

# EFFECT OF CARBONATION ON MICROBIAL CORROSION OF CONCRETES

Nasir ISMAIL\*, Tsuguhiro NONAKA\*\*,  
Shuji NODA\*\*\* and Tadahiro MORI\*\*\*\*

Carbonation process involves the reduction of surface pH of concrete and is the prerequisite to microbial corrosion to occur. The highest carbonation rate was found in specimens exposed to 0.5% CO<sub>2</sub> gas, followed by 5% and control (0.03%) specimens. The carbonation rates for 5%, 0.5%, and control were 7.1, 16.4, and 4.3 mm/year, respectively. Microbial corrosion experiment showed that 0.5% specimens had the highest corrosion rates and percentage mass loss of 3.8 mm/year and 13.9 percent/year, respectively. It can be concluded that carbonation stimulated microbial corrosion process. However, under quite high CO<sub>2</sub> gas concentration (5%), corrosion process was reduced due to formation of much calcite in the carbonated zone. Growth of *T. thiooxidans* was stimulated on the reduced pH of carbonated surface.

**Key Words** : microbial corrosion, concrete, carbonation, *T. thiooxidans*, XRD

## 1. INTRODUCTION

The corrosion of concrete sewers and wastewater treatment facilities are wellknown and widely reported<sup>(1,2)</sup>. Due to huge economic loss and maintenance problems, the control of corrosion process is one of the primary concerns because more treatment plants facilities will be built in near future. Despite numerous findings and progresses have been made in corrosion control, degradation of concrete structures by microbial corrosion still occur. It means that there are certain areas which remain unexplored and need further study.

Microbial corrosion of concrete in wastewater treatment facilities is stated as follows.

1. Sulfate-reducing bacteria, *Desulfovibrio* reduces sulfate in wastewater to hydrogen sulfide H<sub>2</sub>S in anaerobic condition.
2. Sulfur-oxidizing bacterias, *Thiobacilli* oxidize H<sub>2</sub>S in the atmosphere into sulfuric acid H<sub>2</sub>SO<sub>4</sub>.
3. The sulfuric acid attacks the concrete by reacting with calcium hydroxide Ca(OH)<sub>2</sub> to form gypsum CaSO<sub>4</sub>·2 H<sub>2</sub>O.
4. Then, gypsum may react with hydrated cement compound as tricalcium aluminate C<sub>3</sub>A forming calcium sulfoaluminate known as ettringite. The formation of gypsum and ettringite may result in complete decomposition of the hardened concrete.

Besides H<sub>2</sub>S gas and other environmental parameters such as moisture, temperature, and nutrient ; CO<sub>2</sub> gas that emanated from sewage into sewer environment also play an important role in corrosion process. On-site investigations revealed that the concentration of CO<sub>2</sub> gas in treatment plants were considerably higher than normally exist in the atmosphere (max. more than 3%). D. Thistlethwayte<sup>3)</sup> reported that CO<sub>2</sub> concentrations in main sewer were about 3%. Corrosion was also detected in compartments with low H<sub>2</sub>S but quite high CO<sub>2</sub>.

It is generally accepted that carbonation process reduced the surface pH of concrete and assist sulfur oxidizing bacterias to colonize and induce corrosion. Despite this detrimental effect, carbonated layer was reportedly responsible for protection against aggressive environments<sup>3)</sup>. The objective of this study was to investigate the effect of carbonation on microbial corrosion of concretes.

## 2. MATERIALS AND METHODS

### (1) Carbonation Experiment

Mortar specimens measuring 40 × 40 × 160 mm were prepared by mix proportion of 520 g cement (OPC), 1040 g Toyora standard sand, and 330 g water. The specimens were cured at 100% RH for one day and subsequent curing in water for 27 days at 20°C. Then, for three months the specimens were stored in humid box at 20°C before the initiation of the experiment. Carbonation experiment was conducted for four months with three different concentrations of CO<sub>2</sub> gas ; 5%, 0.5%, and control (atmospheric air). The concentration of CO<sub>2</sub> were adjusted by regulating the air and CO<sub>2</sub> flowmeters and measured by gas chromatography (HITACHI 2E 3.30). Specimens were placed in

\* Former Graduate Student, Ms. Agr., Dept. of Biochemical Engineering, Shimane University (Matsue 690, Japna)

\*\* Member of JSCE, Dr. Agr., Associate Professor, Dept. of Regional Development, Shimane University

\*\*\* Chief Research Engineer, Dr. Eng., Institute of Industries and Technology, Shimane Pref.

