ELSEVIER Science Press

Trans. Nonferrous Met. Soc. China 19(2009) s134−s142

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Evaluation of properties of concrete using fluosilicate salts and metal (Ni, W) compounds

Gyu-Yong KIM[1], Eui-Bae LEE[1], Bae-Su KHIL[2], Seung-Hun LEE[3]

1. Division of Architecture Engineering, Chungnam National University, Daejeon, Korea;
2. Research Institute of Technology, Tripod Co., Daejeon, Korea;
3. Research Institute of Technology, Samsung Construction and Engineering, Sungnam, Korea

Received 2 March 2009; accepted 30 May 2009

Abstract: To improve watertightness and antibiosis of sewage structure concrete, the antimicrobial watertight admixture was made with fluosilicate salts and antimicrobial compounds. And fresh properties, watertightness, harmlessness and antibiosis of concrete were investigated experimentally. As a result, the fresh properties of concrete were similar to those of an ordinary concrete, without setting time delay. Compressive strength and carbonation resistance of concrete were better than those of an ordinary concrete. Finally it was confirmed that the antimicrobial watertight admixture of concrete had an antibiosis inhibiting SOB growth.

Key words: concrete; fluosilicate salts; antimicrobial metal; biochemical corrosion

1 Introduction

Sewage structures like sewer pipes and clarifiers are mostly of the underground or closed type, and their interiors come into constant contact with sewage containing pollutants and corrosive substances, a great amount of moisture content and harmful gases. Due to these physical and chemical deterioration factors, sewage structures undergo a faster deterioration than those of aboveground concrete structures and have a remarkably lowered durability.

PAKER[1−2] reported that, in addition to various physical and chemical factors responsible for the corrosion of sewage structure concrete, the biochemical corrosion by microbes like SOB (sulfur-oxidizing bacteria) accelerates the deterioration of sewage structure concrete. Since his study, there has been extensive research on the biochemical corrosion of sewage structure concrete[3−6].

Considering those various corrosive factors, many improved performances were more needed in sewage structure than in any other ordinary concrete structures: 1) watertightness resisting to penetration of outer corrosive factors, 2) antibiosis inhibiting SOB growth, and 3) harmlessness relating with the water quality. Undoubtedly fresh properties and compressive strength of concrete are basically needed for construction.

In these days, to improve performance of concrete structures, various functional materials are used and are attempted to hybrid. This study aimed especially at watertightness and antibiosis for the sewage concrete structures. So the antimicrobial watertight admixture is manufactured and main ingredients of it are as follows: 1) watertight ingredients (fluosilicate salts) and 2) antibiosis ingredients (Ni and W). This admixture was made liquid because it was profitable for the admixture dispersion in concrete and homogeneity of concrete.

In the experiments, the concrete mixed with the antimicrobial watertight admixture was compared with plan concrete in workability, watertightness, harmlessness and antibiosis totally to evaluate application feasibility to sewage structure concrete.

2 Composition and function of antimicrobial watertight admixture

$ZnSiF_6$ and $MgSiF_6$ are used as fluosilicate salts in the antimicrobial watertight admixture. When these fluosilicate salts and cement hydrates come together,

Foundation item: Brain Korea 2th (BK21) funded by the Korean Government
Corresponding author: Eui-Bae LEE; Tel: +82-42-821-7731; E-mail: mir2468@cnu.ac.kr

CaF_2 and MgF_2 that have insoluble, stable and fine crystal structure are generated. These products make concrete watertight, so the strength and durability of concrete can be improved. The reactions between fluosilicate salts and cement hydrates are as follows.

$$MgSiF_6+2Ca(OH)_2 \rightarrow 2CaF_2+MgF_2+SiO_2+2H_2O$$
$$MgSiF_6+2CaCO_3 \rightarrow 2CaF_2+MgF_2+SiO_2+2CO_2$$
$$ZnSiF_6+2Ca(OH)_2 \rightarrow 2CaF_2+ZnF_2+SiO_2+2H_2O$$
$$ZnSiF_6+2CaCO_3 \rightarrow 2CaF_2+ZnF_2+SiO_2+2CO_2$$

Furthermore, soluble SiO_2 was used in making admixture as a watertightness ingredient. It has a pozzolan reaction with cement hydrate ($Ca(OH)_2$) and accelerates generation of C-S-H gel. It improves the strength and durability of concrete too and is usually used in concrete admixture in these days.

Ni and W were used as antimicrobial ingredients and were dissolved in the admixture. Surely, their antibiosis inhibiting the SOB growth was reported already. MAEDA et al[7−11] attempted to inhibit the SOB growth by mixing metal ingredients (Ni, W) into concrete. The validity of his research was confirmed through an exposure experiment in an actual sewage environment.

The schematic about the functions of admixture ingredients is shown in Fig.1. Table 1 shows ingredients and composition rate of admixture and Table 2 shows the physical properties of admixture.

