

# Effects of Sulfuric Acid Solution on Cement Mortar

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## Abstract

To elucidate effects of a sulfuric acid environment on a hardened cement body, the mass change and carbonation depth were examined after environmental operations. For that purpose, the mortar specimens were immersed in sulfuric acid solution and examined using this accelerated experiment. The experimental factors were concentrations of sulfuric-acid solution and mortar water-cement ratios. The measurement items were the change of pH and ion concentration for environment solution, and the mass change and carbonation depth change of the mortar. Results of this study show that the environment operation and the mass change, and the environment operation and carbonation change respectively showed a good correlation.

**Key words:** sulfuric acid, mortar, immersion, pH, ion concentration, mass change, carbonation depth

## 1. Introduction

Reports on typical deterioration mechanisms establish investigation methods and maintenance management [1]. In addition, reports clarify deterioration mechanisms. However, unsolved problems of chemical corrosion mechanisms remain. For example, accelerated experiments of chemical corrosion examinations are so diverse that results of one which include some actual environment are sometimes difficult to apply to another actual environment. Diverse conditions used for experimentation are the acid type, the operation situation and period of the actual environment. These disparate parameters might make it difficult to apply results to expansive actual environments and to establish a unified index.

Regarding chemical corrosion mechanisms, a

corrosion factor permeates to the interior of a hardened cement body through corrosion of the surface of its body. This mechanism differs from that of salt damage or carbonation mechanisms; these characteristics of permeation render the corrosion mechanism more complicated.

Actual acid environments are assumed to be spa zones, sewers, acid rain affected areas, and so on. Therefore, the present study of chemical corrosion examines an accelerated environment using a highly concentrated specified acid. [2] The respective results were obtained mainly from the experiment with a purpose of application in the assumed environment. Such results are therefore almost impossible to apply to other environments. This reason was described above as the kind of acid, the diversity of the

conditions, and different acid concentrations, in addition to complicated deterioration mechanisms.

The present study was therefore undertaken based on the contents shown below, including the evaluation of the extensive applicability of the acceleration experiment result for the chemical corrosion mechanism. As for the chemical erosive (corrosive) phenomenon, it was verified by mass measurement as expansion and corrosion. Using measurements of carbonation depth, its invasion route

was evaluated as permeation by the corrosion factor into the mass.

Effects of the environment operation were identified from the elapsed change of the pH and the ion concentration in the setting environment. These results were examined with correlation between the environment operation and the corrosion and evaluated the ability for applying a result of one concentration to another different environmental concentration.

## 2. Experimental Outline

Experimental conditions shown in Table 1 are obtained from references [3]; results are shown following these.

### 2.1 Materials

Mortar was used as the cement hardening agent. Materials used were a commercially available ordinary Portland cement (specific gravity: 3.15) for cement and river sand (specific gravity: 2.57) as fine aggregate. In addition, the best available quality reagent of sulfuric acid was used as the environment solution.

### 2.2 Mix proportions, shape and treatment

The water cement ratios (W/C) of the mortar were 40, 50 and 60%. The mass ratio of the cement and river sand was a constant value of 1:3. As for the mortar test specimen shapes, A and B were rectangles and C was a column. For A, both sides of the section were 55 mm; it had 80-mm height. For B, both sides of the section were 40 mm, with 25-mm thickness. For C, the diameter was 25 mm, with 50-mm height. Aside from one 40 × 40 mm section of specimen (B) and the side surface of specimen (C), all surfaces were painted with resin.

### 2.3 Environmental condition

The initial concentrations of the sulfuric acid solution were 2% (specimen (A) and (B)) and 3% (specimen (C)). The replacement time for old acid solution in tank with new solution was basically at

every 1-wk or 2-wk until 4-wk. Thereafter, it was done every fixed period. Each environmental tank was kept covered to prevent evaporation from the solution surface in the indoor air environment.

### 2.4 Measurements

Each test specimen was removed from the mold on the day after casting; it was cured in water for 4 wk and then cured in an air environment for 2 wk. After the treatment described above, test specimens by group (classified by water-cement ratio) were immersed individually in the sulfuric acid tank. Items such as pH and ion analysis for environmental solution, and mass weight and carbonation depth were examined based on following conditions.

#### (1) pH and ion concentration

The time for measurement of the pH and sulfuric ion concentration were approximately every after 1 wk for 4 wk and every after 2 wk for 4–16 wk in all concentration cases. These measurements were done at the time of replacement of the old acid solution with the new acid. Measurements were done after 1, 3, 6, and 24-hours from the immersion beginning to grasp a change in the early stages. Personal pH meter and ion analysis meter were used for each measurement.

