DEVELOPMENT OF A CRACK REPAIR METHOD USING YEAST-INDUCED CALCIUM CARBONATE PRECIPITATION

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ABSTRACT: Although many examples of water leakages are observed between the high column of the bridge and the deck, the gaps in between them are not recognized as degradation. However, if water leaks from the gap, deterioration of the reinforced concrete becomes faster than expected, so even though this is not an urgent matter, some inexpensive repairs would be necessary. In this study, the applicability of bio-grout using microbial metabolism for crack repairs was investigated. Bio-grout is a repair material using microbial metabolism, mainly based on water. Therefore, bio-grout is expected to penetrate cracks more easily due to a capillary tension that is quite different from conventional inorganic or organic grout. Therefore, it is unnecessary to press fit the grout into cracks, and this grout is environmentally friendly. This study examined the mixture proportion of the bio-grout used to produce a significant amount of calcium carbonate. Further, the precipitation amount of calcium carbonate was investigated via sedimentation analysis using a geochemical code. The simulation model based on the geochemical code successfully reproduced, the precipitation amount of calcium carbonate with reasonable precision.

Keywords: Grout, Calcium carbonate, Calcite, Microbial metabolism

1. INTRODUCTION

In Japan, post-war reconstructed bridges are currently in a state of deterioration, and repair is required. However, the municipalities in Japan are in severe financial straits; hence, allocating a sufficient budget for repair expenses is difficult and thus, sufficient repair measures for all bridges are unattainable.
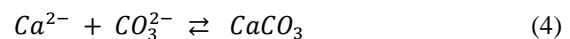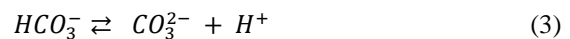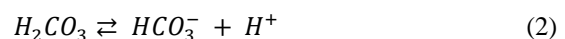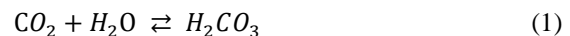
Although not classified as deterioration, many reported cases of water leakage occur from the gap between the high column and the floor slab of a bridge; it is not a pressing matter, but restoration plans and action are required. Because of water leakage from the gaps, deterioration of the reinforced concrete becomes faster than expected. Therefore some low-cost countermeasures are required.

A conventional crack-repairing method is to fill the crack with epoxy resin via press fitting, which is laborious and expensive, mainly due to the material cost. It may also cause a leakage of the grout and produce a pervasive smell. Therefore, a method of repairing gaps and cracks using naturally derived bio-grout is proposed herein. In previous studies, calcium carbonate was precipitated from bio-grout, but that was not enough to repair the gaps. [1-9]

The purpose of this research is to design a repair model using a geochemical code to develop a more optimal blending condition. [10]

2. MATERIALS AND METHOD

Bio-grout formation comprises two reactions: biological and chemical. The former involves microorganisms consuming nutrients and releasing carbon dioxide, whereas the latter involves producing calcium carbonate from the generated carbon dioxide reacting with a calcium source. The chemical reactions can be simulated using PHREEQC, and they are outlined as follows:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \tag{1}$$

$$H_2CO_3 \rightleftarrows HCO_3^- + H^+ \tag{2}$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \tag{3}$$

$$Ca^{2-} + CO_3^{2-} \rightleftarrows CaCO_3 \tag{4}$$

In producing bio-grout, we referred to the reaction condition as shown in Table 1. [1]

The buffer is added here because of the precipitation of calcium carbonate is a reversible reaction, and as the pH decreases, calcium carbonate dissolves, as shown in Eq. (4). Therefore, to maintain the production of calcium carbonate, tris(hydroxymethyl)aminomethane (THAM) is added to capture the released protons to induce more carbonate ion (refer to Eq. (2) and (3)).

Table 1 Formulation of bio-grout as a reference.

	Materials	Con.
Microbe	Saccharomyces Cerevisiae	9.0 g/L
Nutrient	D-glucose	0.10 M
Calcium	Calcium acetate	0.05 M
Buffer	Tris(hydroxymethyl) aminomethane	0.5 M

Note: The pH was set to 9.0 and the experimental temperature was 20°C.

2.1 Experiments with Bio-grout

In this study, the type of microbe and nutrient used were fixed. The calcium source, buffer concentration, pH adjuster of the buffer, and reaction temperature were varied.