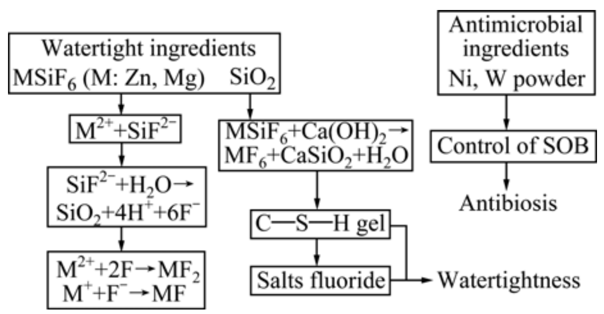

Fig.1 Functions of admixture ingredients

Table 1 Ingredients of admixture

Ingredient	Composition
Fluosilicate salt ($ZnSiF_6$, $MgSiF_6$)	15.0
Soluble silica	25.0
Nickel compound (Ni)	5.0
Tungsten compound (W)	2.5
Diluted solution	52.5

3 Experimental plan and methods

3.1 Experimental plan

Table 3 shows items and methods to evaluate various properties of concrete mixed with the antimicrobial watertight admixture. First slump, air content and setting time of concrete were tested to evaluate fresh properties for concrete. To evaluate watertightness, the compressive strength, resistance to carbonation, inner pore volume and microstructure were tested by SEM. And to evaluate harmlessness, the harmful ingredients elution test by ICP-MASS (Thermo Elemental IRIS DUO) was conducted. Finally, to evaluate antibiosis, Broth Microdilution MIC test, color change test, total colony test and simulation test were conducted.

Table 2 Physical properties of admixture

Item	Measured value
Solid concentration/%	13±2
Density/($kg \cdot m^{-3}$)	1.20±0.05
pH	3.0±0.5

Table 3 Evaluation items and methods

Item	Value of measurement
Workability	• Air content • Slump • Setting time
Watertightness	• Compressive strength • Resistance to carbonation • Pore volume • Microstructure(SEM)
Harmlessness	• ICP-MASS (Thermo Elemental IRIS DUO)
Antibiosis	• Broth Microdilution MIC test • Color change test • Total colony test • Simulation test

3.2 Mix proportions and materials of concrete

Table 4 shows the mix proportions of concrete in this study. In evaluating workability and watertightness, two water/cement ratios of 0.45 and 0.50 were applied. To evaluate harmlessness, water/cement ratios of 0.50 was applied. And, to evaluate antibiosis, the mortar mix proportion was applied; water:cement:fine aggregate= 1:1.67:4 (mass ratio). Aimed slump and air content of concrete were (180±25) mm and (4.5±1.5)%.

Two types of specimen were made: plain-concrete (mixed without the antimicrobial watertight admixture, in mortar was plain-mortar) and AW-concrete (mixed with the antimicrobial watertight admixture, in mortar was AW-mortar). The antimicrobial watertight admixture was added in amount of 1% to cement mass. Physical

Table 4 Mix proportions of concrete

Item	W/C	S/a	Water/(kg·m^{-3})	Cement/(kg·m^{-3})	Fine aggregate /(kg·m^{-3})	Coarse aggregate /(kg·m^{-3})
Workability	0.45	0.45	170	378	783	991
	0.50	0.45	175	350	792	1 001
Watertightness	0.40	0.45	170	378	783	991
	0.50	0.45	175	350	792	1 001
Harmlessness	0.50	0.45	175	350	792	1 001
Antibiosis[1)]	(1:1.67:4)					

1) Mix proportion for antibiosis evaluation shows mortar mix proportion with weight rate.

properties of cement, fine aggregate, coarse aggregate and a superplasticizer used in the experiment are shown in Table 5.

Table 5 Physical properties of materials

Item	Value of measurement
Cement	• Ordinary portland cement • Density: 3.15 g/cm^3
Fine aggregate	• Sea sand • Density: 2.58 g/cm^3 • Fineness modulus: 2.84
Coarse aggregate	• Crushed stone • Density: 2.62 g/cm^3 • Max. size: 20 mm
Superplasticizer	• Napthalene • Density: 1.1 8g/m^3

3.3 Test methods

3.3.1 Fresh properties

The slump, air content and setting time of concrete were tested according to standards: KS F 2402 Method of test for slump of concrete (ASTM C143/C143M-98), KS F 2421 Method of test for air content of fresh concrete by pressure method (ASTM C231-97) and KS F 2436 Testing method for time of setting of concrete mixture by penetration resistance (ASTM C403/C403M-08).

3.3.2 Watertightness

The compressive strength of concrete was tested according to KS F 2405 Method for compressive strength of concrete (ASTM C873-99). To evaluate the carbonation resistance, the concrete specimen with size of 100 mm×100 mm×400 mm was made. It was cured in water at 20 ℃. After 28 d curing, the specimen was moved into carbonation chamber with temperature 20 ℃, relative humidity 60% and CO_2 5%. And the specimen was split and was measured carbonation depth using phenolphthalein solution at every carbonation curing 1, 2, 4 and 8 weeks. Then the carbonation coefficient was calculated through the following equation.

$$C=A\cdot t^{1/2} \tag{1}$$

where C denotes carbonation depth, mm; A denotes coefficient of carbonation velocity, mm/a$^{0.5}$; t denotes age, a.

3.3.3 Harmlessness

First, the specimen powder was gathered by crushing concrete specimen. It was mixed in water with mass ratio of 1:10. And pH was regulated to 5.8−6.3 by using hydrochloric acid. The powder solution was shaken for 6 h, then pH of the solution was analyzed by ICP-MASS (Thermo Elemental IRIS DUO).

