Response of Concrete to Sulfuric Acid Attack

by Emmanuel K. Attiogbe and Sami H. Rizkalla

The response of four different concrete mixes to sulfuric acid attack was evaluated in an accelerated laboratory test program. Small test specimens cut from standard concrete cylinders and a 1 percent sulfuric acid solution with a pH of 1 were used in the test program. Changes in weight and thickness of the test specimens were used as physical indicators of the degree of deterioration, while increase in sulfur content of the test specimens was used as a chemical indicator of the degree of deterioration.

The study shows that all three indicators of deterioration are effective measures of concrete response to the acid attack. However, the study suggests that the increase in thickness (expansion) of small specimens (with large surface area-to-volume ratios) may be a more consistent measure than the weight loss of larger specimens when comparing the effects of different sulfuric acid concentrations on concrete. Photomicrographs of the concrete microstructure show that the concrete deterioration starts from the acid-exposed surface and progresses inward. The degree of concrete deterioration is increased by alternate wet-dry cycles of exposure to sulfuric acid. The rate of concrete deterioration along the penetration depth of sulfuric acid could be described by a variation in sulfur concentration with the depth of acid penetration.

Keywords: acids; chemical attack; concrete; deterioration; electron microscopes; expansion; measurement; microstructure; pH; sulfur; sulfuric acid; thickness; weight (mass).

Concrete is susceptible to attack by sulfuric acid produced from either sewage or sulfur dioxide present in the atmosphere of industrial cities. This attack is due to the high alkalinity of portland cement concrete, which can be attacked by other acids as well. Sulfuric acid is particularly corrosive due to the sulfate ion participating in sulfate attack, in addition to the dissolution caused by the hydrogen ion. Since sulfur compounds are formed as a result of the sulfuric acid-cement paste reaction, the increase in sulfur content of concrete specimens could be used as a measure of the chemical manifestation of deterioration.

In previous studies, weight loss, reduction in compressive strength, and change in dynamic modulus of elasticity were used to evaluate the extent of concrete deterioration due to sulfuric acid attack. These studies indicate that damage starts at the surface of the concrete and progresses inward. However, the extent of damage along the depth of penetration of acid is not clearly defined. This information is necessary to accurately estimate the minimum thickness of the concrete cover in reinforced concrete structures or to adequately design for sacrificial layers in concrete structures exposed to sulfuric acid solutions.

As expected, the previous studies have generally shown that weight loss of the test specimens increases with a decreasing pH level of the acid solutions. However, in a recent study, a solution with a pH of 3 produced a greater weight loss than one with a pH of 2. This apparent anomaly needs to be resolved for an adequate comparison of the resistance of different concrete mixes to acid attack.

The present study is aimed at evaluating the response of different concrete mixes to sulfuric acid attack, using both physical and chemical indicators of the degree of deterioration. An accelerated laboratory test program was conducted. The program involved alternate acid immersion and drying of test specimens, as well as continuous acid immersion of other test specimens. Changes in weight and thickness of the test specimens were used to evaluate the physical degree of deterioration of the concrete, while the increase in sulfur content of the test specimens, as measured with a scanning electron microscope (SEM) equipped with an energy-dispersive x-ray analyzer, was used to evaluate the chemical change in the concrete. Photomicrographs of the test specimens were used to study the extent of the acid attack.

RESEARCH SIGNIFICANCE

This research sheds new light on the mechanism of sulfuric acid attack on concrete. The experimental techniques used in the study provide information on the extent of damage that occurs in concrete as a result of acid attack. Photomicrographs show the nature of the
pressive strength of each concrete mix. To induce
period, two cylinders were used to determine the
derers were made from each concrete mix. The cylinders
were moist-cured for 28 days. At the end of the curing
the characteristics and composition of the different
mix. A superplasticizer was used in all mixes to
increase slump. Siliceous fine aggregate and a blend of
CSA concrete mixes. Three of the mixes were made with
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The study shows that the increase in thickness
ration. The effect of wet-dry cycles of concrete
specimens are good indicators of the degree of
deterioration. The test specimens completely disintegrated in the acid. The test specimens for weight and
evaluation from the University of Kansas. His research interests include durability and micromechanics of concrete.