Table 2 shows the condition of the bio-grout. Table 3 lists the conditions of the experiments.

The experiment began by adding the pH adjuster into the buffer solution to set a specific pH. 40 mL of the buffer solution was taken into a conical tube, to which D-glucose and calcium source were added. Next, baker's yeast (*S. cervisiae*) was added. Following this, the mixture was kept at a constant temperature. Finally, the pH and the amount of calcium carbonate thus produced were measured.

pH change and crystal appearance confirmed the precipitation of calcium carbonate, and the precipitation amount was measured. Further analysis of the obtained crystals was done via X-ray diffraction (XRD) to examine the crystal structure.

Table 2 Proposed formulation of bio-grout.

	Materials	Con.
Microbe	Saccharomyces cerevisiae	6.0 g/L
Nutrient	D-glucose	0.4 M
Calcium	Calcium lactate	0.2 M
Buffer	Tris(hydroxymethyl)- aminomethane	Varied

Table 3 Different experimental conditions using the components from Table 2.

	Con. of THAM	Temp.
Case 1	-	25°C
Case 2	-	40°C
Case 3	0.3 M THAM	25°C
Case 4	0.3 M THAM	40°C
Case 5	0.75 M THAM	25°C
Case 6	0.75 M THAM	40°C

3. RESULTS AND DISCUSSION

3.1 Experimental Results

From Fig. 1 and Fig. 2, the pH remarkably decreased over time in Cases 1, 2, and 4.
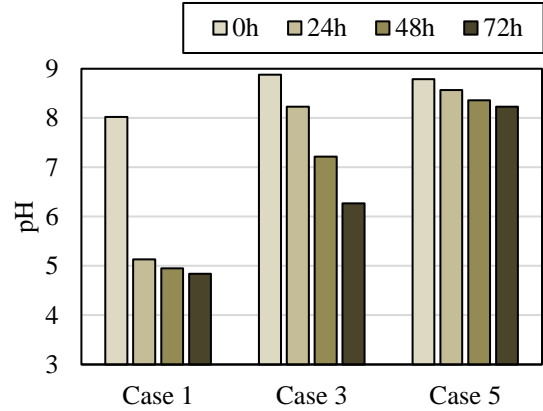

Fig. 1 pH change trends for different experimental cases when the reaction was maintained at 25°C.
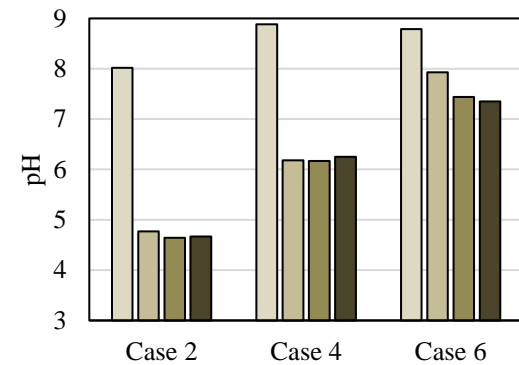

Fig. 2 pH change trends for different experimental cases when the reaction was maintained at 40°C.

Adding THAM resulted in a gentler pH change. Figures 1 and 2 show that the higher the concentration, the slower the pH change. For example, when the temperature was 40°C, the concentration of carbon dioxide increased and many protons were generated because the microbes breathed more actively thereby producing more carbon dioxide. Figure 2 shows that using only 0.3M THAM resulted in a thin concentration and insufficient effect. However, 0.75M THAM was effective.

In Cases 1 and 2 where the buffer was not introduced, calcite and aragonite, which are crystals of calcium carbonate, did not precipitate (Figs. 3 and 4).
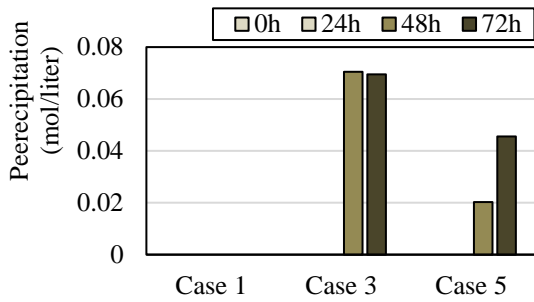
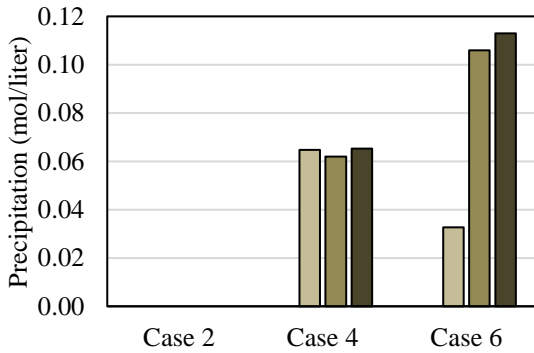Fig. 3   Precipitation trend of calcium carbonate at 25°C