3.3.4 Antibiosis

1) Broth Microdilution MIC test

This test is for antibiosis evaluation of antimicrobial watertight admixture. First, SOB (*Thiobacillus novellus*) was put in saline solution and SOB density of the solution was controlled to 3.75×10^8/mL. The nutrient agar was covered with the SOB solution and the antimicrobial watertight admixture was dropped on it. This nutrient agar was cultured for 2 days and the clear zone created on the surface was measured.

2) Color change test

The culture solution mixed with SOB (*Thiobacillus novellus*) was prepared and an indicator was put into it. The mortar specimen with size of 40 mm×40 mm×10 mm was soaked into the culture solution for 4 weeks. Then pH of the culture solution was measured by color change of the culture solution. The color changing point of an indicator is shown in Table 6.

Table 6 Properties of indicator

Indicator	pH	Color
Bromo cresol	＞6.6	Purple
Purple	＜6.6	Yellow

3) Total colony test

The mortar specimen with size of 40 mm×40 mm ×10 mm was soaked into culture solution of SOB (*Thiobacillus novellus*, 3.75×10^8/mL) and was cultured for 2 days. At initial time and after 12, 24 and 48 h, the culture solution of 100 μL was put on the nutrient agar and was cultured again for 2 days. Then total colony on the nutrient agar was counted.

4) Simulation test

The mortar specimens transplanted with *Thiobacillus novellus* were put into the simulation test device. The inner temperature and humidity of the simulation test device were controlled to optimize the conditions for *Thiobacillus novellus*, as shown in Table 7. During the simulation test, SEM and EDX were used to examine the growth of *Thiobacillus novellus* and the elements on the specimen surface. The schematic of simulation test is shown in Fig.2.

Table 7 Conditions of simulation test

Item	Content
SOB	*Thiobacillus novellus*
Temperature/℃	29±1
Humidity/%	90±5
H_2S	50×10^{-6}

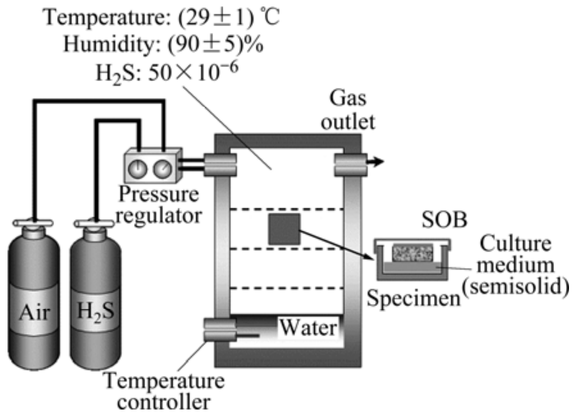

Fig.2 Schematic of biochemical simulation test

4 Results and discussion

4.1 Fresh properties

The results of slump and air content of the concrete are presented in Fig.3 and Fig.4. The slump and air content of all mixture in this experiment met the aimed values.

Fig.5 shows the initial and final setting time of all mixture. The setting time of AW-concrete mixed with the antimicrobial watertight admixture was more delayed about 6.5−7 h than that of plain-concrete. When fluoric ion(F^-) which is an main ingredient of antimicrobial watertight admixture comes together calcium ion(Ca^{2+}) eluted by cement hydration, $CaF_2{\cdot}SiO_2$ is generated. It is a corpuscle and covers the surface of cement particle. Then the connection between cement and water is inhibited and the setting time of concrete is delayed[12]. So when the antimicrobial watertight admixture is used in real construction, the setting delay of the concrete should be considered.

