EFFECTS OF ORGANIC AND CARBONIC ACIDS ON CONCRETE DETERIORATION CAUSED BY AEROBIC MICROOGANISMS

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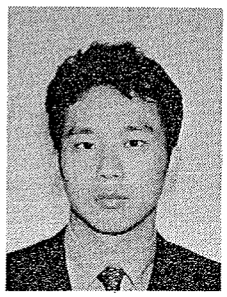

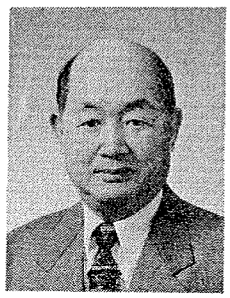

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Biological deterioration of concrete has been reported previously. Most degradations were caused by mainly sulfur bacteria, and many studies regarding anaerobic and aerobic sulfur bacteria have been carried out. In an earlier study it was clarified that concrete deterioration was also caused by solely aerobic bacteria. In this study, effects of metabolites of microorganisms on concrete deterioration were investigated with regard to aerobic universal bacteria and fungi. It was found that organic and carbonic acids metabolized by these microorganisms caused concrete deterioration in the same degree as that of aerobic sulfur bacteria. In this deterioration process, organic acids decomposed and dissolved out calcium salts, while carbonic acid mainly decomposed cement hydrates.

Keywords: *concrete, deterioration, aerobic microorganisms, bacteria, fungi, metabolites, weak acid, organic acid, carbonic acid*

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1. INTRODUCTION

In previous studies [1]-[2], the deterioration of certain underground concrete structures was found to be related to microorganisms. After microorganisms isolated from this biodegraded concrete structure were cultured, simulation tests of mortar deterioration and analysis of metabolites were carried out using *Xanthomonas* sp. and *Thiobacillus intermedium* which were thought to be involved in the concrete deterioration. As a result, it was verified that the deterioration was mainly caused by organic acids metabolized by microorganisms and carbonic acid produced as a byproduct of microorganisms respirations [3]-[5].

Previous reports of biological deterioration of concrete have mainly regarded sewage plants. In these reports, only sulfur bacteria such as anaerobic sulfate-reducing bacteria and aerobic sulfur-oxidizing bacteria were used as test bacteria [6]-[9]. But the previously-mentioned results showed that concrete deterioration could be caused in an aerobic condition where bacteria could carry out respiration and metabolize organic acids with high activity of bacteria. It can be said that underground structures have a possibility of biological deterioration since an aerobic condition may be generated due to artificial works such as boring of soil.

In this study, not only sulfur bacteria, but other varied aerobic microorganisms were used as test specimens. The aim of this study was to clarify the effects of metabolites of microorganisms on concrete deterioration and to discuss the effects of metabolized organic and carbonic acids on the deterioration.

2. EXPERIMENTS

The experiments were composed of two types of tests. A simulation test of deterioration was carried out in order to understand the deterioration of cement paste specimens using various aerobic microorganisms. An accelerated test using synthesized solutions was performed to understand the effects of organic acids on the deterioration of cement paste.

The former was a simulation test to decide whether the deterioration focused on in this study was caused only by a particular microorganism such as sulfur bacteria or by some other microorganism.

The latter was a test to clarify each effect that organic and carbonic acids had on concrete deterioration. Since it was difficult to measure the concentration of carbonic acid in solution, the effect of carbonic acid was indirectly discussed by knowing both the extent of deterioration caused by synthesized organic acids and the results of the former simulation tests using microorganisms.

2.1 Simulation tests of deterioration

a) Microorganisms
Universal bacteria and fungi were used as aerobic microorganisms in this study.

Bacillus subtilis HUT 8049 (*B.subtilis*) and *Esherichia coli* N 17 (*E.coli*) were used as universal bacteria. *B.subtilis* universally inhabits the soil and air, and *E.coli* inhabits waste water and the intestines of mammals.

Penicillium expansum HUT 4122 (*P.expansum*) and *Aureobasidium pullulans* HUT 5041 (*A.pullulans*) were used as fungi. *P.expansum* is a kind of green mold which is concerned with the soiling of concrete surfaces [10]. *A.pullulans* is a kind of black mold which forms black soiling in wet places such as bathrooms.

b) Media
Ordinary liquid medium (10 g of glucose, 10 g of peptone and 10 g of nutrient broth in 1000 ml of distilled water) and potato dextrose medium (10 g of dextrose in 1000 ml of potato extract solution) were used as culture medium regarding bacteria and fungi respectively.

c) Specimens
Cement pastes were prepared with water-cement ratios of 0.30 and 0.40, using ordinary Portland cement, and were cast in 40 x 40 x 40 mm cubes. After the specimens were cured in water until they reached the age of 28 days, they were used in the following experiments.

d) Experimental methods
After the logarithmic growth phase in which a microorganism showed the most active growth, determined from growth curves of bacteria and fungi, microorganisms in this logarithmic phase were used for simulation tests. The growth curve was measured as absorbance (wavelength: 660 nm) of culture medium for bacteria, and as dry weight of microorganisms for fungi. As a result the following were collected, *B.subtilis* at 5 hours, *E.coli* at 5 hours, *P.expansum* at 3 days and *A.pullulans* at 10 days after culture [11].