#### (2) Mass change and carbonation depth

Each mass weight measurement was done at the time of replacing the old environment solution with

**Table 1 Experimental outline**

Material	Ordinary Portland cement (specific gravity : 3.15), river sand (specific gravity : 2.57)
Mix proportion	Water - cement ratio (W/C, %) : 40, 50, 60, weight ratio of cement / sand : 1 / 3
Test specimen size	(A) 55mm×55mm×80mm, (B) 40mm×40mm×20mm, (C) Φ25mm×50mm
Curing condition	Water curing : 4 wk, air curing : 2 wk
Environment	Sulfuric acid solution (weight concentration (%)) : 0.5, 2.0, 3.0
Measurement	Environmental operation : pH and ion concentration, chemical erosion (corrosion) : mass and carbonation depth

the new one, as described in the section "2.2" in all cases of the (A), (B) and (C). Regarding the standard mass of each test specimen, the resin coat weight was added to the specimen weight after curing in water for 4 wk. To assess the carbonation depth, for test specimens of (B) and (C) were measured using the following procedure. The test specimen was taken out at 1, 2, 4, 8 and 16 wk from the start of exposure in solution and was cut using the dry cutter. Test specimens were cut respectively at right angles to the

exposure surface (in the case of (B)) and at the long axis (in the case of (C)). These cut surfaces were sprayed with phenolphthalein solution and were measured from the corroded surface to the boundary position of carbonation/non-carbonation. Each carbonation depth was used as an average with five measured values for (B). The value was subtracted from the diameter of non-carbonation from the initial diameter before exposure for (C).

### 3. Results

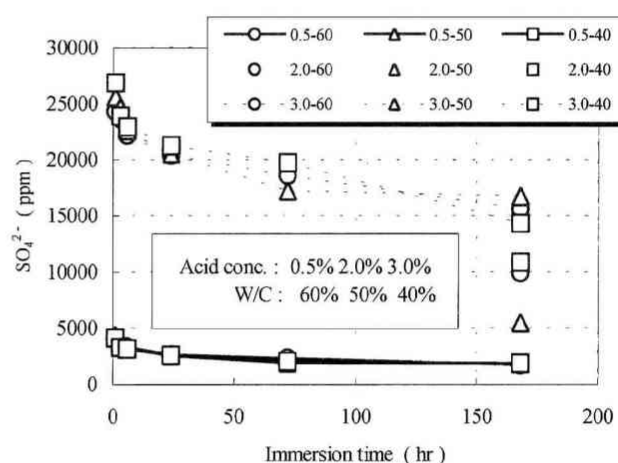
The pH measurement is used generally. For a strong acid environment, it is difficult to assess the degree of the environment operation by dissociating the acid degree and the pH meter coverage region. Nevertheless, ion measurements can better reflect reaction phenomena than the pH measurements because the quantity related with the reaction is obtained directly.

Therefore, it is expected that environmental action can be estimated using the ion measurement method. In this report, some of these examination results are discussed as the following.

#### 3.1 Change of environmental operation

The change in sulfuric acid ion concentration of each environment is shown in Fig. 1.

From a relative point of view, it is assumed that the immersion periods were "the first period" for 1 day from the start of immersion without the case of 2% (because of measurement in every 1 wk) and "the long-term" after "the first period" in all cases.



**Fig. 1 Change in sulfuric acid ion concentration**

In every environment, the sulfuric acid ion concentration decreased with immersion time.

At initial concentrations of 0.5% and 3%, long-term comparison of the early stages of exposure to the rate during the time of the sulfuric acid ion

decrease was remarkable. Especially, a change is remarkable for 1 h from the beginning of immersion from other periods: it increases greatly just at the start of immersion. After 24 hr, the rate of change is low.

### 3.2 Operation and corrosion by acid

The result shown in Fig. 1 depicts each environment in this experiment. The results suggest that the pH and the ion quantity depend on the number of test specimens and the gross volume of environment solutions in cases under the same conditions. Therefore, to alleviate these influences (the number of test specimens and the gross volume of acid solution) the results were converted to the value per unit quantity of test specimen. Therefore, the value of environment operation was calculated for the test specimen unit area.

On the other hand, the change of test specimen was a summation of the mass variation (the corrosion quantity) and the carbonation depth.

The environment operation on each specimen, which was the accumulated measured change of environment until carbonation testing, was reflected by the accumulated value per unit area of the test specimen. The relationship between the accumulation value of the hydrogen ion, which was converted from the pH of 2%-solution, and the corrosion and carbonation depth for unit area of test specimen, is shown in Fig. 2.