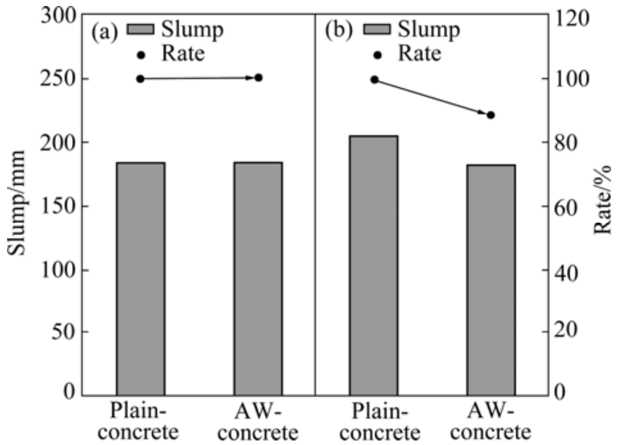

Fig.3 Comparison of slump between plain-concrete and AW-concrete

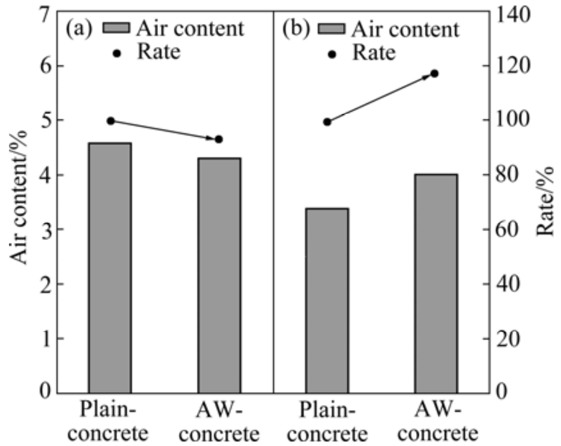

Fig.4 Comparison of air content between plain-concrete and AW-concrete

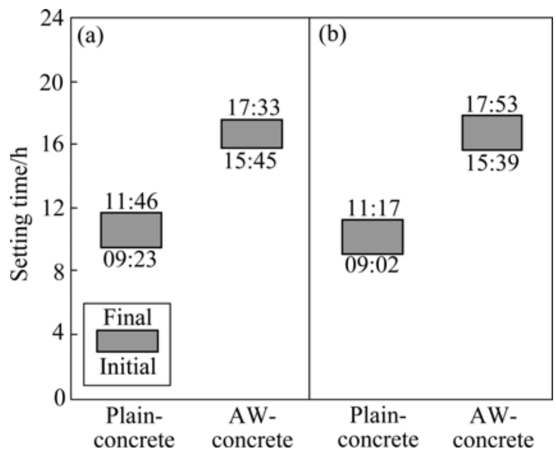

Fig.5 Comparison of setting time between plain-concrete and AW-concrete

4.2 Watertightness

In this study, the compressive strength was measured at 3, 7, 14, 28, 56 and 91 days, respectively. The results of compressive strength are presented in

Fig.6. In case of W/C 0.45, the compressive strength of AW-concrete at 3 days was about 23% less than that of plain-concrete. But after 7 days, the compressive strength of AW-concrete was maximum 28% higher than that of plain-concrete. In case of W/C 0.50, until 14 days the compressive strength of AW-concrete was about 5%−18% less than that of plain-concrete, but after 28 days the compressive strength of AW-concrete was 4%−7% higher than that of plain-concrete. As using the antimicrobial watertight admixture in the concrete, the compressive strength of the concrete at an early age was decreased but the long term compressive strength was increased.

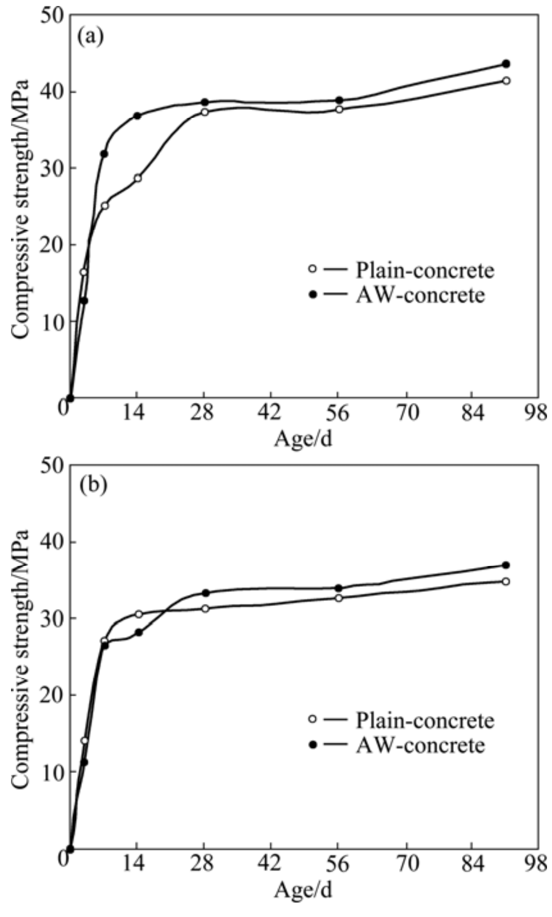

Fig.6 Comparison of compressive strength between plain-concrete and AW-concrete: (a) W/C=0.45; (b) W/C=0.50

Fig.7 shows the predicted carbonation depth through Eq.(1). The carbonation coefficients were calculated based on the real data measured in the concrete specimen. In case of W/C 0.45, the carbonation coefficients of plain-concrete and AW-concrete were 4.2 mm/a$^{0.5}$ and 3.3 mm/a$^{0.5}$. In case of W/C 0.50, the carbonation coefficient was 5.2 mm/a$^{0.5}$, about 50% less than that of plain-concrete. As using antimicrobial watertight admixture in the concrete, the resistance to carbonation (resistance to penetration of the corrosive factors) of concrete was increased.

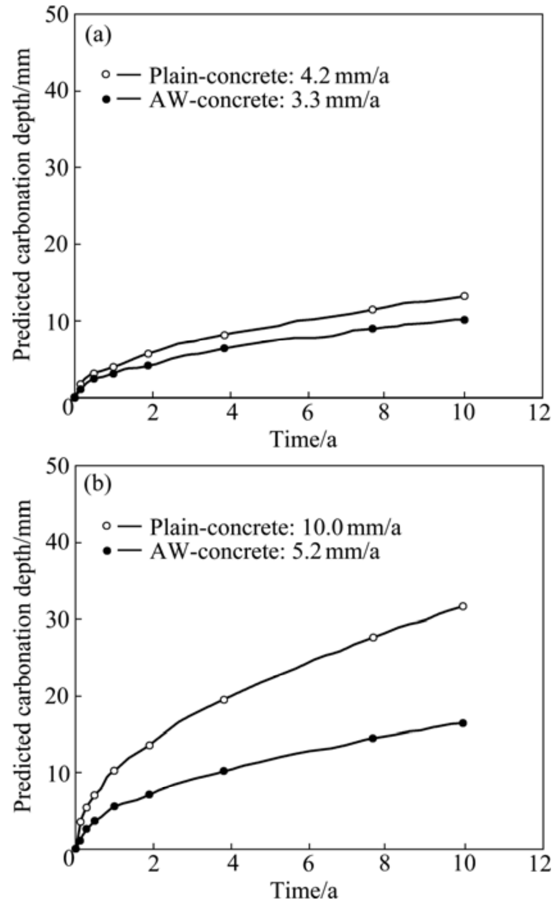

Fig.7 Comparison of predicted carbonation depth between plain-concrete and AW-concrete: (a) W/C=0.45; (b) W/C=0.50