Cement paste specimens with water cement ratios of 0.30 and 0.40 were used for tests using *B.subtilis* and cement paste specimens with a water cement ratio of 0.40 were used for *E.coli*, *P.expansum* and *A.pullulans*. A cement paste specimen was immersed in 300ml of medium in a culture bottle and sterilized for 20 minutes at 120℃ and 1.5 atm. Microorganisms in the logarithmic growth phase were then inoculated upon the medium. A medium containing a specimen and no microorganisms (Blank A) and a medium containing no specimen and a microorganism (Blank B) were also prepared as control. These experiments were carried out at 37℃ for bacteria and at 28℃ for fungi, the optimum temperature for each microorganism.

Culture media and specimens were collected after a specifed culture duration and analyzed. Two samples were analyzed every culture duration and the average of the two was used as a value of measurement. Concentrations of calcium ion were measured with a flame emission spectrophotometer, sodium and potassium ions with an atomic absorption spectrophotometer, inorganic anions with an ion chromatoanalyzer and organic acids with a gas chromatoanalyzer, all derived from culture mediums. With respect to specimen, after samples were extracted, at a depth of up to 2 mm from the surface of the specimen, and were ground, contents of calcium hydroxide and calcium carbonate were determined with TG-DTA, and mineral compositions were identified with powder X-ray diffraction analysis.

2.2 Accelerated tests using synthesized solutions

Solutions containing chemical compositions of bacteria metabolites were synthesized on the basis of a previous study [12]. The metabolite of *Xanthomonas* sp. which is a hydrogen sulfide-producing bacterium was referred to as a composition of the synthesized solution. From the change in the composition until the logarithmic growth phase (about 3 hours after culture in the case of *Xanthomonas* sp.), a solution having a composition which had been metabolized after the logarithmic growth phase of the bacterium continued for one day, was synthesized. Solutions which were 10, 50, and 100 times as concentrated as the original solution, were also synthesized. With respect to acetic acid, propionic acid and hydrogen sulfide, solutions having each composition alone were synthesized. Running water was used as a control. Types and compositions of synthesized solutions are listed in Table 1.

A cement paste specimen was prepared with a water-cement ratio of 0.50 and was cast in ϕ 20 x 40 mm cylinder. After curing in water until reaching the age of 28 days, it was placed in a culture tube of ϕ 30 x 120 mm in size. The tube was then filled with synthesized solution, and plugged with silicon rubber. Specimens were immersed for 1, 2, 4, 8, 16 and 32 days. Synthesized solution was renewed every eighth day in cases where the immersed duration exceeded 8 days.

Synthesized solutions and specimens were collected after a specified culture duration and analyzed. Concentrations of calcium ion were measured with a flame emission spectrophotometer, sodium and potassium ions with an atomic absorption spectrophotometer, inorganic anions with an ion chromatoanalyzer, organic acids with a gas chromatoanalyzer, and dissolved hydrogen sulfide with the methylene blue method [13], respectively, all being derived from culture mediums. The pH value of the culture medium was measured with a pH meter. With respect to specimen, after

Table 1 Synthesized solutions by type and composition

Mark	Compositions (in 1 liter of distilled water)					
	CH_3COOH	C_2H_5COOH	K_2SO_4	KNO_3	$NaHCO_3$	H_2S
MIX-1	0.652 ml	0.440 ml	23.14 mg	57.37 mg	480 mg	ca. 0.6 mg
MIX-2	6.52 ml	4.40 ml	231.4 mg	573.7 mg	4800 mg	ca. 6 mg
MIX-3	32.6 ml	22.0 ml	1157 mg	2869 mg	24000 mg	ca. 30 mg
MIX-4	65.2 ml	44.0 ml	2314 mg	5737 mg	48000 mg	ca.60 mg
ACE-1	0.652 ml	----	----	----	----	----
ACE-2	6.52 ml	----	----	----	----	----
ACE-3	32.6 ml	----	----	----	----	----
ACE-4	65.2 ml	----	----	----	----	----
PRO-1	----	0.440 ml	----	----	----	----
PRO-2	----	4.40 ml	----	----	----	----
PRO-3	----	22.0 ml	----	----	----	----
PRO-4	----	44.0 ml	----	----	----	----
H2S-1	----	----	----	----	----	ca. 0.6 mg
H2S-2	----	----	----	----	----	ca. 6 mg
H2S-3	----	----	----	----	----	ca. 30 mg
H2S-4	----	----	----	----	----	ca.60 mg

samples were extracted at a depth up to 3 mm from the surface of the specimen and were ground, contents of calcium hydroxide and calcium carbonate were determined with TG-DTA, and mineral compositions were identified with powder X-ray diffraction analysis.