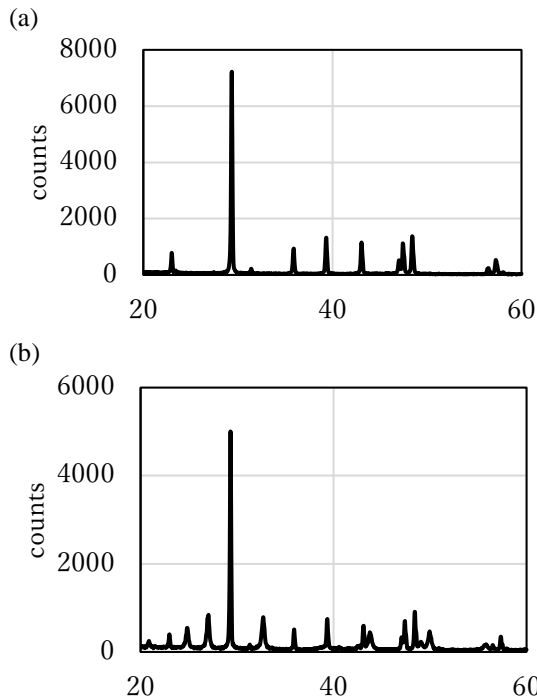Fig. 4   Precipitation trend of calcium carbonate at 40°C

(a)

(b)

Fig. 5   XRD results for crystalline precipitates; (a) Calcite, (b) Crystalline precipitates in the Tris-buffer solution

The solid precipitates associated with yeast were identified by XRD analysis. A SHIMADZU LabX XRD-6100 X-ray diffractometer with Cu-Kα radiation in the theta/theta configuration was used. The diffractometer was operated at 40 kV and 30 mA. Measurements were made from 3° to 60° 2θ at a rate of 2°/min with a step size of 1° 2θ.

The results from XRD analysis are shown in Fig. 5. The data strongly suggested that these crystalline precipitates were calcium carbonate. The sharp peak at around 30° 2θ suggests the presence of highly crystalline phases of the calcium carbonate mineral calcite. The carbonation is the result of the dissolution of CO_2 in the concrete pore fluid and its reaction with calcium ion.

The solid precipitates associated with yeast and the $CaCO_3$ crystals were analyzed using a JEOL JSM-5500s SEM and a JSM-7001F Schottky FE-SEM with an Oxford instruments X-Max energy-dispersive X-ray spectrometer (EDS).

The samples were completely dried in the oven at 100 ℃ for 1 day, and then were mounted on sample board and chemical vapor deposited with gold to ensure electrical conductivity for the examination of crystal morphology and distribution. The elemental composition of the precipitates was investigated by EDS analysis.

The SEM images are shown in Fig. 6. It can be seen that a large number of mineral crystals grew around yeast. The mineral crystals showed evidence of yeast involvement. Round-shaped holes having an average diameter of 3 μm were found on the surface of the minerals, which presumably means the space occupied by yeast. These holes also indicated that yeast served as nucleation sites during the mineral precipitation process. EDS analysis demonstrated that the crystal is composed of Ca, C, and O with an atomic percentage almost closely matching that of $CaCO_3$, however, C was slightly more amount than Ca, implying that the crystal is composed of calcium carbonate and yeast.

Fig. 6   Observation of precipitates in the SEM image

Table 4 EDS of the calcium carbonate precipitation.

Element	Wt%	At%
C	22.68	35.15
O	41.40	48.16
Ca	35.92	16.68

3.2 Geochemical Code: PHREEQC

PHREEQC [11] is a computer program written in the C and C++ programming languages that are designed to perform various aqueous geochemical calculations.