Fig.8 presents the SEM images on microstructure of pore surface in the concrete with W/C 0.50. The crystals observed on the pore surface in AW-concrete, were more than those in plain-concrete. And Fig.9 shows the pore size and volume of the concrete cured for 28 days. The pore volume of AW-concrete was less than that of plain-concrete. Especially for the pore size under 0.1 μm, the pore volume of AW-concrete was 5%−15% lower than that of plain-concrete, because the fine pores with the pore size under 0.1 μm were filled with additional crystal generated from fluosilicate salts and soluble SiO_2, as shown in Fig.8. The data clearly confirm the improvement effect of the antimicrobial watertight admixture on concrete watertightness.

4.3 Harmlessness

To use the antimicrobial watertight admixture in sewage concrete structures, it is important to test harmlessness of the antimicrobial watertight admixture on the quality of water. In this study, the elusion test for heavy metals and harmful ingredients was conducted. The result of the test is presented in Fig.10. All values measured each day were much lower than 100×10^{-9} and met the standard. Furthermore, the elusion of watertight

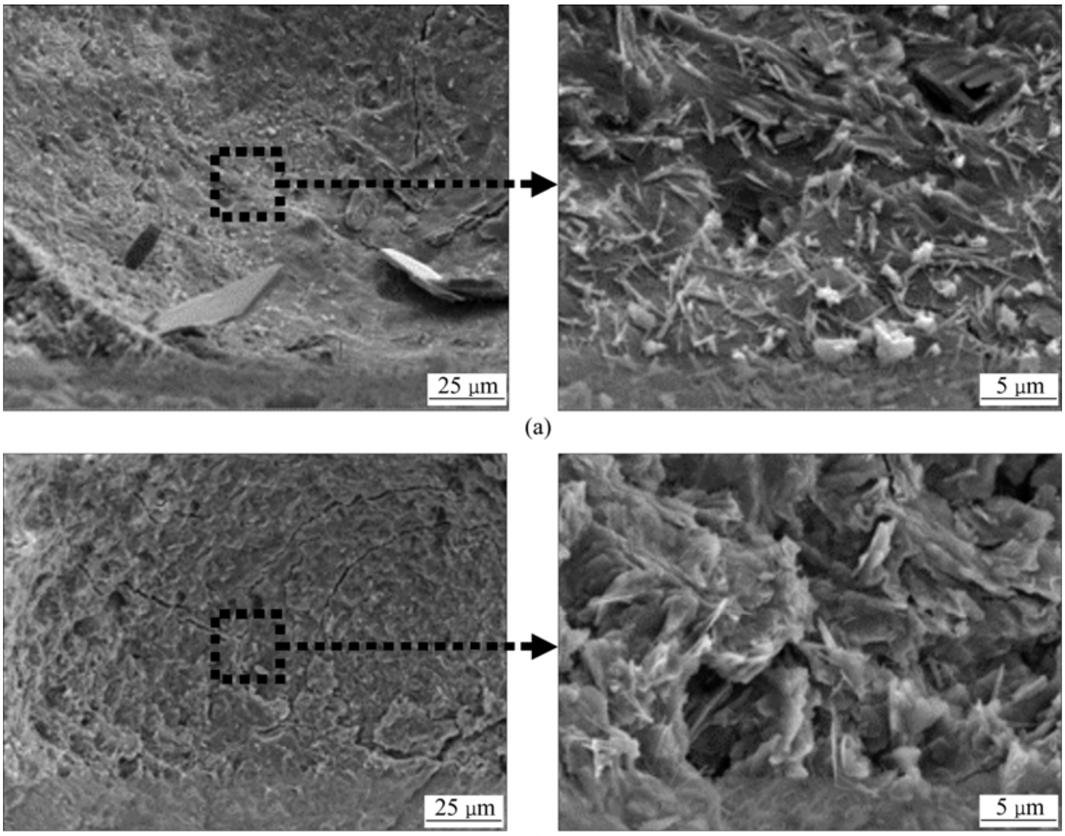

Fig.8 Comparison of microstructure on pore surface (W/C 0.50, SEM): (a) Plain-concrete; (b) AW-concrete

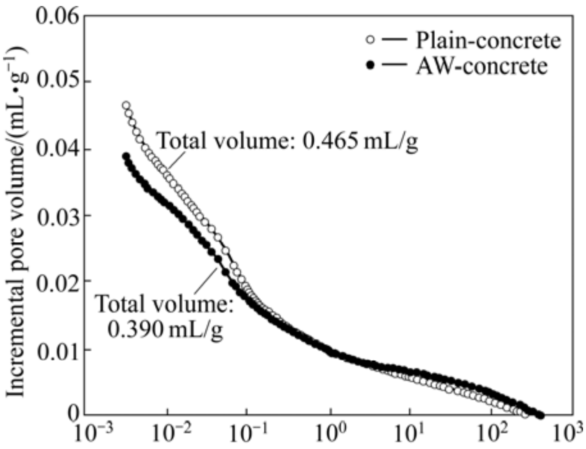

Fig.9 Comparison of pore volume between plain-concrete and AW-concrete (W/C 0.50)