3. RESULTS OF DETERIORATION SIMULATION TESTS

3.1 Analytical results of medium

Changes in concentrations of calcium ion, sodium ion, potassium ion, sulfate ion and organic acids in culture medium, in simulation tests using each microorganism are shown in Figs. 1, 2, 3, 4 and 5 respectively. The value of concentration of each ion and acid measured in Blank A test, in which a specimen is immersed and no microorganism is inoculated, has been deducted from the value in the vertical coordinate. From the results of Blank B test, it was confirmed that microorganisms

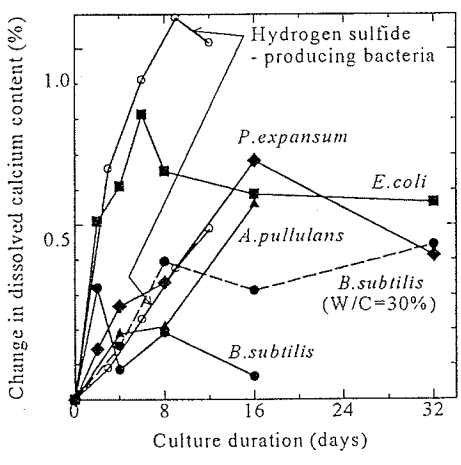

Fig. 1 Change in calcium ion concentration in culture medium

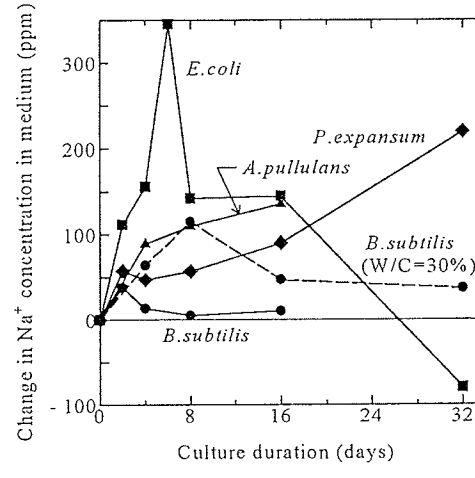

Fig. 2 Change in sodium ion concentration in culture medium

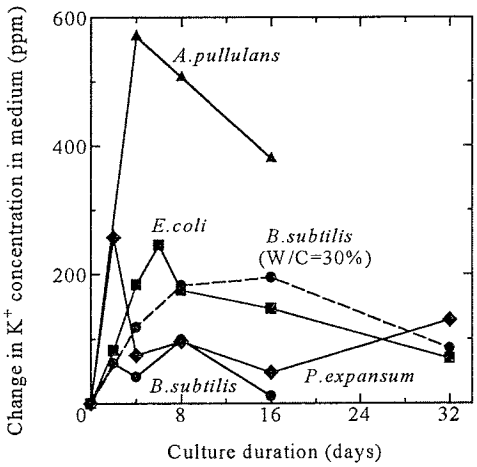

Fig. 3 Change in potassium ion concentration in culture medium

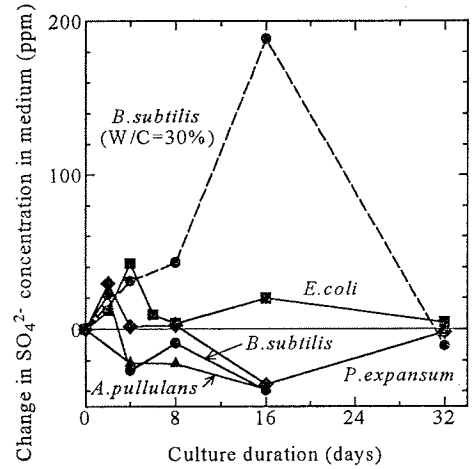

Fig. 4 Change in sulfate ion concentration in culture medium

produced no inorganic ions.

Change in calcium ion concentration is represented as a change in the percentage of dissolved calcium content to calcium content in the cement paste. Results of simulation tests using hydrogen sulfide-producing bacteria in the previous study [2] are also shown in Fig. 1. The only other inorganic anions detected were hydroxide, carbonate and sulfate ions. A reliable concentration of carbonate ion could not be obtained because organic acids were highly concentrated and volatile organic acids were present in culture medium when the attempt was made to measure the concentration with a total organic carbon analyzer and a gas chromatoanalyzer [14].

