Concrete Deterioration Caused by Sulfuric Acid Attack

K. Kawai, S. Yamaji, T. Shinmi
Department of Social and Environmental Engineering, Graduate School of Engineering, Hiroshima University
1-4-1, Kagamiyama, Higashi-Hiroshima, 739-8527 Japan
kkawai@hiroshima-u.ac.jp
TT1-199

ABSTRACT

Recently, biological deterioration of concrete in sewage and wastewater treatment plants has been reported. This deterioration is caused by sulfuric acid attack and is dependent on the concentration of sulfuric acid, this in turn being a function of both the specific location within the plant and also the time over which the concrete is exposed to elevated concentrations of acid. Given that concrete may often be exposed to very strong acid solutions, resin coatings are applied to the concrete to protect them. However these coating are only effective if there are neither pinholes nor defects due to coating operations. Otherwise, the deterioration of the concrete may proceed rapidly by sulfuric acid and sulfate. The method of predicting deterioration of coated concrete when subjected to sulfuric acid and sulfate attack has not yet been established. It is understood that the depth of deterioration of concrete due to sulfuric acid attack is proportional to the square root of the exposure time. This relationship is based on results of laboratory tests where specimens are continuously immersed in acid solutions over a specified period of time. But in actual structures, concrete is often exposed to flowing water that contains an acid solution such as sewage. In other words, concrete is subjected to the shearing force of fluid that erodes the surface of areas of deteriorated concrete. In these instances, it is predicted that concrete deterioration caused by sulfuric acid attack will proceed at a greater rate than that predicted from the square root relationship. Hence in this study concrete deterioration caused by sulfuric acid attack was investigated considering the effects of the flow of acid solution over the surface of concrete with the intent of proposing a prediction method for the deterioration of concrete due to sulfuric acid. Cylindrical concrete specimens and mortar prisms were immersed in various concentrations of sulfuric acid. In certain tests the sulfuric acid solution was circulated onto concrete specimens. In both instances, the depths of zones eroded and neutralized by acids were measured. As well, the zones of deteriorated concrete were analysed with an XRD and an ion chromatoanalyzer. It was found that the rate of concrete deterioration caused by sulfuric acid attack depended on the pH value of acid solutions and that the depth of erosion of concrete was nearly proportional to the exposure time of flowing acid solution to which concrete was exposed.

KEYWORDS

Concrete, Chemical Deterioration, Acid Attack, Sulfuric Acid, Flowing Water
1 INTRODUCTION

Sulfuric acid solution in sewage, wastewater treatment plants and hot spring places deteriorates concrete structures hard by reacting with cement hydrates. Concrete is not a chemically stable material under the condition of acidic environment. Although acid attack is one of the primary chemical deterioration of concrete for many years, the prediction method for this kind of deterioration has not been established yet. In Japan, the JSCE (Japan Society of Civil Engineers) Standard Specification [2001] mentions about countermeasures against chemical deterioration and maintenances, but does not describe the prediction method.

As a study of the prediction method for deterioration by sulfuric acid attack, many kinds of immersion tests using mortar specimens have been carried out. But actual structures are made from concrete and concrete deterioration due to acid attack should be predicted. Those studies are not so much so far.

It is generally said that the deterioration depth of concrete due to acid attack including sulfuric acid attack is proportional to the square root of the exposure time, according to Sakamoto [1972], Pavlik [1994], and so on, as follows:

\[ y = b \sqrt{t} \]

where, \( y \) the deterioration depth (mm)
\( t \) the exposure time in acid solution (year)
\( b \) constant (mm/√year).

In this equation, the rate of deterioration is governed by the diffusion rate of acid in deteriorated zones from concrete surfaces to non-deteriorated concrete under the assumption that corrosion products keep to remain on concrete surfaces. In actual deteriorated structures of sewage and wastewater treatment plants, however, it is found that deterioration products have been removed from concrete surfaces and coarse aggregates are exposed on surfaces. This should be because the deterioration products of mainly gypsum are subjected to the shearing force of flowing water and/or splashing water.