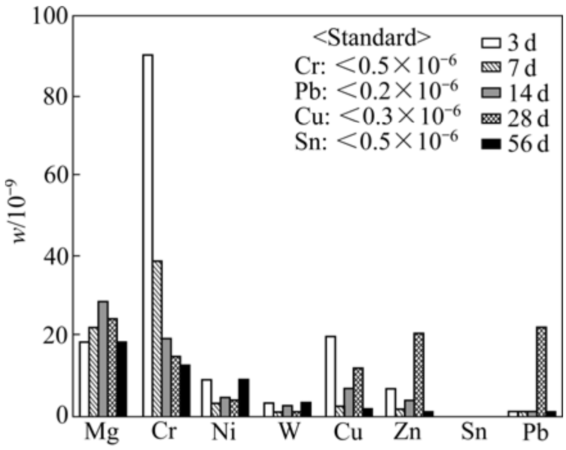

Fig.10 Result of elusion test of AW-concrete

ingredients (Zn, Mg) and antimicrobial ingredients (Ni, W) which are main ingredient of admixture was much lower, under 30×10^{-9}. This indicates that the effective ingredients of the admixture were fixed stably in the concrete, and that the watertightness and antibiosis of the concrete were maintained.

4.4 Antibiosis

Fig.11 shows the antibiosis test results of the antimicrobial watertight admixture with different concentration. The clear zone was made on nutrient agar by dropping of the antimicrobial watertight admixture. It means that *Thiobacillus novellus* could not live in the area admixture dropped. And the diameter of clear zone was increased as increasing concentration of admixture. So it is concluded that the antimicrobial watertight admixture has an antibiosis.

Fig.12 shows the antibiosis test results of mortar mixed with the antimicrobial watertight admixture. The

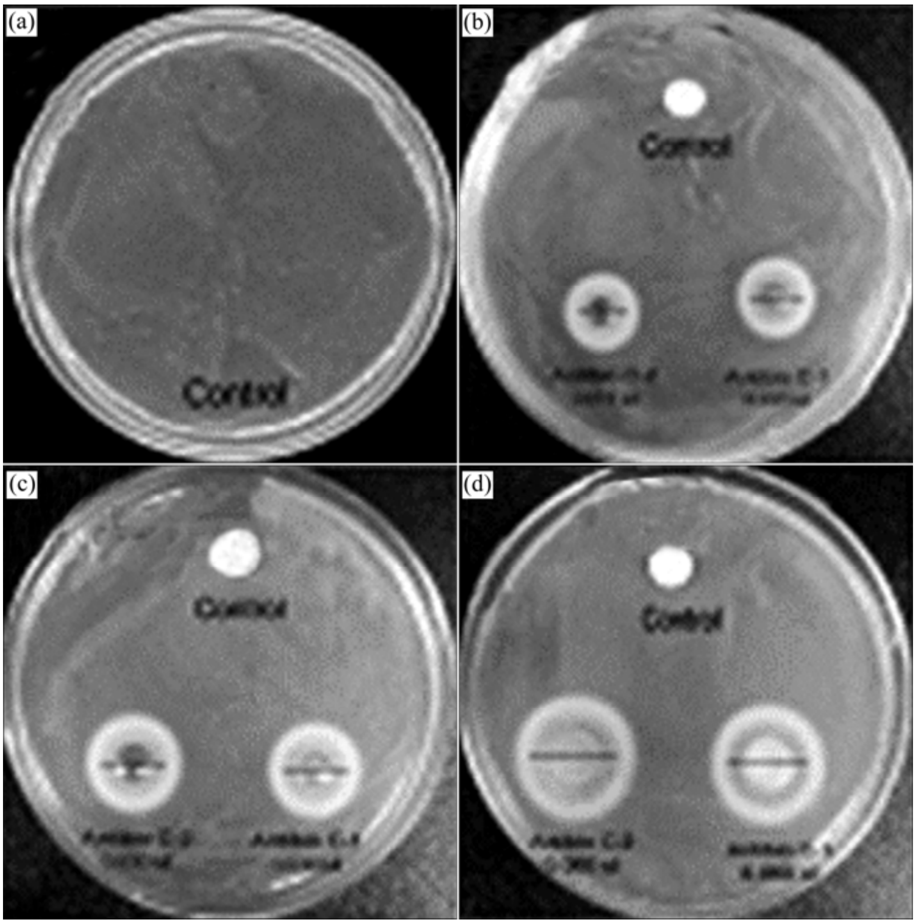

Fig.11 Change of clear zone with different admixture concentrations: (a) No dropping; (b) 0.015 μL; (c) 0.030 μL; (d) 0.060 μL