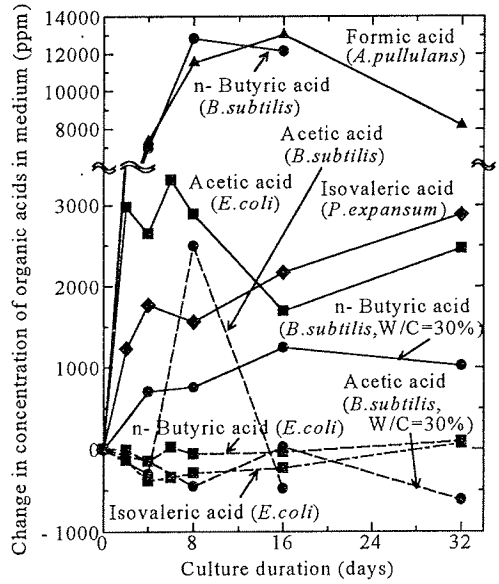

Fig. 5 Change in concentration of organic acids in culture medium

It was found that highly concentrated organic acids were metabolized by microorganisms and a large amount of calcium ion was dissolved out of the cement paste specimen in simulation tests involving each microorganism. The results of dissolved calcium content showed that the extent of deterioration caused by universal bacteria and fungi was almost equal to that of sulfur bacteria. After an initial increase, dissolved calcium content became stagnated or decreased. One of the reasons for this decrease was that calcium ion was ingested as a nutrient by microorganisms since nutrients in the culture medium became insufficient as microorganisms grew. Another was that calcium ion reacted with carbonate ion produced through the respiration of microorganisms therefore calcium carbonate was produced and was precipitated. White precipitation could be seen in the culture bottle. But the content of calcium carbonate precipitated could not be determined because the white substance could not be separated from other precipitation including autolyzed microorganisms.

It could be seen that some changes in organic acids became negative. This meant that microorganisms ingested organic acids when nutrients in the culture medium became insufficient.

The dissolved calcium content out of the specimen with W/C=0.40 in the simulation test using *B.subtilis* was higher in the early stage of culture than that of the specimen with W/C=0.30. This meant that the density of the specimen influenced the extent of deterioration. However, the dissolved calcium content of the specimen with W/C=0.30 became higher than that of the specimen with W/C=0.40 as culture duration was longer. It was thought that this was due to the difference in activity levels of the bacteria used in both tests. Since the concentration of organic acid in the culture medium where the specimen with W/C=0.40 was immersed reached very high values in the early stages of culture before becoming stagnated, *B.subtilis* in the same culture medium also grew very quickly and entered the stationary growth phase from the logarithmic growth phase.

Types of organic acids metabolized by each microorganism vary by type of microorganism and are shown in Table 2. Since samples of solution were vaporized at 175℃ in this study, only lower organic acids could be detected. Even if microorganisms metabolized organic acids containing a large number of carbons, these organic acids were not included in the results shown here. These organic acids were not considered because they were hardly dissociated in water and did not act as acids compared with lower organic acids.

Table 2 Organic acids metabolized by microorganisms

	Formic acid	Acetic acid	n-Butyric acid	Isovaleric acid
B.subtilis	----	Little detected	Much detected	----
E.coli	----	Much detected	Little detected	Little detected
P.expansum	----	----	----	Much detected
A.pullulans	Much detected	----	----	----

No remarkable change could be seen with respect to sodium, potassium and sulfate ions. A decrease of sulfate ion concentration as shown in some cases resulted in producing $CaSO_4 \cdot 2H_2O$. It was found that potassium ion was largely dissolved in simulation tests using *A.pullulans*. This was because of selective dissolution of potassium ion from the fact that *A.pullulans* metabolized a large amount of formic acid as shown in Fig. 5 and solubility of potassium formate was very large (331 g/100 g at 18℃ [15]).

3.2 Analytical results of specimens

In simulation tests utilizing each microorganism, the contents of calcium hydroxide and calcium carbonate in the surface area of specimens immersed in culture medium are shown in Fig. 6. The calcium carbonate content was converted to the equivalent calcium hydroxide content.

The sum of the contents of calcium hydroxide and calcium carbonate was increased in simulation tests utilizing each microorganism. The increase of the sum regardless of dissolution of calcium ion as shown in Fig. 1 meant decomposition of calcium hydrates besides calcium hydroxide. Assuming that the difference between the increment of calcium carbonate content and

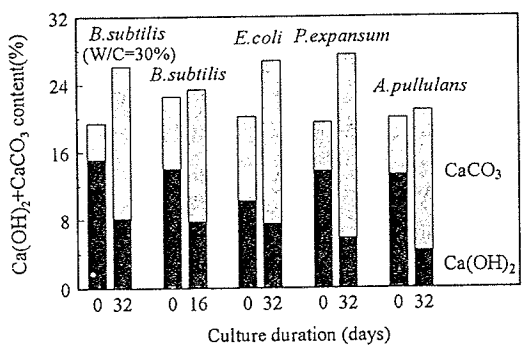

Fig. 6 Calcium hydroxide and calcium carbonate contents of specimen immersed in culture medium

the decrement of calcium hydroxide content is the calcium content produced by carbonation of calcium compounds except calcium hydroxide, changes in composition of calcium compounds in the cement hydrates is shown in Fig. 7. Unhydrated cement was included in calcium compounds except calcium hydroxide and calcium carbonate, and calcium ion dissolved in culture medium was neglected. This figure shows that composition of calcium compounds was greatly affected after simulation tests.

The only mineral components in specimens identified with powder X-ray diffraction were unhydrated cement, portlandite, calcite and ettringite.