Table 1 — Characteristics and composition of the concrete mixes

<table>
<thead>
<tr>
<th>Concrete components</th>
<th>Mix number</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse aggregate, lb/yd³</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
</tr>
<tr>
<td>Fine aggregate, lb/yd³</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
</tr>
<tr>
<td>Water, lb/yd³</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>310</td>
</tr>
<tr>
<td>Type 10 cement, lb/yd³ (ASTM Type I)</td>
<td>540</td>
<td>540</td>
<td>540</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Type 50 cement, lb/yd³ (ASTM Type V)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>Water-reducing agent, oz</td>
<td>-</td>
<td>22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Superplasticizer, oz</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Air-entraining agent, oz</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Slump, in.</td>
<td>7.0</td>
<td>8.0</td>
<td>7.0</td>
<td>6.5</td>
<td>-</td>
</tr>
<tr>
<td>Air content, percent</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>Average 28 day compressive strength, psi</td>
<td>5640</td>
<td>4670</td>
<td>5220</td>
<td>6230</td>
<td></td>
</tr>
</tbody>
</table>

Note: 1 lb/yd³ = 0.593 kg/m³; 1 oz = 29.6 ml; 1 psi = 6.895 kPa; 1 in. = 25.4 mm.

acid damage to the cement paste matrix of concrete. The study shows that the increase in thickness (expansion) and the increase in sulfur content of concrete specimens are good indicators of the degree of deterioration. The effect of wet-dry cycles of concrete exposure to sulfuric acid was investigated.

**EXPERIMENTAL PROGRAM**

**Materials and test procedures**

The experimental program utilized four different concrete mixes. Three of the mixes were made with CSA Type 10 (ASTM Type I) portland cement, while one mix was made with CSA Type 50 (ASTM Type V) portland cement. A water-reducing agent was used in one mix and an air-entraining agent was used in another mix. A superplasticizer was used in all mixes to increase slump. Siliceous fine aggregate and a blend of calcareous and siliceous coarse aggregate were used. The characteristics and composition of the different concrete mixes are shown in Table 1.

Standard 152 x 305 mm (6 x 12 in.) concrete cylinders were made from each concrete mix. The cylinders were moist-cured for 28 days. At the end of the curing period, two cylinders were used to determine the compressive strength of each concrete mix. To induce stresses similar to those that exist in concrete under service load conditions, a third concrete cylinder for each mix was loaded to 40 percent of the compressive strength. From this cylinder, small test specimens were cut and used in the acid attack test program.

**Test specimens**—The test specimens for each concrete mix were obtained as follows. A disk approximately 6 mm (¼ in.) thick was cut near the midheight of each cylinder. Each disk was then cut into small 12 mm (½ in.) wide specimens. The final prismatic test specimens, approximately 100 mm (4 in.) long x 12 mm (¼ in.) wide and 6 mm (¼ in.) thick, were used to evaluate the sulfuric acid resistance of the concrete mixes. A total of six test specimens were used for each concrete mix: two for periodic physical measurements, two for continuous immersion in the acid solution, and the remaining two for microscopic examination. The test specimens were oven-dried to a constant weight for 24 hr at about 100 C, and their weights and thicknesses were measured prior to the start of the acid attack test program. The weight was measured using a balance with a 0.01 g sensitivity; the thickness was measured with a pair of calipers. The average thickness for three locations along the length was recorded for each specimen. These locations were marked with waterproof ink for subsequent thickness measurements following periodic immersion of the specimens in the acid solutions. The marks were retouched after taking measurements.

Additional test specimens for Mix M1 were covered with two coatings and used in the acid attack test program. These coatings were applied to the test specimens with a brush and allowed to air dry for 2 days before being immersed in the acid. The first coating, a methyl methacrylate sealant, provided a visible layer about 1 mm (0.04 in.) thick on the surface of the test specimens, while the second coating, an acrylic sealer, penetrated without any visible layer on the surface of the test specimens.

**Sulfuric acid solutions**—The test specimens were immersed in jars filled with equal quantities of 1 percent sulfuric acid solutions (pH = 1). This concentration of sulfuric acid is representative of that found in sewers that are in the process of deterioration.25 The pH levels of the acid solutions were monitored at an average interval of 2 days with a portable pH meter. All solutions were replaced with fresh 1 percent solutions if the pH of any solution exceeded a value of 1.1. All solutions were also replaced prior to reimmersion of the test specimens after taking measurements. The periodic use of fresh acid solutions along with the use of small test specimens provided an accelerated evaluation of the acid resistance of the concrete mixes. The test program was concluded after about 10 weeks when some of the test specimens completely disintegrated in the acid solutions.