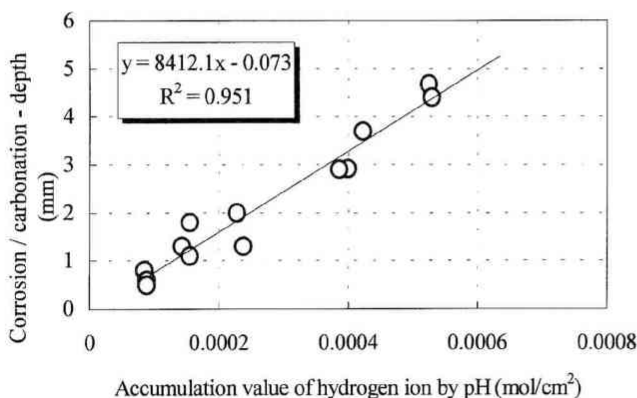


Fig. 2 Relationship between operation/damage by pH measurement (operation: 2%-acid)

The general relation showed no significant difference resulting from the different water cement ratio. However, the depth of the corrosion and carbonation as the damage seems to increase concomitant with the accumulated value of hydrogen ion as the environmental operations increase. Therefore, this relationship is regarded to be a linear expression.

Furthermore, less sulfuric acid ion is assumed to accumulate as the ion disappeared through the reaction. The relation to the corrosion and carbonation depth in this case is shown in Fig. 3. This correlation has a good relation, as shown by a linear expression similar to that shown in Fig. 2.

### 3.3 Relation between operation/damage

Regarding the 2% acid environment, it was presumed to be possible to expect the effect to the cement hardened body by the environment using with the pH/ion measurement. Using the relation described in "3.2", the ability of applying another acid concentration was examined. An example of this case is portrayed in Fig. 4.

This result was based on Fig. 3, showing a correlation between the damage and the accumulated disappeared quantity of sulfuric acid ion as an environment operation.

In Fig. 4, the results of 3% were plotted using the same calculated method as that of the 2% case.

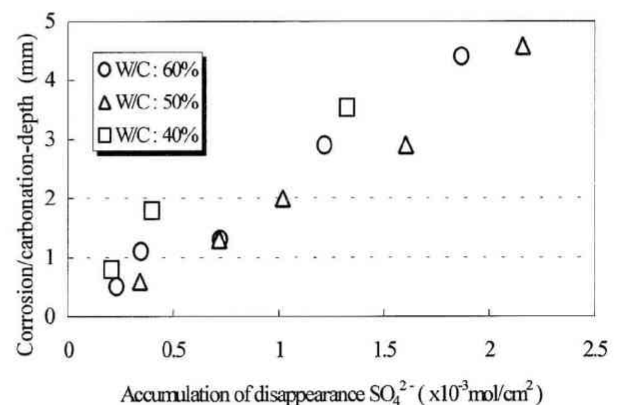


Fig. 3 Relationship between operation/damage by SO<sub>4</sub><sup>2-</sup> ion measurement (operation: 2%-acid)

Result points of the 3% case were not plotted out of range of the 2% result. The shape of the test-specimen in the case of 3% is not identical to that for 2%, but both values might be under identical conditions in terms of calculations for their unit area. Regarding these points, the damage imparted by the acid with 0.5% of low concentration is based and must be examined. In future studies, these conjectures must be investigated in detail and must be assessed using experiments with lower concentrations than those used for this experiment.

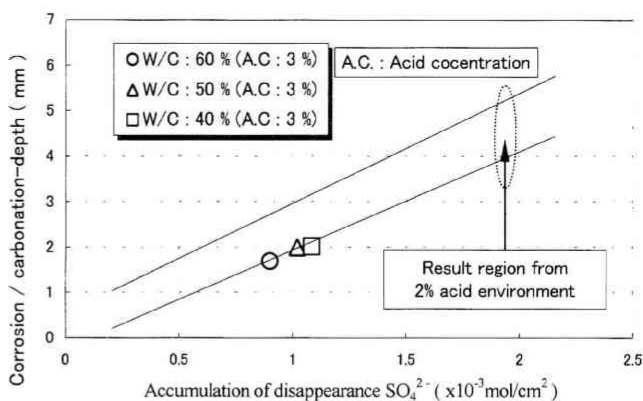
## 4. Conclusion

Operation of the specific acid environment was estimated as the hydrogen ion concentration as indicated by the pH/ion measurement. These accumulated values of environmental operation were related with the depth of the corrosion and carbonation depth, which reflect the degree of damage. Some conclusions from obtained results are as follows.

- (1) In each environment, sulfuric acid ion decreased according to the immersion period of the test specimen. Especially, the rate of decrease in the early stages was remarkable compared to that for other periods.
- (2) It was assumed that the environmental operation can be assessed according to the accumulation value

## References

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**Fig. 4 Application of 3% measurement result to 2% measurement result**

by hydrogen ion concentration or the disappeared sulfuric acid ion for unit area of test specimen. The damage was assumed as a summation with the corrosion and carbonation depth. Good correlation existed between the operations and their respective damage levels.

- (3) The same degree of damage might not always be shown, even with identical operations (the mass decrease and the carbonation rate) because of different acid concentrations if a relation between operation and damage obtained from the specific acid environment is applied to another acid environment. Therefore, detailed examinations are necessary for other subjects, as in this report.