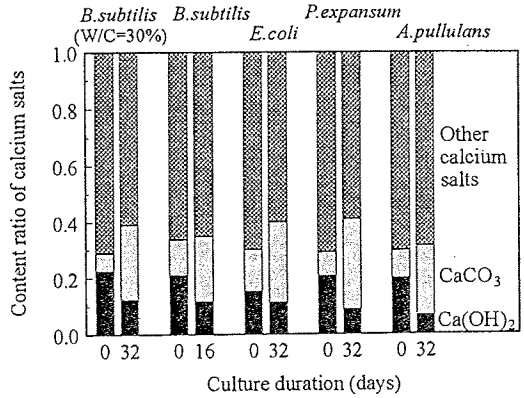

Fig. 7 Changes in types of calcium salts before and after simulation test

4. RESULTS OF ACCELERATED TESTS USING SYNTHESIZED SOLUTIONS

Figures 8, 9, 10 and 11 show changes in calcium ion concentration in each synthesized solution of MIX, ACE, PRO and H2S respectively. In the cases of MIX, ACE and PRO solutions, dissolved calcium ion content was nearly proportional to the concentration of synthesized solution, while changes in calcium ion concentration were almost unchanged regardless of concentration of synthesized solutions in the case of H2S solutions. By using the following dissociation coefficients of hydrogen sulfide [16], the percentage of existence of H_2S in water having various pH values is shown in Fig. 12.

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 0.9 \times 10^{-7} \qquad (1a)$$

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = 0.12 \times 10^{-14} \qquad (1b)$$

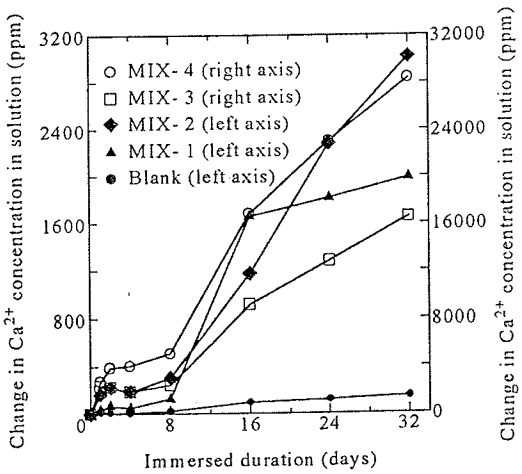

Fig. 8 Change in calcium ion concentration in synthesized solutions (MIX-1, MIX-2, MIX-3 and MIX-4)

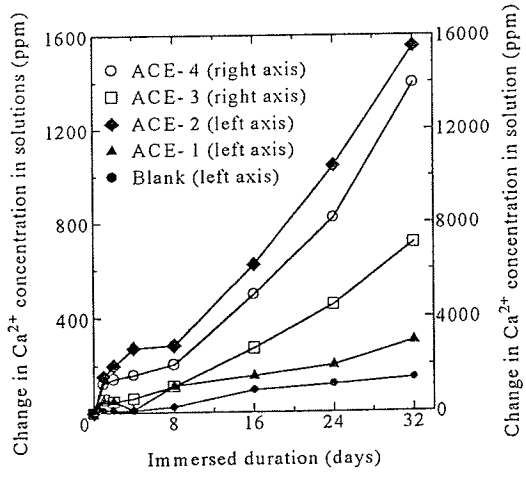

Fig. 9 Change in calcium ion concentration in synthesized solutions (ACE-1, ACE-2, ACE-3 and ACE-4)

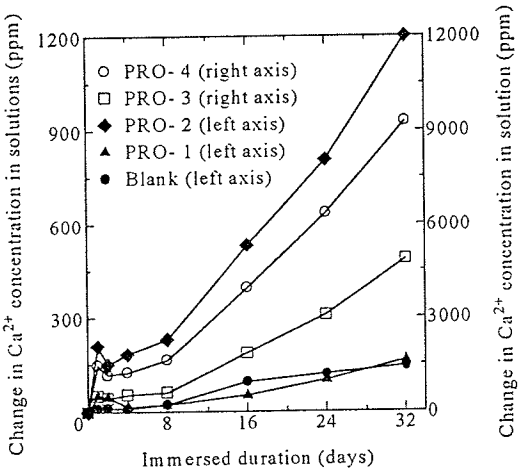

Fig. 10 Change in calcium ion concentration in synthesized solutions (PRO-1, PRO-2, PRO-3 and PRO-4)

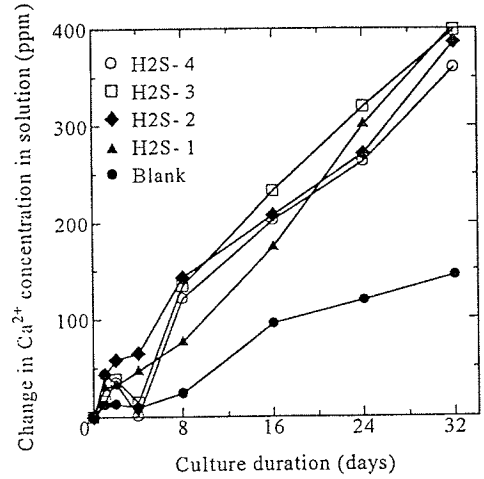

Fig. 11 Change in calcium ion concentration in synthesized solutions (H2S-1, H2S-2, H2S-3 and H2S-4)

Since the pH values in every synthesized solution reached over 11.5 one day after immersion of specimens into solution, H_2S in the solution was completely dissociated to produce H^+ and S^{2-}. Consequently, it was thought that dissolution of calcium ion did not proceed because of low solubility of CaS.