**Test measurements**—Measurements of the test specimens were performed after selected periods of immersion in the acid. The test specimens for weight and thickness measurements, as well as those for SEM examination, were removed from the acid, immersed in fresh water several times, and oven-dried to a constant weight for 24 hr. Upon removal from the oven, the two test specimens of each mix that had been marked for
measurements were lightly brushed, weighed, and their thicknesses measured.

**Scanning electron microscope (SEM) examination**—For the SEM examination of each concrete mix, small fractured specimens, approximately 6 mm (¼ in.) thick x 12 mm (½ in.) long x 6 mm (¼ in.) high, were prepared from one of the test specimens that had been marked for microscopic examination. A typical specimen, as mounted on a stud, is shown in Fig. 1. To obtain clear photomicrographs, the top surface of the fractured specimens was rendered conductive with a layer of aluminum about 0.02 μm thick. No conductive coating was used on specimens for the energy-dispersive x-ray analysis.

Photomicrographs were taken of both unattacked and acid-attacked specimens. Quantitative elemental analysis of the specimens was performed at a magnification of 500X, using computer software available on the energy-dispersive system. Changes in sulfur content were of primary interest in this analysis. The elemental analysis was performed at three locations along the length of each specimen. At each location, the analysis was performed on the cement paste matrix within an area approximately 0.25 mm² (0.01 in.²), and three adjacent areas along the thickness of the specimen were analyzed.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Expansion of test specimens**

Percentage change in thickness of the test specimens versus immersion time in the acid solutions are shown in Fig. 2 through 5. Immersion time as defined in these figures does not include the time used in drying the specimens. Each data point is an average of two specimens of the same mix. The data for the individual specimens varied less than 5 percent from the average values. The increases in thickness indicate that the specimens undergo volume expansion or swelling as a consequence of the sulfuric acid attack.

Fig. 2 shows percentage change in thickness versus immersion time for the concrete mixes without and with a water-reducing admixture, Mixes M1 and M2, respectively. The test specimens for Mix M2 expand more...
than the specimens for Mix M1. This larger expansion of Mix M2 is probably due to its lower compressive strength compared to Mix M1 (Table 1). The lower compressive strength is thought to be due to an excessive amount of air entrainment caused by the addition of the water-reducing admixture.

In Fig. 3, concrete mixes with and without air entrainment are compared. The air-entrained concrete has a slightly smaller expansion. Air entrainment improves the chemical resistance of concrete insofar as it helps to produce a more uniform, well-compacted, and, hence, denser concrete.\(^6\)

Fig. 4 shows that beyond about 20 days' immersion in the sulfuric acid solution, the test specimens for the concrete made with sulfate-resistant Type 50 (ASTM Type V) cement expand more than those for the concrete made with Type 10 (ASTM Type I) cement. Thus, in the long run, sulfate-resistant cement does not appear to provide concrete a better resistance to sulfuric acid attack than that provided by normal Portland cement. This observation is consistent with the findings of previous studies\(^2^9\) and is explained by the fact that sulfate attack is only one aspect of sulfuric acid attack on concrete.\(^1\)

As shown in Fig. 5 for test specimens of Mix M1, coated specimens expand less than uncoated specimens. Also, the coated specimens with a protective surface layer expand less than those without a visible protective surface layer. These results support the well-known fact that measures aimed at making concrete more impermeable to ingestion of chemical solutions are the most efficient in providing resistance to chemical attack.

The preceding discussions show that expansion of the small test specimens used in this study provides a consistent measure of the deterioration of concrete due to sulfuric acid exposure.

**Wet-dry cycles versus continuous immersion**—Fig. 6 compares the expansion of test specimens that were alternately immersed in the acid solutions and dried to that of specimens that were continuously immersed until the end of the test program. Specimens that underwent alternate immersion and drying showed a greater expansion than those that were continuously immersed. This suggests that wet-dry cycles of exposure to sulfuric acid solutions increase the degree of concrete deterioration. The increased permeability of concrete due to drying cracks would lead to a greater volume of material being attacked by the sulfuric acid.