\*\*\*\* Member of JSCE, Dr. Sci., Professor, Dept. of Biochemical Engineering, Shimane University

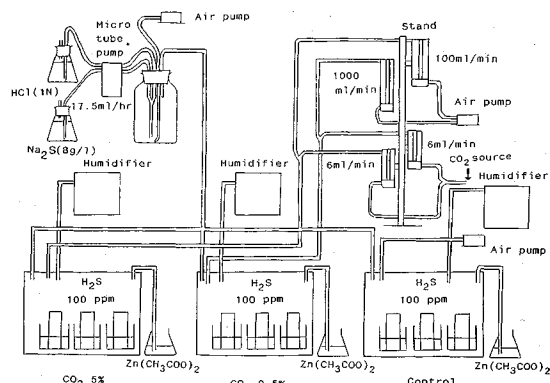


Fig.1 Set-up of carbonation and microbial corrosion experiment.

plastic chambers measuring W 400 × L 300 × H 300 mm. The thicknesses of carbonated layer were measured periodically by treating the freshly-broken surface of specimens with 1% phenolphthalein solution.

### (2) Microbial Corrosion Experiment

After four months, raw sewage influent was introduced with 6 cm of the mortar specimens was immersed in the influent. 10 ml broth of *Thiobacillus thiooxidans* (about  $10^9$  viable bacteria) was inoculated weekly for one month period. In addition to  $CO_2$  gas, hydrogen sulfide  $H_2S$  gas of 100 ppm was also introduced into each chamber as shown in Fig.1. The concentration of  $H_2S$  was measured  $H_2S$  test tube (GASTECH No.4 M). 100% humidity was kept by using humidifiers, since *T. thiooxidans* prefers humid condition. Temperature was according to room temperature. pH changes, corrosion depths, mass loss, and colony numbers of *T. thiooxidans* were investigated. pH changes were measured by pH papers (TOYO test paper). The value of mass losses were obtained by subtracting the weight of corroded specimens after brushing from the original weight. The colony number of *T. thiooxidans* on corroded materials indicates the number of viable bacteria. The colony number was determined as follows: One gram wet of corroded material was placed in 9 ml of distilled water, and homogenized by ultrasonic disruption for 1 min. at 40 W. After serial dilutions with distilled water, the suspensions were spread on colloidal silica gel AT media. After incubating the media at 30°C for 2-3 weeks, the colonies, which were appeared on the media, were counted. The compositions of the AT medium were as follows:

Solution 1 (per 70 ml)  
 $(NH_4)_2SO_4$  3.0 g;  $K_2HPO_4$  0.5 g  
 KCL 0.1 g;  $MgSO_4 \cdot 7H_2O$  0.5 g

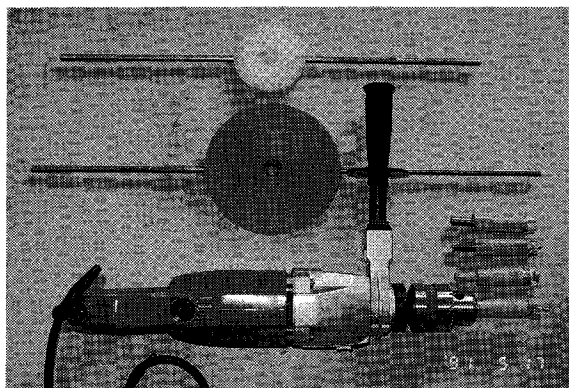


Fig.2 Concrete core sampler apparatus.

Table 1 Carbonation depth of mortar specimens.

Specimens	Carbonation Depth (mm)						
	Days	19	32	55	80	96	120
Control		1.70	2.90	1.60	3.00	2.65	3.30
0.5%		3.00	4.20	5.30	5.40	6.80	8.00
5%		2.95	5.60	6.40	4.40	5.50	6.50

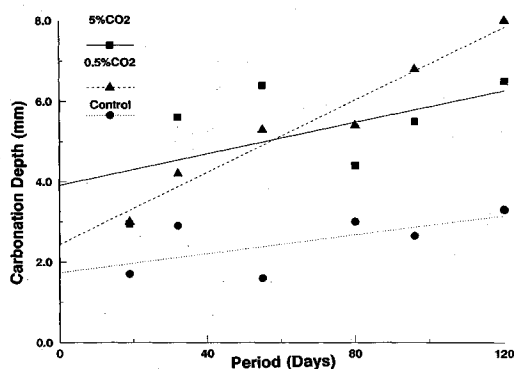


Fig.3 Change of carbonation depth with time.