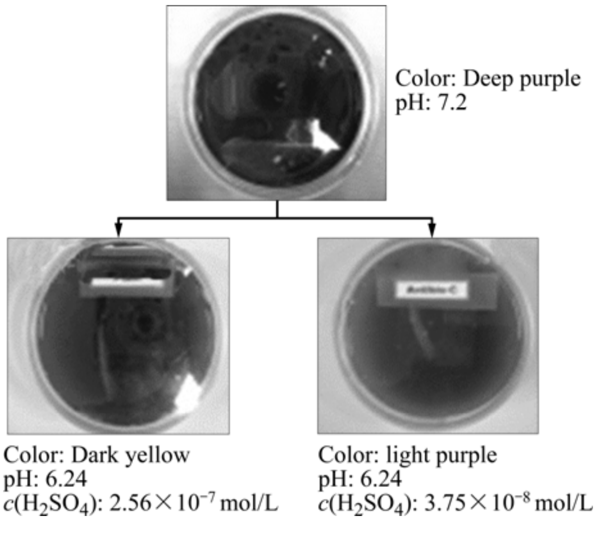

Fig.12 Change in color of culture solutions in which plain-mortar and AW-mortar were sunk: (a) Initial; (b) Plain-mortar; (c) AW-mortar

initial color of the culture solution mixed with *Thiobacillus novellus* and an indicator (bromo cresol purple) was deep purple. After 4 weeks, the color of the culture solution with plain-mortar changed to dark yellow. The pH of it was 6.24 (under 6.6) and the concentration of H_2SO_4 of it was 2.56×10^{-7} mol/L. But, in case of WA-mortar, the color of culture solution was light purple. The pH of it was 6.86 (over 6.6) and the concentration of H_2SO_4 was 3.75×10^{-8} mol/L. This result indicates that the antimicrobial ingredient of specimen inhibited the growing of *Thiobacillus novellus* and the production of H_2SO_4 was controlled.

Effect of the antimicrobial watertight admixture on *Thiobacillus novellus* proliferation was investigated numerically in total colony test. The results of it were presented in Fig.13. Total colony per unit culture solution (mL) at initial was 1.68×10^5/mL. In case of SOB (no specimen in culture solution) and Plain-Mortar, the cells of *Thiobacillus novellus* were increased and were uncountable after 24 h. But *Thiobacillus novellus* in culture solution with WA-mortar were disappeared after 24 h.

Fig.14 shows the results of biochemical corrosion simulation test. The AW-mortar specimen has a lower number of *Thiobacillus novellus* than the Plain-mortar specimen, as shown in Fig.14. As the test time elapsed, the transformed *Thiobacillus novellus* are observed. As shown in Fig.14(d), *Thiobacillus novellus* destroyed cell membranes are observed on the AW-Mortar specimens at

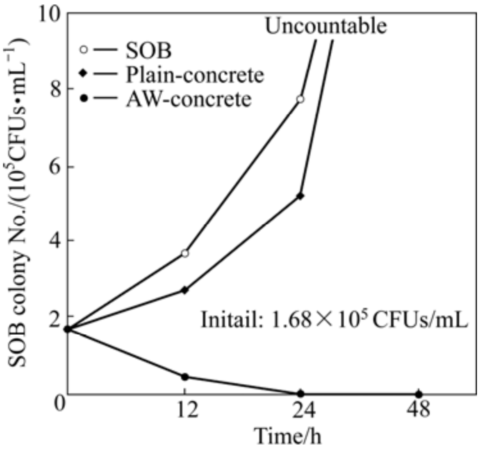

Fig.13 Results of total colony counting test

age 17 weeks. And dead *Thiobacillus novellus* with destroyed internal organizations were observed also on the AW-Mortar specimens at age 20 weeks. In general, the antibiosis mechanism of antimicrobial metal is that the cell membrane or internal protein tissue of microbial is destroyed by it [13]. This antibiosis mechanism is clearly shown in Fig.14.

5 Conclusions

1) The fresh properties of concrete mixed with the antimicrobial watertight admixture are similar to those of an ordinary concrete. But the setting time of concrete is delayed because of fluoric ion in it. So when the antimicrobial watertight admixture is used in real construction, the setting delay of concrete should be considered.

2) The watertight ingredients in the admixture make an additional fine crystal and a reduction of fine pore in concrete. And the compressive strength and carbonation resistance of concrete mixed with the antimicrobial watertight admixture are improved.

3) The antibiosis of the antimicrobial watertight admixture and the concrete mixed with it were confirmed through broth microdilution MIC test, color change test, total colony test and simulation test. Especially, the destruction of cell membrane or internal protein tissue of microbial was observed in simulation test.