**Weight loss of test specimens**

Percentage changes in weight of the test specimens are shown in Fig. 7 through 10. Fig. 7 shows that weight loss is greater for the test specimens of Mix M2, which contained a water-reducing admixture, than for the specimens of Mix M1. Weight loss of the test specimens for the air-entrained concrete, Mix M3, is smaller than that of the specimens for the non-air-entrained concrete, Mix M2 (Fig. 8). As shown in Fig. 9, the weight loss is slightly greater for the test specimens of Mix M4 with Type 0 (ASTM Type V) cement than for the specimens of Mix M1 with Type 0 (ASTM Type I) cement. The effect of using surface coats is shown in Fig. 10 by the smaller weight loss of the coated specimens in comparison to the uncoated specimens. The weight loss is smaller for coated specimens with a protective surface layer than for those without a visible protective surface layer. These results (Fig. 7 through 10) are consistent with those discussed in the previous section based on the expansion of the test specimens.

It should be noted that the test specimens initially gain weight followed by weight loss. The weight gain cannot be attributed to saturation of the specimens since the specimens were oven-dried prior to weighing. The reaction between sulfuric acid and the cement constituent of concrete results in the conversion of calcium hydroxide to calcium sulfate (gypsum) which, in turn, may be converted to calcium sulfoaluminate (ettringite). Each of these reactions involves an increase in volume of the reacting solids by a factor of about two.\(^1^0\) The formation of calcium sulfate leads to softening (decrease in density) of the concrete. Since weight depends on both volume and density, the initial weight gain of the test specimens is probably due to the increase in volume of the reacting solids. The weight loss is then due to the conversion of calcium sulfoaluminate to calcium sulfate (gypsum) which, in turn, may be converted to calcium sulfate (gypsum) which, in turn, may be converted to calcium sulfate (gypsum) which, in turn, may be converted to calcium sulfate (gypsum).
gain of the test specimens is probably due to the relative increase in volume being greater than the relative decrease in density.

Both the increase in volume and the decrease in density of the concrete due to the sulfuric acid-cement-paste reaction would be larger the higher the acidity (the lower the pH) of the acid solution. This implies that a stronger acid solution could produce a smaller weight loss in a concrete specimen than that produced by a weaker solution due to a significant increase in the volume of the concrete in comparison to the reduction in the density. This phenomenon explains the results of the study reported in Reference 6, in which the weight loss of concrete cylinders exposed to sulfuric/nitric acid solutions with pH of 2 was smaller than the weight loss of identical specimens exposed to the acid solutions with pH of 3. In the same study, the weight loss of the concrete cylinders produced by other acid concentrations increased with growing acidity, as expected.

It seems, therefore, that weight loss may not be a consistent measure when comparing the effects of different sulfuric acid concentrations on concrete. The expansion of concrete specimens may be a more consistent measure than the weight loss of the specimens since the sulfuric acid-cement-paste reaction entails a volume increase. In this regard, the use of test specimens with large surface area-to-volume ratios (such as those used in this study) may be preferred since the acid attack is a surface phenomenon, as indicated by previous studies and supported by results discussed in a subsequent section of this paper. Further investigation is needed to evaluate specimen expansion and weight loss as measures of concrete deterioration due to acids with different strengths and for specimens with different surface area-to-volume ratios. In such an investigation, more than two test specimens would need to be used for the expansion and weight loss measurements to clearly establish the statistical reliability of the tests.

**Scanning electron microscope (SEM) analyses**

*Micrographs* — Photomicrographs of unattacked and acid-attacked specimens are presented in Fig. 11 and Fig. 12 through 15, respectively. Fig. 12 through 14 are micrographs of specimens that were not coated prior to immersion in the acid solutions, while Fig. 15 is a micrograph of a coated specimen. The changes in microstructure, as discussed later, are typical for all the concrete mixes studied. However, as discussed in earlier sections, the extent of deterioration as a function of acid immersion time varies among the concrete mixes due to differences in mix composition, such as the type of cement and the admixtures used.
Figs. 11, 12, 13, 14, and 15 show the microstructure of specimens under different conditions. Fig. 11 is a micrograph of an unattacked specimen, showing a typical microstructure of the cement paste matrix on a fractured surface of matured concrete. The predominant structure appears to be a modified Type III calcium silicate hydrate (CSH), one of the prime hydration products of Portland cement. A calcium hydroxide crystal is visible in the lower right corner of the micrograph.