$Ca(NO_3)_2$  0.01 g  
 Solution 2  
 (1 : 5)  $H_2SO_4$  : Water 14 ml  
 Solution 3 (per 116 ml)  
 $Na_2S_2O_3 \cdot 5H_2O$  5.0 g  
 Solution 4  
 Colloidal Silica 800 ml

Solution 1, 2, and 3 were mixed and autoclaved together whereas solution 4 was autoclaved separately. After cooling at room temperature, all solutions were mixed and pH was adjusted to about 1.5. Solidification was done at 55°C for few days.

### (3) On-site Investigation

Several sites had been selected to investigate the  $H_2S$ ,  $CO_2$  gasses, concrete surface pH, carbonation depth as well as corrosion process. Concrete core samples were collected by using the concrete core sampler as shown in Fig.2.

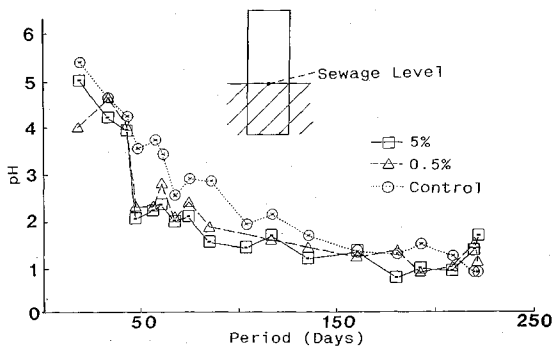


Fig.4 Decrease in mortar surface pH in chamber receiving 100 ppm H<sub>2</sub>S and CO<sub>2</sub> gas.

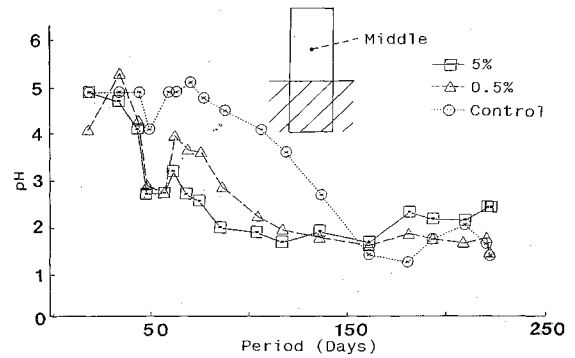


Fig.5 Decrease in mortar surface pH in chamber receiving 100 ppm H<sub>2</sub>S and CO<sub>2</sub> gas.

### 3. RESULTS AND DISCUSSION

#### (1) Carbonation

Effect of carbon dioxide gas concentrations on the thickness of carbonated layer is shown in Table 1 and Fig.3. Control specimens had a gradual increase in carbonation depth as compared to 5% and 0.5% specimens. Results indicate that 0.5% specimens had the highest carbonation rate. In case of 5% specimens, they can be divided into two groups. The first one achieved the highest carbonation rate during the first 55 days. The second group had an increase in carbonation depth with slower carbonation rate till the end of experiment. These results show that carbonation was stimulated when specimens were exposed to high concentration of CO<sub>2</sub> gas. Exposure to 5% CO<sub>2</sub> concentration however, reduced the rate of carbonation. There are two explanations. According to Neville's research<sup>3)</sup>, in 5% case, the diffusion rate of moisture released by reaction of CO<sub>2</sub> was possibly too slow after 55 days causing an increased in vapor pressure into saturation and clogging the pore volumes and slow further CO<sub>2</sub> penetration. Another explanation from Osborne's research<sup>4)</sup> was the formation of much calcite during early carbonation process which increased formation of fine pores preventing CO<sub>2</sub> penetration later.