PHREEQC is capable of speciation and saturation-index calculations; batch-reaction and one-dimensional (1D) transport calculations with reversible and irreversible reactions, including aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria; specified mole transfers of reactants; kinetically controlled reactions; mixing of solutions; pressure and temperature changes; inverse modeling.

3.3 Simulation Results Obtained via PHREEQC

In the simulation, besides the calcium ion concentration, the pH value and the temperature obtained from the experiment were used. THAM was not found in the database of PHREEQC; hence, an assumed compound as a pseudo buffer was set and used.

Similar to the experiment, precipitation of calcite and aragonite was not observed in Cases 1 and 2 (without buffer), and the change in pH was remarkable (Fig. 5).

However, the addition of a pseudo buffer resulted in a gentler pH drop, as depicted in Fig. 6, and the precipitation amount of calcite, a crystal of calcium carbonate, is shown in Fig. 7. Furthermore, no precipitation of aragonite was observed in any of the cases.
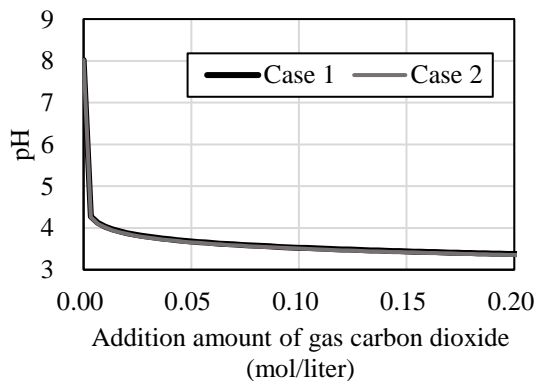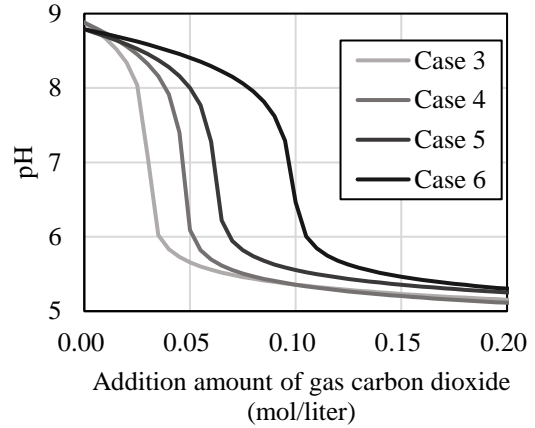

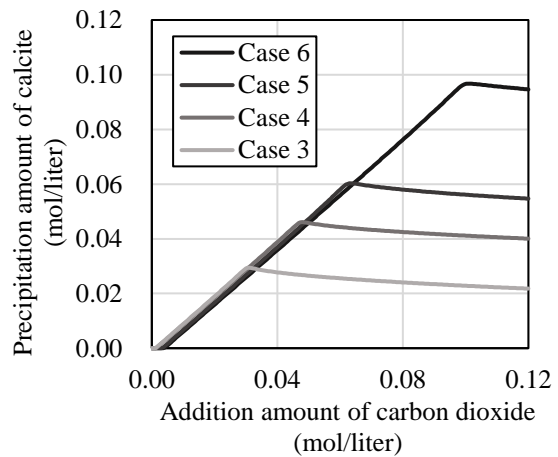Fig. 7   pH change in Cases 1 and 2

Fig. 8   pH change in Cases 3-6

Fig. 9   Precipitation amount of calcite in Cases 3-6

3.4 Comparison Between Experimental and Simulation Results

Comparing the experimental values with the simulation values, where *x*-axis denotes pH and *y*-axis denotes the precipitation of calcite (Fig. 8), it can be observed that the simulation values accurately followed the experimental values.