As shown in Figs. 8 to 10, the sum of dissolved calcium contents of cement paste immersed in acetic and propionic acid was slightly smaller than the calcium content of specimens immersed in mixed solution. This was due to the effect of not hydrogen sulfide but carbonic acid, taking account of no identification of sulfate such as gypsum in the surface area of specimens from the results of powder X-ray diffraction analysis.

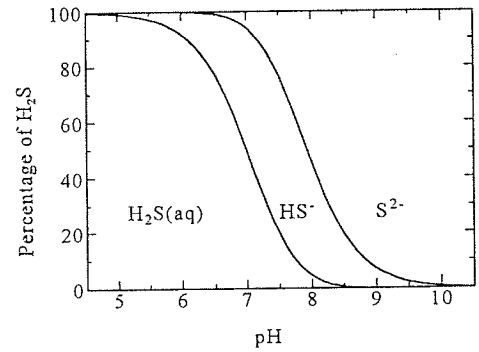

Fig. 12 Percentage of H_2S in water having various pH

Change in pH values in MIX solutions is shown in Fig. 13. The pH value in MIX-1 solution increased up to 11 one day after immersion of specimen, while the pH values in MIX-2 to MIX-4 solutions kept a 5 to 6 value of weak acidity. By using the following dissociation coefficients of carbonic acid [17], the percentage of existence of H_2CO_3 in water having various pH values is shown in Fig. 14.

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.4 \times 10^{-7} \qquad (2a)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.62 \times 10^{-11} \qquad (2b)$$

From this figure it can be seen that 10 to 30 % of H_2CO_3 exist as HCO_3^- producing soluble calcium salt with a pH range of 5 to 6. It was thought that this HCO_3^- accelerated dissolution of calcium ion in MIX-2 to MIX-4 solutions. On the other hand, drastic changes in the pH value in MIX-1 solution caused precipitation of calcium carbonate as well as dissociation of calcium ion. After that, calcium ion was dissolved out of the specimen because of an increase in HCO_3^- including a slight decrease in pH.

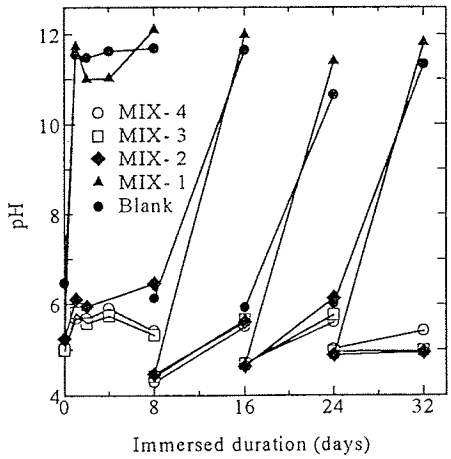

Fig. 13 Value of pH in synthesized solutions (MIX-1, MIX-2, MIX-3 and MIX-4)

Changes in the contents of calcium hydroxide and calcium carbonate in the surface area of the specimens immersed in MIX, ACE and PRO solutions are shown in Figs. 15, 16 and 17, respectively. The content of calcium hydroxide was remarkably decreased when the specimen was immersed in highly concentrated organic acid solutions, especially in MIX-3 and MIX-4 solutions. The increase of calcium carbonate did not mean production of calcium carbonate in specimen, but showed production of calcium carbonate by thermal decomposition of carboxylate in the specimen

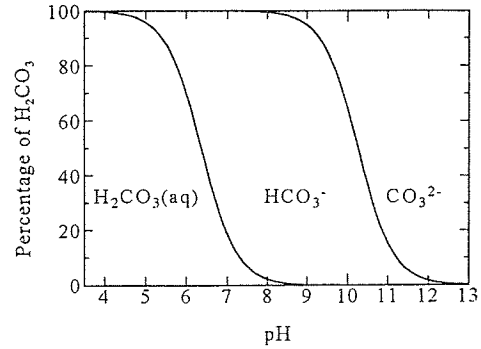

Fig. 14 Percentage of H_2CO_3 in water having various pH

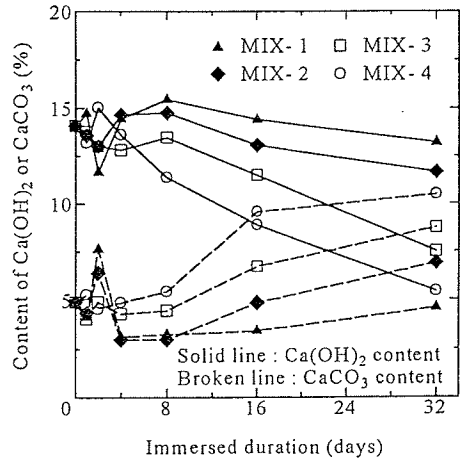

Fig. 15 Change in calcium content in immersed specimens (MIX-1, MIX-2, MIX-3 and MIX-4)