#### (2) Corrosion

##### a) Microbial corrosion

Microbial corrosion process in laboratory is shown by surface pH decrease as shown in Fig.4. Surface pH started to drop when H<sub>2</sub>S gas and *T. thiooxidans* were introduced. It took about 20 days before surface pH reduced from about 8 to 5. Then, pH of 5% and 0.5% specimens dropped drastically from about 3.9 and 4.0 to 2.2 and 2.3, respectively. The drastic drop of pH were due to maximum growth of *T. thiooxidans* species during this period. Control specimens exhibited a gradual decline in pH instead. However, after 160 days

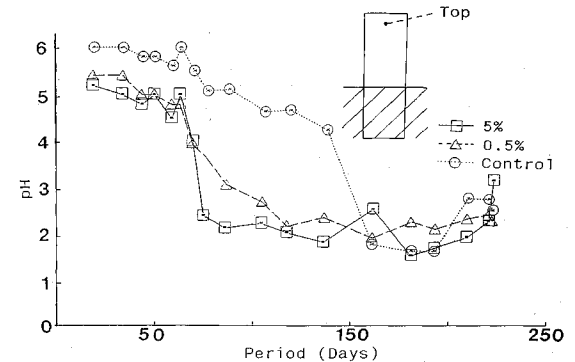


Fig.6 Decrease in mortar surface pH in chamber receiving 100 ppm H<sub>2</sub>S and CO<sub>2</sub> gas.

onward surface pH were about the same in all categories.

Similarly but at lower decreasing pH rate, the middle and upper parts of mortar specimens also exhibited the same pattern of declining pH as shown in Fig.5 and Fig.6. The lowest pH level was measured at areas near sewage level. Therefore, corrosion depth measurements were taken at this zone where corrosion was the severest. Greater supply of humidity and nutrients provided a conducive environment for growth of *T. thiooxidans*.

##### b) Corrosion depth and corrosion rate

Measurement of corrosion depth revealed that 0.5% specimens had the highest corrosion rate followed by 5% and control specimens as shown in Fig.7. Higher carbonation rate in 0.5% as consequence of carbonation provided more carbonated areas susceptible to sulfuric acid attack resulting higher microbial corrosion rate. The increase of corrosion depths were greater from period of 120 days to 160 days because low pH of about 2.0. The consistency of results illustrate that corrosion rate corresponds with the carbonation rate. It is clearly shown that carbonation acceler-

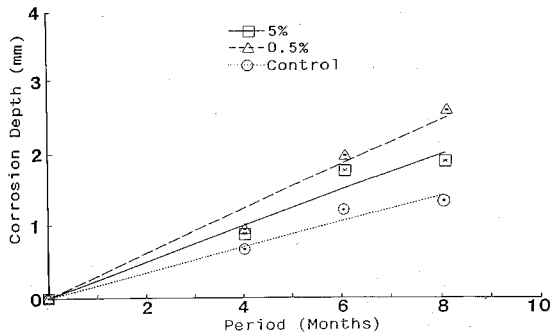


Fig.7 Corrosion depth of mortar specimens at sewage level during microbial corrosion.

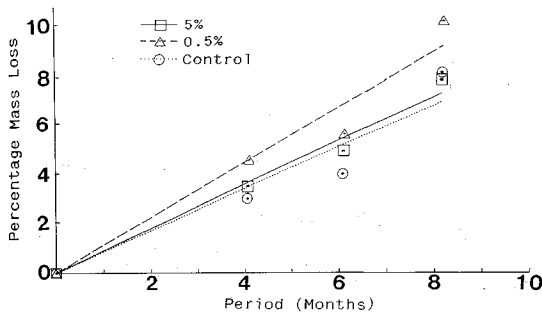


Fig.8 Mass loss percentage of mortar specimens during microbial corrosion process.

ated the microbial corrosion process at early stage.

c) Percentage mass loss

The results of percentage weight loss also in agreement with the order of carbonation and corrosion rates. As shown in Fig.8, percentage mass loss of control began to exceed the 5% specimens after 8 months as a result of continuous pH drop. Physical appearance evaluation showed the surface of control experienced more attack.

d) Colony number of *T. thiooxidans*

Colony counting of *T. thiooxidans* per gram corroded material is shown in Table 2. The cell number of *T. thiooxidans* was in order of  $10^5$  to  $10^8$ .

e) Carbonated surface layer

Corrosion rate of 0.5% specimen was the highest due to largest effect of carbonation process. Formation of calcite caused a decreased in pores volumes<sup>6)</sup> in 5% preventing further  $CO_2$  penetration and ingress of sulfuric acid. Osborne reported that the carbonated outer layer was beneficial in protection against sulfate attack<sup>4)</sup>. Neville<sup>5)</sup> stated that concrete permeability decrease as result of drying out. Formation of calcite in carbonated mortar is shown in Fig.9. In control specimens, the effect of carbonation was not as significant as in 5% and less calcite formed allowing more sulfuric acid penetration. This is confirmed by steady decline of