Usually experimental studies on concrete deterioration due to sulfuric acid attack are performed using specimens statically immersed in acid solutions. In this case, because concrete surfaces are not subjected to the shearing force, deterioration products will remain on the surfaces. It is concerned that the results obtained from these experiments could evaluate lesser deterioration than actual deterioration of sewage and wastewater treatment plants subjected to the shearing force of flowing water.

In this study, in order to clarify the effects of the shearing force of flowing water on the concrete deterioration due to sulfuric acid attack, concrete and mortar specimens are immersed in sulfuric acid solutions that are circulated by pumps. This circulation generates the flow of solutions and the shearing force of the flow is applied to the surfaces of the specimens.

2 EXPERIMENTAL PROCEDURES

2.1 Materials and specimens

Ordinary Portland cement was used as cement. Blast furnace slag and fly ash were used as mineral admixtures. Concrete cylinders of φ150×300 mm in size and mortar prisms of 40×40×160 mm in size were made with water binder ratios of 0.35, 0.50 and 0.65. The replacement ratio of cement with mineral admixtures was 0.30. The properties of materials used in this study and the mix proportions are shown in Table 1 and Table 2, respectively. Comparing the chemical resistivity at a certain age, it
is supposed that specimens containing mineral admixtures should be weaker than those containing no mineral admixtures because of slow hydration. In this study, therefore, specimens containing mineral admixtures were cured until those compressive strengths became almost equal to specimens containing no mineral admixtures with the same water cement ratio cured for 28 days. It is assumed here that the pore structures in specimens are almost same if compressive strengths are same with a certain water cement ratio whether mineral admixtures are contained or not. The test results of compressive strength of specimens are also shown in Table 2.

2.2 Experimental method

The concentrations of sulfuric acid solutions in immersion tests were 2.0 mol/L for concrete specimens and about 0.09 mol/L (adjusted to pH=1.0) and about 0.06 mol/L (adjusted to pH=2.0) for mortar specimens. The immersion tests contain two types of Method 1 and Method 2. In the Method 1, specimens were immersed statically in sulfuric acid solutions and in the Method 2 they were immersed in sulfuric acid solutions that were circulated with a pump and flowed in a tank (Table 3). To keep the concentration of sulfuric acid solution constant, sulfuric acid was added suitably to the solution. At this time, a pH meter was used to measure the value of pH and the concentration of sulfuric acid solution was adjusted to the initial value of pH.

After the immersion tests were started, the erosion depth was measured with a vernier micrometer every seven days. The erosion depth is defined as a distance between the initial surface and current

Table 1. Physical properties of materials used in this study

<table>
<thead>
<tr>
<th>Cement</th>
<th>Density (g/cm³), Blaine fineness (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary Portland cement</td>
<td>3.16, 3080</td>
</tr>
<tr>
<td>Fly ash</td>
<td>2.30, 4160</td>
</tr>
<tr>
<td>Blast furnace slag</td>
<td>2.91, 6220</td>
</tr>
<tr>
<td>Iwase crushed stone</td>
<td></td>
</tr>
<tr>
<td>Maximum Size : 20 (mm)</td>
<td></td>
</tr>
<tr>
<td>Density (SSD) : 2.65 (g/cm³)</td>
<td></td>
</tr>
<tr>
<td>F.M. : 6.52, Water absorption : 0.74%, Solid content : 61.2%</td>
<td></td>
</tr>
<tr>
<td>Ogasa crushed sand</td>
<td></td>
</tr>
<tr>
<td>Density (SSD) : 2.61 (g/cm³), F.M. : 2.82, Water absorption : 1.44%</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Mix proportions and compressive strengths of specimens used in this study