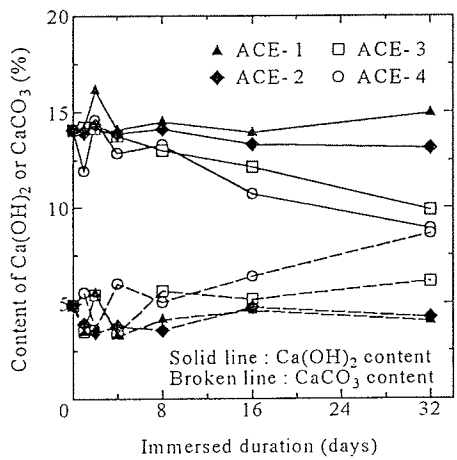

Fig. 16 Change in calcium content in immersed specimens (ACE-1, ACE-2, ACE-3 and ACE-4)

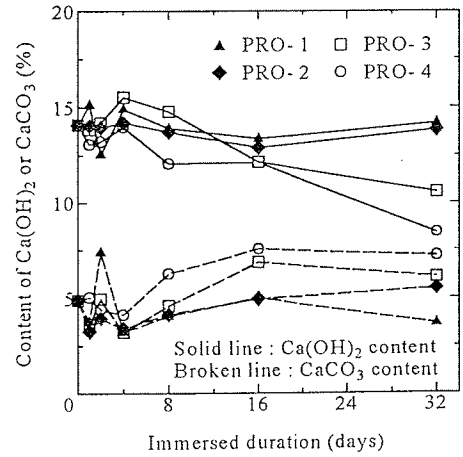

Fig. 17 Change in calcium content in immersed specimens (PRO-1, PRO-2, PRO-3 and PRO-4)

during TG-DTA. This fact was confirmed by identification of $Ca(CH_3COO)_2$ in the surface area of the specimen, which had been immersed in ACE-4 solution, by powder X-ray diffraction analysis.

5. ROLE OF ORGANIC AND CARBONIC ACIDS IN DETERIORATION PROCESS

Since *E.coli* metabolized acetic acid, results of simulation tests using *E.coli* and accelerated tests using acetic acid solution were compared and discussed. Calcium ion concentrations shown in Figs. 1 and 9 could not be directly compared because the mix proportions, specimen size and the volume of solution in which specimens were immersed differed. Dissolved calcium content per unit of surface area of specimen is shown in Fig. 18 since the calcium ion is dissolved out of the specimen's surface. As mentioned above, it was thought that the logarithmic growth phase of *E.coli* had already finished before the dissolved calcium content decreased. Therefore, results until 6 days after culture, the logarithmic growth phase of *E.coli*, were discussed.

Dissolved calcium content in the culture medium of the simulation test using *E.coli* exceeded dissolved calcium content in the ACE-4 solution even though the water-cement ratio of the specimen used in accelerated tests was 0.10 higher than that used in simulation tests. It is well known that organic acids which react with calcium hydroxide to produce soluble salts, severely erode concrete. This fact was confirmed in accelerated tests using synthesized solutions in this study. Since the dissolved calcium content in simulation tests was much higher than that in accelerated tests, it was thought that carbonate ion produced by the respiration of microorganisms accelerated dissolution of calcium ion in simulation tests.

Figure 19 shows fluctuations in acetic acid, both in culture mediums in simulation tests and in synthesized solutions in accelerated tests. Since the solution was renewed 8 days after immersion of specimen in accelerated tests, changes until 8 days after culture and immersion were focused on. The vertical coordinate in the figure was represented by a concentration of acetic acid because it was not the total content, but the concentration of acetic acid attacking the specimen that governed deterioration of the specimen. From this figure, it was found that the concentration of acetic acid in culture mediums in the simulation test using *E.coli* corresponded to the concentration of acetic acid in the accelerated test where the specimen was immersed in 800 to 1000 mmol/l of acetic acid. It was shown in Fig. 18 that the dissolved calcium content in the simulation test using *E.coli* was nearly twice that in the accelerated test using ACE-4 solution. Consequently, a factor besides acetic

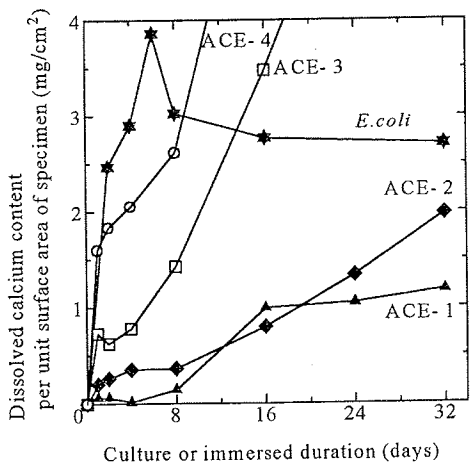

Fig. 18 Comparison of dissolved calcium content between simulation tests and acceleration tests