Fig. 12 is a micrograph of an acid-attacked specimen immersed for 32 days, showing the region near the acid-exposed surface of the specimen. Fig. 13 shows a region farther from the acid-exposed surface of the same specimen. These micrographs indicate that the deterioration is smaller in the region farther from the acid-exposed surface than in the region near the acid-exposed surface. This result supports previous studies and clearly indicates that the acid attack is a surface phenomenon: the deterioration starts at the surface of the concrete and progresses inward.

Fig. 14 is a micrograph of a specimen that had been immersed in the acid for 71 days, showing the total surface of the specimen at this stage of the acid attack. The spherical fibrous structures visible in several locations on this micrograph are Type I CSH. These structures are usually not visible on the fractured surfaces of matured cement paste and concrete. The fracture path usually passes through Type III CSH (see Fig. 11 and References 13 through 15). Comparing Fig. 14 to Figs. 11 and 12, it appears that after 71 days immersion, the acid has dissolved the Type III CSH to a large extent exposing the Type I structures.

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Fig. 16 — Elemental energy-dispersive spectrum for an unattacked specimen

A micrograph of a specimen that was coated before being immersed in the acid for 49 days is presented in Fig. 15. The protective surface layer of the coating is shown as a dark vertical band on the left side of the micrograph. A comparison of this micrograph to Fig. 12 shows that the extent of deterioration is less in the coated specimen, even though it was immersed in the acid for a longer duration.

Elemental analysis — Typical energy-dispersive spectra obtained from the quantitative elemental analysis are shown in Fig. 16 and 17 for unattacked and acid-attacked specimens, respectively. These spectra were obtained within three adjacent regions, each approximately 0.25 mm (0.01 in.) wide, along the thickness of the specimens. Since sulfur compounds are formed as a result of the reaction between sulfuric acid and cement paste, sulfur components of the spectra are of primary interest in these figures and are highlighted by the dark shadings. The figures show that the sulfur content of the acid-attacked specimen is higher than that of the unattacked specimen.

Sulfur concentrations obtained from the elemental spectra, such as those in Fig. 16 and 17, are shown in Fig. 18 versus specimen immersion time in the acid solution for the three adjacent regions analyzed along the depth of acid penetration. Each data point is an average of the sulfur concentrations for three locations along the length of the SEM specimen. For both the uncoated and coated specimens, the sulfur concentration is higher in the region near the acid-exposed surface than in the regions farther from the acid-exposed surface. The coated specimen has a smaller sulfur concentration within each region than the uncoated specimen. The smaller sulfur concentrations for the coated specimen correspond to smaller expansion (Fig. 5) and weight loss (Fig. 10) when compared to uncoated specimens.

To accurately estimate the minimum thickness of concrete cover in reinforced concrete members exposed...
CONCLUSIONS

The following conclusions are drawn from the test results and analysis presented in this paper.

1. The increase in sulfur content of test specimens, as measured with an SEM equipped with an energy-dispersive x-ray analyzer, is a good indicator of the extent of damage in concrete due to exposure to sulfuric acid.

2. Photomicrographs, as well as the variation in sulfur concentration with the depth of acid penetration, clearly show that deterioration of concrete due to sulfuric acid attack starts at the surface and progresses inwards.

3. The increase in thickness (expansion) of small specimens (with large surface area-to-volume ratios) may be a more consistent measure than the weight loss of larger specimens when comparing the effects of different sulfuric acid concentrations on concrete.

4. Wet-dry cycles of exposure to sulfuric acid increase the degree of concrete deterioration.

5. The relationship between degree of concrete deterioration and depth of penetration of sulfuric acid could be represented by the variation in sulfur concentration with the depth of acid penetration.

ACKNOWLEDGMENTS

This research was performed at the Structural Engineering and Materials Laboratory of the University of Manitoba. Electron microscope analysis was carried out on the JEOL JXA-840 Scanning Electron Microscope of the Department of Mechanical Engineering, University of Manitoba. The authors are grateful for the technical and financial assistance provided by Barkman Concrete Ltd., Steinbach, Manitoba.

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