Table 2 Colony number of *T. thiooxidans* per gram corroded materials

Specimens Receiving $CO_2$	4 Months	6 Months	8 Months
Control	$3.06 \times 10^5$	$1.66 \times 10^7$	$1.84 \times 10^6$
0.5%	$2.43 \times 10^6$	$1.81 \times 10^7$	$5.45 \times 10^6$
5%	$5.50 \times 10^4$	$1.40 \times 10^6$	$1.90 \times 10^6$

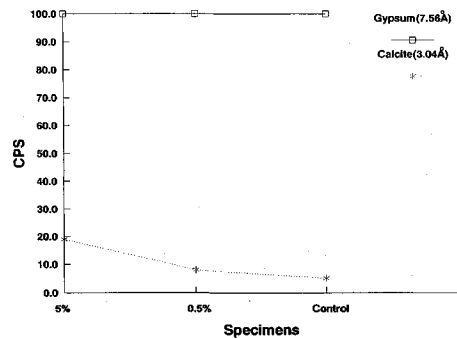


Fig.9 (a) Results of X-ray diffraction analysis with mortar specimens. (Corroded Zone)

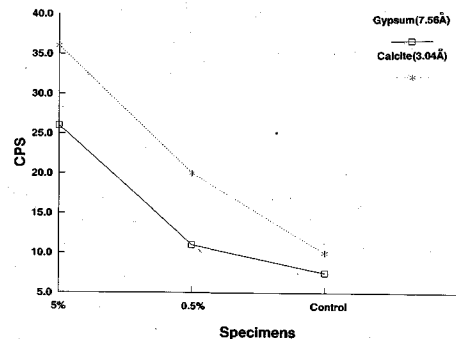


Fig.9 (b) Results of X-ray diffraction analysis with mortar specimens. (Carbonated Zone)

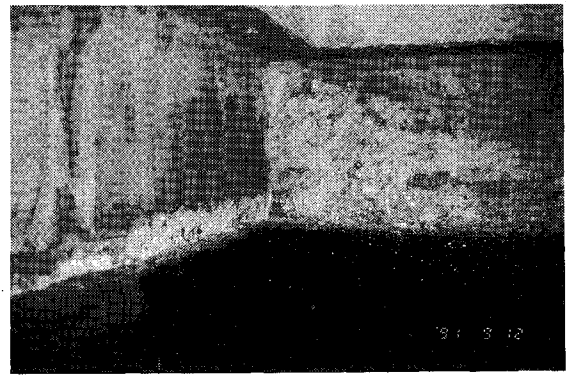
pH and higher percentage mass loss than 5% specimens after 8 months (Fig.4). Microscopic investigation is needed to confirm this pores volume changes.

(3) On-site Investigation

Results of on-site investigation of wastewater treatment plants are shown in Table 3. Apparently, low concentration of  $CO_2$  produced carbonation depths of 4 mm to 8 mm and surface pH of 4 to 5, at contact aeration of *M* treatment plant. High concentration of  $CO_2$  gas from 4 000 ppm to 8 100 ppm resulted higher carbonated depth and very low surface concrete pH. Low pH range from 1 to 3 and high concentration of  $H_2S$  showed strong corrosion at second and third anaerobic tanks in *K* treatment plant. Microbial corrosion was stimulated by high rate of carbonation of 4.33 mm per year. In case of *Y* treatment plant, eventhough  $H_2S$  concentration