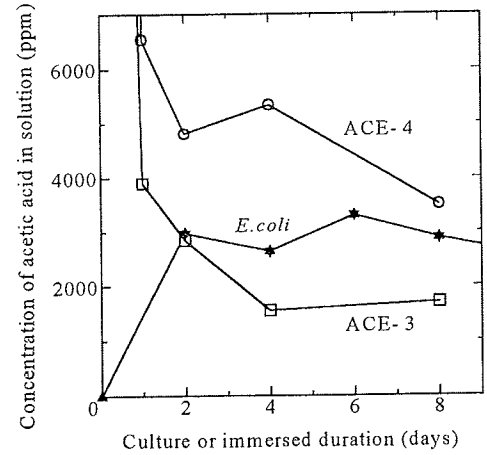

Fig. 19 Change in concentration of acetic acid in simulation test and acceleration test

acid doubled the dissolved calcium content in the simulation test. This factor was carbonic acid a byproduct of *E.coli*'s respiratory process. It has been known that almost all calcium compounds in cement hydrate are decomposed by carbonic acid [18]. It was thought that calcium carbonate produced by carbonic acid was dissolved out of the specimen through its pores by organic acid whose calcium salts were very soluble.

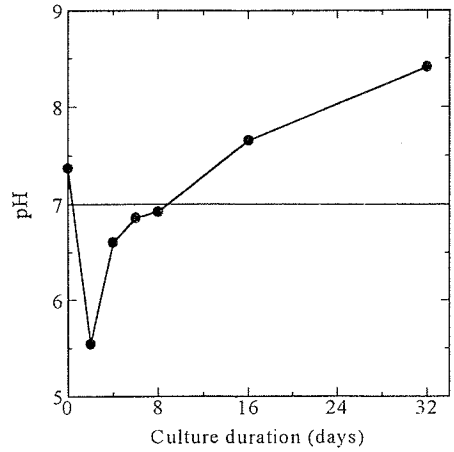

Fig. 20 Value of pH in culture medium inoculated with *E.coli*

Culture medium pH value fluctuations in simulation tests using *E.coli* are shown in Fig. 20. From Figs. 1 and 20, after the pH value lowered to 5.5 in the early stages of culture of *E.coli*, the value shifted towards neutrality as calcium ion was dissolved. In the region of neutrality, most of carbonic acid exists as HCO_3^- seen in Fig. 14 and very soluble $Ca(HCO_3)_2$ is produced as calcium salts. Since soluble $Ca(HCO_3)_2$ in highly concentrated carbonic acid severely eroded concrete [19], carbonic acid produced as a byproduct of microorganisms respirations not only played a role in the decomposition of cement hydrates, but also contributed to the dissolution of calcium ion out of specimens as did the organic acids.

From the above-mentioned discussion, it was thought that organic acids metabolized by aerobic microorganisms and carbonic acid produced through the respiration of aerobic microorganisms played the following roles in concrete deterioration caused by aerobic microorganisms.

1) With respect to calcium salts in cement hydrates; organic acids decomposed calcium hydroxide, while carbonic acid decomposed all calcium compounds including calcium hydroxide.

2) Calcium carbonate precipitated in pore by carbonation of calcium salts was dissociated by organic acids. Carbonic acid contributed to this dissociation as the pH value in pore solution lowered.

3) Dissolution of calcium ion out of concrete was mainly caused by organic acids. Contribution of carbonic acid to this dissolution depended upon the pH value in pore solution.

In summary, organic acids were greatly involved with all phases of decomposition, dissociation and dissolution processes of the deterioration, while carbonic acid greatly contributed to the process of decomposition and accelerated the deterioration.

In this study, effects of weak acids on concrete deterioration caused by organic acids metabolized by aerobic microorganisms and carbonic acid produced through the respiration of aerobic microorganisms were discussed using universal bacteria and fungi as aerobic microorganisms. Since the aim of this study was to clarify the mechanism of the deterioration, highly concentrated culture medium cultured with microorganisms and highly concentrated organic acids in synthesized solutions were used. For these reasons, there might be little correspondence between the results of this study and existing phenomena. It is very difficult to correlate results obtained by laboratory tests with existing phenomena, considering that it is not exaggerating to say that species of microorganisms are infinite and that types of microorganisms vary with places and districts.

6. CONCLUDING REMARKS

In this study, contribution of organic and carbonic acids to concrete deterioration caused by organic acids metabolized by aerobic microorganisms and carbonic acid produced through the respiration of

aerobic microorganisms was investigated. In conclusion, the following concepts were clarified.

(1) Organic acids metabolized by aerobic microorganisms were greatly involved in the decomposition of calcium salts in cement hydrates, dissociation of calcium carbonate in pore solution and dissolution of calcium ion out of the hardened cement.

(2) Carbonic acid produced through the respiration of aerobic microorganisms was a large factor in the decomposition of calcium salts in hardened cement. Contribution to dissociation of calcium salts depended upon the pH value in pore solution.

(3) The extent of deterioration caused by organic acids was almost half as much as that caused by organic and carbonic acids. That is to say, carbonic acid accelerated deterioration caused by organic acids.

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