<table>
<thead>
<tr>
<th>Mark</th>
<th>Binder</th>
<th>Percentage of Replacement (%)</th>
<th>W/</th>
<th>Compressive Strength [N/mm²] (Age: days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC35</td>
<td>Ordinary Portland cement</td>
<td>—</td>
<td>0.35</td>
<td>65.5 (28)</td>
</tr>
<tr>
<td>NC50</td>
<td>Ordinary Portland cement</td>
<td>—</td>
<td>0.50</td>
<td>43.5 (28)</td>
</tr>
<tr>
<td>NC65</td>
<td>Ordinary Portland cement</td>
<td>—</td>
<td>0.65</td>
<td>32.6 (28)</td>
</tr>
<tr>
<td>BS30-65</td>
<td>Ordinary Portland cement</td>
<td>30</td>
<td>0.65</td>
<td>36.3 (42)</td>
</tr>
<tr>
<td>FA30-50</td>
<td>Ordinary Portland cement</td>
<td>30</td>
<td>0.50</td>
<td>43.1 (91)</td>
</tr>
<tr>
<td>FA30-65</td>
<td>Ordinary Portland cement</td>
<td>30</td>
<td>0.65</td>
<td>33.7 (417)</td>
</tr>
<tr>
<td>NC35</td>
<td>Ordinary Portland cement</td>
<td>—</td>
<td>0.35</td>
<td>47.2 (28)</td>
</tr>
<tr>
<td>NC50</td>
<td>Ordinary Portland cement</td>
<td>—</td>
<td>0.50</td>
<td>41.3 (28)</td>
</tr>
</tbody>
</table>
surface. Before every measurement, intentional removal of deteriorated zones on the surfaces was not carried out.

After specimens were immersed for certain periods, mineralogical changes in the specimens were analyzed with an XRD and the distribution of sulfate ions in the specimens was measured with an ion chromatoanalyzer.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Effects of the flow of fluid on erosion

The erosion depth of concrete specimens immersed in 2.0 mol/L of sulfuric acid solution with the Method 1 and Method 2 is shown in Fig. 1. For specimens with every water cement ratio, the erosion depth with the Method 2 was larger than with the Method 1. Especially it is remarkable for specimens of NC50 and NC65 after 60 day immersion. As shown in Fig. 2, reaction products of gypsum remained on the surfaces of concrete specimens immersed with the Method 1, while any products could not be seen on the surfaces of concrete specimens immersed with the Method 2. The reaction products of concrete specimens are shown in Fig. 3.
products on the surfaces of concrete specimens immersed with the Method 2 should be driven out by the flow of fluid without being precipitated on the surfaces. As a result, sulfuric acid always attacks concrete surfaces without the necessity of diffusing into deteriorated zones. Reaction products could not be seen on the surfaces of concrete specimens NC35 immersed with the Method 1. Because of dense microstructures, it is thought that reaction products of gypsum could not be precipitated in microstructures and was driven out by the flow of fluid.

The erosion depth of mortar specimens immersed in ca. 0.09 mol/L (pH=1.0) of sulfuric acid solution with the Method 1 and Method 2 is shown in Fig. 3. For NC35, erosion of specimens can be seen after 49 day immersion with the Method 1 and after 28 day immersion with the Method 2. For NC50, erosion of specimens immersed with the Method 2 can be seen after 63 day immersion. The XRD patterns of surface areas for mortar specimens of NC50 immersed for 63 days are shown in Fig. 4. Gypsum was clearly identified for specimens immersed with both the Method 1 and Method 2. These results show that reaction products of sulfuric acid attack are mainly gypsum. On the other hand, as shown in Fig. 5, for mortar specimens of NC35 immersed in ca. 0.09 mol/L (pH=1.0) of sulfuric acid solution for 63 days no reaction products can be seen on the surface of the mortar specimen immersed with Method 2, while a layer of reaction products can be seen on the surface of the mortar specimen immersed with the Method 1. Since reaction products were precipitated on the surface when the specimen was immersed statically, reaction products would have been seen on the surface also in the case of Method 2. But the flow of the solution swept reaction products on the surface.

The erosion depth of mortar specimens immersed in ca. 0.06 mol/L (pH=2.0) of sulfuric acid solution with the Method 1 and Method 2 is shown in Fig. 6. Every specimen immersed in sulfuric acid solution of pH=2.0 was hardly eroded but swelled a little. Reaction products were found on
every surface of the specimens as shown in Fig. 7. But compared with specimens immersed in ca. 0.09 mol/L (pH=1.0) of sulfuric acid solution shown in Fig. 5, reaction products were not remarkable. The specimens immersed in ca. 0.06 mol/L (pH=2.0) of sulfuric acid solution were not reacted heavier than those immersed in ca. 0.09 mol/L (pH=1.0) of sulfuric acid solution.