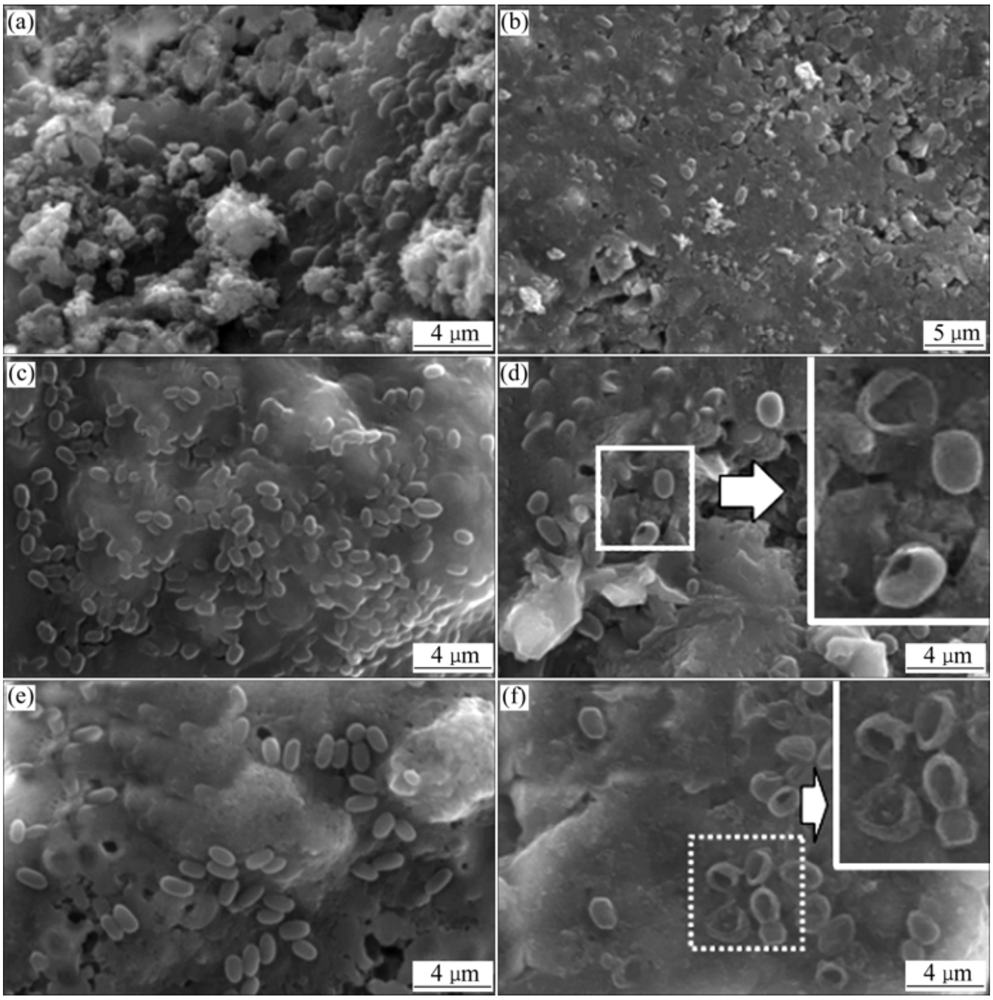

Fig.14 SEM images of specimen surface submitted to simulation test: (a) After 4 weeks plain-mortar; (b) After 4 weeks AW-mortar; (c) After 17 weeks plain-mortar; (d) After 17 weeks AW-mortar; (e) After 20 weeks plain-mortar; (f) After 20 weeks AW-mortar

References

[1] PARKER C D. The corrosion of concrete (I): The isolation of a species of bacterium associated with the corrosion of concrete exposed to atmospheres containing hydrogen sulfide [J]. Aust J exp Viol Med Sci, 1945, 23: 81−90.

[2] PARKER C D. The corrosion of concrete (I): The function of Thiobacillus concretivorus nov. spec. in the corrosion of concrete exposed to atmospheres containing hydrogen sulfide [J]. Aust J exp Viol Med Sci, 1945, 23: 91−98.

[3] MIDDLE K, SAND W, BOCK E. Thiobacilli of the corroded concrete wall of the Hamburg sewer system [J]. Journal of General Microbiology, 1983, 129: 1327−1333.

[4] SAND W, BOCK E, WHITE D C. Biosystem for rapid evaluation of concrete resistance to sulfur-oxidizing bacteria [J]. Mater Perform, 1987, 26: 14−17.

[5] ISMAIL N, NONAKA T, NODA S, MORI T. Effect of carbonation on microbial corrosion of concretes [J]. Journal of Construction Management and Engineering, 1993, 20: 133−138.

[6] JAFFREY L D, DANA N, KAMERON S, DEBORAH J R. Analysis of concrete from corroded sewer pipe [J]. International Biodegradation & Biodeterioration, 1998, 42: 75−84.

[7] MAEDA T. A study on the development of antibiotics for concrete corrosion [D]. Okayama: Okayama University, 1999.

[8] MAEDA T, NEGISHI A, NOGAMI Y, SUGIO T. Nickel inhibition of the growth of a sulfur-oxidizing bacterium isolated from corroded concrete [J]. Biosci Biotechnol Biochem, 1996, 60: 626−629.

[9] NOGAMI Y, MAEDA T, DEGISHI A, SUGIO T. Inhibition of sulfur oxidizing activity by nickel ion in *Thiobacillus thiooxidans* NB1-3 isolated from the corroded concrete [J]. Biosci Biotechnol Biochem, 1997, 61: 1373−1375.

[10] MAEDA T, NEGISHI A, OSHIMA Y, NOGAMI Y, KAMIMURA K, SUGIO T. Isolation of a sulfur-oxidizing bacterium that can grow under alkaline pH from corroded concrete [J]. Biosci Biotechnol Biochem, 1998, 62: 1087−1092.

[11] MAEDA T, NEGISHI A, KOMOTO H, OSHIMA Y, KAMIMURA K, SUGIO T. Isolation of iron-oxidizing bacteria from corroded concretes of sewage treatment plants [J]. Ferment Bioeng, 1999, 88: 300−305.

[12] KIM S M, MOON J H, LEE B K, LEE B J, KIM C G, RHO J S. The characteristics of cement sludge treated with hydrofluorosilicic acid and its effects on properties of cement paste and mortar [J]. J Korea Solid Wastes Engineering Society, 1998, 15(4): 386−392.

[13] CLOETE T E. Resistance mechanisms of bacteria to antimicrobial compounds [J]. International Biodegradation & Biodeterioration, 2003, 51: 272−282.

(Edited by HE Xue-feng)