chemical treatment in sawn concrete surface substrates, but by the use of concrete surfaces as cast against formwork. Those kinds of surfaces are rich in calcium hydroxide but lack exposed coarse aggregates which could contribute to improve bond strength due to silica dissolution from the aggregate surface. This is consistent with previous research by the authors [29].

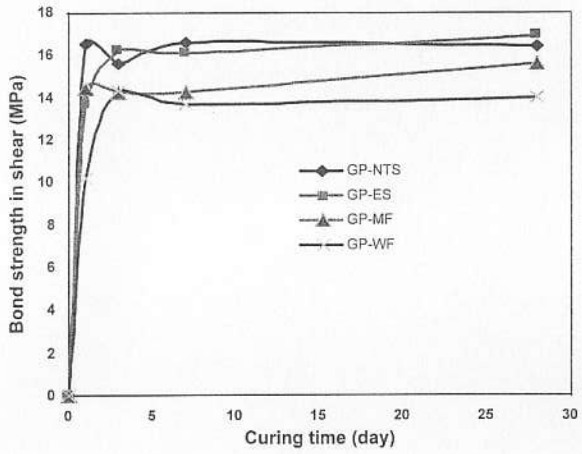

Figure 3. Slant shear test results.

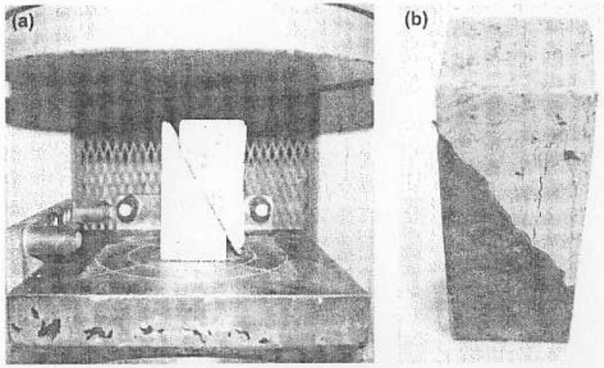

Figure 4. Slant specimens failure mode; (a) Adhesive failure and (b) Monolithic failure.

Table 4 shows the number of specimens that had an adhesive failure. As can be seen, only the slant specimens repaired with the geopolymeric binder and saw concrete substrates present monolithic failures due to is high bond strength.

Table 4. Specimens with an adhesive failure

		Concrete surface treatment			
		ES	NTS	MF	WF
Curing days	1	2	0	4	4
	3	0	0	4	4
	7	0	0	4	4
	28	0	0	4	4

Table 5 shows the coefficient of variation (COV) of bond strengths according to curing age. The results show that in all cases, COV decreases with curing age and shear strength increases except in the case of the specimens repaired with the TMWM geopolymeric binder and with chemical surface treatment (GP-ES). The specimens repaired with the TMWM geopolymeric binder show low COV values even at early ages and are not influenced by the chemical treatment.

Table 5. Coefficient of variation of bond strength (%)

		Concrete surface treatment			
		ES	NTS	MF	WF
Curing days	1	6,7	6,7	12,5	14,8
	3	5,6	6,4	8,4	6,3
	7	5,6	6,0	7,7	5,8
	28	6,0	6,1	7,0	1,4

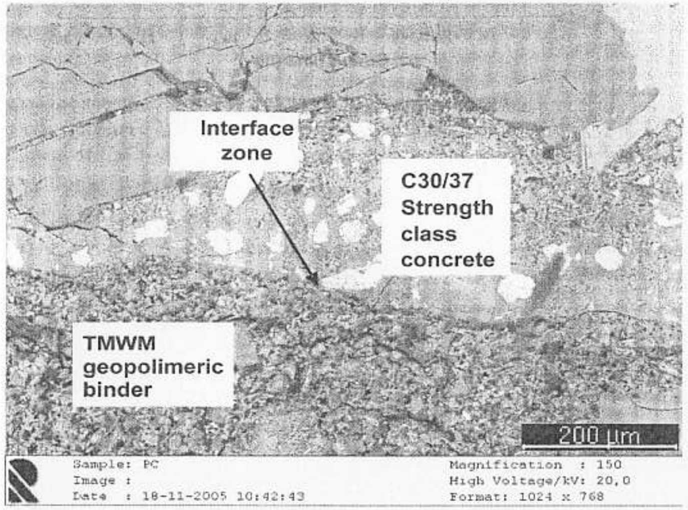

Figure 5. **SEM micrographs of interfacial transition zone between concrete substrate and geopolymeric binder.**

The explanation for this behaviour lies in the fact that OPC concrete substrate surfaces are rich in calcium hydroxide, that reacts to geopolymeric based binders due to the need for positive ions such as Ca^{++} to be present in the framework cavities to balance the negative charge of Al^{3+} ions and also to the mechanical interlock yield by silica dissolution from aggregate surface when subject to the high alkaline activator. Thus, the concrete substrate chemically bonds to the geopolymeric phase, as it can be seen by the absence of a clear interfacial transition zone on a microstructural level (see Figure 5).

4 CONCLUSIONS

The following conclusions can be drawn from this study:

TMWIP geopolymeric binder present high bond strength even at early ages (just after the first day). Furthermore bond strength is not affected by low roughness surface treatment of concrete substrate. Since bond strength is still very high for concrete substrate specimens as cast against metallic formwork which represents the majority of concrete structures surfaces it means TMWIP could be used to replace epoxy resins when CFRP strips are used in retrofitting operations.

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Durability Performance of Barrier Penetrants on Concrete Surfaces

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ABSTRACT

Various barrier penetrants have been used to improve the durability and to prevent the fouling of fair-faced concrete. However, there have been insufficient studies on their durability. This paper describes the results of durability tests (accelerated carbonation, chloride ion penetration, freeze-thaw and accelerated weathering) on the mortars coated with major commercial silane-, acrylic-resin- and silicate-based barrier penetrants used in Japan. The following conclusions were reached. (i) Coating with barrier penetrants can improve the resistance to carbonation and chloride ion penetration of mortar. However, the effects depend on the main ingredient of the barrier penetrants. (ii) Coating with barrier penetrants can improve the freeze-thaw durability of mortar. However, the effect of the main ingredient of the barrier penetrants on freeze-thaw durability is unclear. (iii) The effect on the water absorption reduction of mortar after accelerated weathering depends greatly on the main ingredient of the barrier penetrants. (iv) Coating with barrier penetrants can improve the durability of mortar. However, the effect depends greatly on the main ingredient of the barrier penetrants.

KEYWORDS: barrier penetrants, concrete, carbonation resistance, chloride ion penetration resistance, freeze-thaw durability, weatherability