Regarding the mechanism of concrete deterioration caused by sulfuric acid, Kurashige [2002] described that sulfuric acid penetrating into mortar or concrete reacts with calcium hydroxide of cement hydrates to produce gypsum and at this time the volume of solid substances increases largely, which causes expansion of reaction products resulting in erosion. This phenomenon is schematically illustrated in Fig. 8. Concrete with a high water cement ratio has larger and more pores than that with a low water cement ratio. These pores play the role of a capacity to absorb expansion caused by the production of gypsum. Therefore concrete with a high water cement ratio has a higher capacity to absorb the expansion of production reaction of gypsum than that with a low water cement ratio, that is to say, concrete with a low water cement ratio erodes earlier than that with a high water cement ratio and its erosion depth is nearly proportional to the exposure time instead of the square root of the exposure time. The results of this study also agreed with this mechanism. It is shown that specimens with a lower water cement ratio eroded heavier regardless of the Method 1 and Method 2 and the erosion depth was nearly proportional to the exposure time.

Ueda et al. [1996] pointed out that sulfuric acid is hard to penetrate into hardened cement. As shown in Fig. 9, sulfate ions did not penetrate very much into mortar or concrete also in this study. The reaction of cement hydrates and sulfuric acid should occur only in the surface portion of specimens. This would be because the reaction of production of gypsum in the surface portion is faster than the penetration of sulfate ions into the specimen. The surface portion, therefore, is a main field of the reaction of sulfuric acid. That is why specimens immersed with the Method 2 eroded much larger than those with the Method 1 since the flow of solution removed the reaction product of gypsum.

3.2 Effects of the addition of mineral admixtures on erosion

The erosion depth of concrete specimens with mineral admixtures immersed in 2.0 mol/L of sulfuric acid solution with the Method 1 is shown in Fig. 10. The erosion depth of specimens containing blast furnace slag and fly ash was smaller than that of specimens containing no mineral admixtures. This is because the production content of calcium hydroxide in concrete

![Figure 8. Mechanism of concrete deterioration due to sulfuric acid attack](image)

![Figure 9. Sulfate ion content in cement paste portion of concrete and mortar (NC35)](image)
containing mineral admixtures was lower than that in concrete containing no mineral admixtures since a part of cement was replaced with the mineral admixtures. As for concrete containing fly ash, since calcium hydroxide produced by cement hydration was consumed by the pozzolanic reaction, the erosion depth was smallest among concrete specimens with the same water cement ratio. Consequently the calcium hydroxide content in concrete is closely related to the volume increase due to the production of gypsum which causes the deterioration and is one of the factors governing the degree of concrete deterioration caused by sulfuric acid.

4 CONCLUSIONS

This study was performed to understand the mechanism of concrete deterioration caused by sulfuric acid. The effects of the flow of fluid, the concentration of sulfuric acid solution, the use of mineral admixtures and the difference of water cement ratio on the deterioration of concrete were investigated. As a result, the following conclusions were obtained.

1. Regarding concrete deterioration caused by sulfuric acid, the flow of fluid accelerates the deterioration and the rate of deterioration of concrete caused by sulfuric acid strongly depends upon the concentration of sulfuric acid solution. In an elevated concentration of sulfuric acid solution, the erosion depth of concrete is nearly proportional to the exposure time instead of the square root of the exposure time. Sulfate ions do not penetrate into concrete very much and the reaction of cement hydrates and sulfuric acid occurs in the surface portion of concrete.

2. When a part of cement is replaced with blast furnace slag or fly ash and the strength of concrete containing the mineral admixture is almost equal to the strength of plain concrete with the same water binder ratio, the erosion depth of concrete containing mineral admixture due to sulfuric acid attack is smaller than that of plain concrete since the content of calcium hydroxide is small.

5. REFERENCES

JSCE, 2001, JSCE Standard Specifications for Concrete Structures [Mentenance], Japan Society of Civil Engineers, Japan. (in Japanese)