**Table 3** On-site investigation of wastewater treatment plants.

Treatment plant	Compartment	Atmospheric		Surface pH
		H <sub>2</sub> S (ppm)	CO <sub>2</sub> (ppm)	
M	Contact Aeration 7cm from top	0.7- 2.7	300-500	4-5
	Contact Aeration 8cm from top	0.7- 2.7	300-500	4-5
K	Contact Aeration 40-60cm from slab	0.9-14.8	5500-6000	4-5
	2nd Anaerobic Tank 5cm above sewage line	10.7-35.4	5400-8100	1-3
	3rd Anaerobic Tank sewage line	7.2-32.2	4000-7600	1
Y	2nd Anaerobic Tank 10cm above sewage line	3.1- 5.5	1700-2500	2-4
	2nd Anaerobic Tank sewage line	3.1- 5.5	1700-2500	2-4
	2nd Anaerobic Tank 10cm below sewage line			7
Treatment plant	Compartment	Carbonation depth(mm)	Carbonation rate(mm/yr)	
M	Contact Aeration 7cm from top	4-8	0.80-1.60	
	Contact Aeration 8cm from top	4-8	0.80-1.60	
K	Contact Aeration 40-60cm from slab	4-5	1.35-1.67	
	2nd Anaerobic Tank 5cm above sewage line	13	4.33	
	3rd Anaerobic Tank sewage line	12	4.00	
Y	2nd Anaerobic Tank 10cm above sewage line	16	4.00	
	2nd Anaerobic Tank sewage line	14	3.50	
	2nd Anaerobic Tank 10cm below sewage line	11	2.75	



**Fig.10** Typical microbial corrosion of wastewater treatment plant.

**Table 4** Microbial analysis of corroded materials from sites.

Treatment plant	Compartment	pH	Colony number per wet gram materials
M	Separation/Settingling	2	5.0×10 <sup>5</sup>
K	2nd Anaerobic Tank	3-4	3.0×10 <sup>4</sup>
	3rd Anaerobic Tank	1	6.0×10 <sup>4</sup>
Y	2nd Anaerobic Tank	3-4	1.3×10 <sup>6</sup>
	1	1	2.2×10 <sup>6</sup>

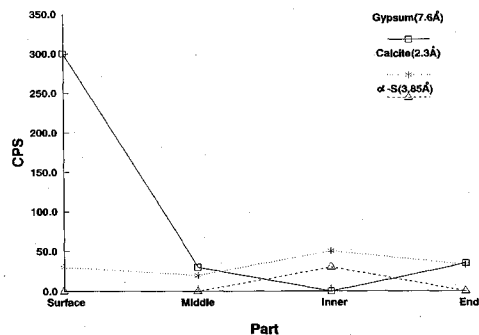
was quite low but with CO<sub>2</sub> concentrations range from 1 700 ppm to 2 500 ppm, corrosion process was considerably strong displayed by low surface pH. Severe microbial corrosion was found at areas above sewage line. Fig.10 shows the microbial corrosion of 3 rd anaerobic tank in K treatment plant.

Corroded samples from sites (Table 4) contained 10<sup>4</sup> to 10<sup>6</sup> of *T. thiooxidans* per gram corroded concrete. Formation of calcite and gypsum in corroded concrete is shown in Fig.11. The result showed that CO<sub>2</sub> gas penetrated deep into inside and the amount of calcite was much more than that of gypsum at the inner part.

**4. CONCLUSIONS**

The following conclusions can be drawn based on the results of this study :

1. Carbonation rates increased with the increased of CO<sub>2</sub> concentrations. However, the results show that 0.5% had the highest carbonation than 5% and control. The carbonation rates of 5%, 0.5%, and control specimens were 7.1, 16.4, and 4.3 mm per year, respectively.



**Fig.11** Results of X-ray diffraction analysis with corroded core samples. (K treatment plant, 2 nd anaerobic tank, sewage level)

2. Carbonated surface layer was essential and accelerated the surface colonization by *T. thiooxidans* and induced microbial corrosion.
3. Corrosion rates corresponded well with the carbonation rates. The corrosion rates for 5%, 0.5%, and control specimens were 3.0, 3.8, and 2.1 mm per year, respectively.
4. However, under quite high CO<sub>2</sub> gas concentration, carbonation and corrosion rates decreased due to formation of much calcite.
5. Results of on-site investigation coincide with that of laboratory experiment. In microbial corrosion, combined effect of H<sub>2</sub>S and CO<sub>2</sub> gases should be considered.

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## コンクリートの微生物腐食に及ぼす炭酸化の効果

Nasir ISMAIL · 野中資博 · 野田修司 · 森 忠洋

コンクリートの炭酸化は表面 pH の低下をもたらす、微生物腐食が起こる前提条件を整える。モルタル供試体を用いて 4 ヶ月の炭酸化試験と 8 ヶ月の微生物腐食試験を行った。二酸化炭素濃度が高くなれば炭酸化も微生物腐食も促進されるが、高濃度すぎると逆に抑制されることがわかった。それは初期のカルサイト生成量の違い等によると考えられる。現場調査の結果は、実際の微生物腐食環境が炭酸化による促進効果の範囲にあることを示している。