Based on these results, the amount of precipitation produced from the bio-grout could be predicted to some extent from the simulation. In addition, Fig. 8 shows that maximum amount of precipitation was obtained between pH 6 and 7; however, when the pH decreased to 6 or less, the calcite dissolved, and the amount of precipitation decreased.
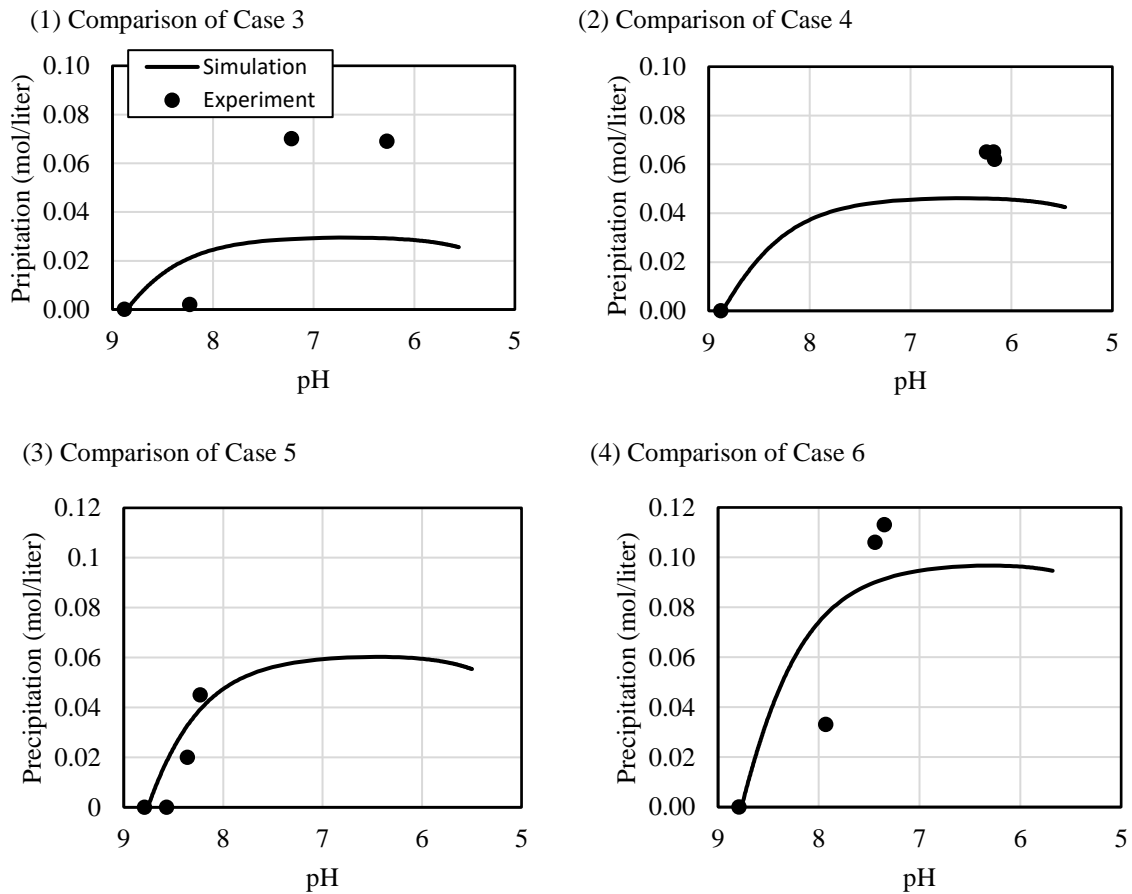
(1) Comparison of Case 3

(2) Comparison of Case 4

(3) Comparison of Case 5

(4) Comparison of Case 6

Fig. 10 Comparison of the precipitation amount between experimental and simulation results as a function of pH

4. CONCLUSION

This study examined the optimum mixture proportion of the bio-grout used to produce a significant amount of calcium carbonate. The type of microbe and nutrient used were fixed. The calcium source, buffer concentration, pH adjuster of the buffer, and reaction temperature were varied. The experiment began by adding the pH adjuster into the buffer solution to set a specific pH.

Further, the precipitation amount of calcium carbonate was investigated via sedimentation analysis using a geochemical code. In the simulation, besides the calcium ion concentration, the pH value and the temperature obtained from the experiment were used. THAM was not found in the database of PHREEQC; hence, an assumed compound as a pseudo buffer was set and used.

The results show that the simulation model followed the same trend as the experimental outcome. In conclusion, the simulation model could be used to predict the amount of precipitation from the bio-grout to some extent.

The simulation also revealed that increasing the precipitation amount of calcium carbonate by setting a higher temperature and preventing the pH from decreasing is possible.

A further study has been planned to test the crack repair in concrete using the new bio-grout.

5. ACKNOWLEDGMENTS

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