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Durability of proprietary cementitious materials for use in wastewater transport systems

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Abstract

Several methods and materials, such as high performance coatings, fiber glass reinforced linings, special mortars, brick or ceramic linings, etc., are used to protect concrete from sulfuric acid attack in a sewage environment. Two proprietary high alumina cementitious lining materials, CC and SC, are recent additions to the list of protective materials used in the Arabian Gulf. This paper documents the findings of a laboratory study under accelerated conditions as well as a two-year field study of CC and SC in a wastewater lift station in Jubail, Saudi Arabia. In the laboratory investigations, 50 mm cube mortar specimens prepared using: (1) SC, (2) CC, (3) Type I + 8% silica fume cement, (4) Type I + 20% fly ash cement and (5) Type I cement were exposed to 2% sulfuric acid for 150 days. The laboratory specimens were tested for weight reduction, compressive strength, sulfate content, and alkalinity. In the field, the walls and ceiling of a wastewater manhole were coated using the proprietary lining materials, SC and CC, and were exposed to a normal sewage service environment. Performance of the liner materials was monitored for sulfate content and alkalinity after 6, 12 and 24 months of exposure. The analysis and evaluation test data generated from the accelerated laboratory study and the field study, which lasted for 24 months, showed that SC performed better than other materials tested in this investigation.

Keywords: Concrete durability; Fly ash; Silica fume; Sulfate resistance; Wastewater transport systems

1. Introduction

Sewer systems in the Arabian Gulf region undergo severe corrosion due mainly to sulfuric acid attack which causes a serious threat to the structural integrity of the system as well as a large amount of maintenance and repair cost. In the environmental conditions of the Arabian Gulf, concrete deterioration in sewer systems due to sulfuric acid formation is enhanced due to the elevated temperature conditions and scarcity of flush water [1].

Under anaerobic conditions in sewage environments, the sulfate-reducing bacteria reduce organic sulfur compounds to hydrogen sulfide (H_2S). As H_2S is a weak acid, it dissolves in the sewage under neutral or alkaline conditions. If the pH value decreases, e.g., due to acidification, it is emitted into the sewage atmosphere. Turbulence in the sewage flow is another cause for H_2S emission. Once H_2S reaches the atmosphere, it is absorbed by the moisture on metallic and concrete surfaces of the structure. H_2S then reacts with oxygen, in the presence of moisture and aerobic bacteria, thiobacilli, to form sulfuric acid, which leads to the corrosion of metallic and concrete surfaces. Several reports were published elucidating the mechanisms of concrete deterioration due to sulfuric acid formation in the sewerage environment [1–4].

Several methods and materials, such as high performance coatings, fiber glass reinforced linings, special mortars, brick or ceramic linings etc., are used to protect concrete from sulfuric acid attack in a sewage environment. Two proprietary cementitious lining materials, "C" and "SC", are recent additions to the list of protective materials in this environment. This paper documents the findings of a laboratory study under accelerated conditions as well as the results of a two-year field study on the performance of "CC" and "SC" in a wastewater lift station in Jubail, Saudi Arabia.

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2. Materials and methods

The field study was conducted in sewage environment and the laboratory study in 2% sulfuric acid. Materials tested were: (1) SC, (2) CC, (3) Type I + 8% silica fume cement, (4) Type I + 20% fly ash cement and (5) Type I cement. SC and CC are high alumina proprietary products. According to the manufacturer's catalogue, SC is a ready to use product consisting of corrosion resistant calcium aluminate cement and specially synthesized aggregates. CC is high alumina cement based on calcium aluminates and developed for resistance to acid and biogenic corrosion. The coating materials CC and SC, and special coarse sand which was mixed with the coating materials were obtained from their supplier in Saudi Arabia. The properties of these proprietary materials, SF, FA and OPC used in this study are given in Table 1 [5].

For laboratory investigation, mortar specimens measuring $50 \times 50 \times 50$ mm^3 were prepared using: (1) Type I + 8% silica fume cement, (2) Type I + 20% fly ash cement, (3) Type I cement, (4) CC and (5) SC. The specimens were cured for seven days under wet burlap followed by 21 days air curing in the laboratory. A sand-to-cementitious materials ratio (s/c) of 2.0 and an effective water-to-cementitious materials ratio (w/c) of 0.45 were used in the mortar specimens. Following curing, the cube specimens for sulfate and alkalinity profile testing were coated with wax on all surfaces except one surface to maintain a unidirectional attack of sulfate ions. The specimens were immersed in a 2% sulfuric acid solution in a Plexiglas container and were kept covered throughout the exposure period to minimize evaporation. The pH and sulfate concentrations of the acid solution were monitored on a weekly basis, and appropriate adjustment of the acid solution was made, as required, by adding acid and distilled water to the acid bath.

Table 1
Chemical analysis of concrete materials [5]

Constituent weight %	Type I	Fly ash	Silica fume	CC	SC
SiO_2	20.96	65.70	90.70	4.0–5.5	4–9
Al_2O_3	5.25	23.10	1.4	50.5–53	40–44
Fe_2O_3	3.56	3.48	2.2	1–3	6–16
CaO	63.67	1.15	0	37–39	35–39
MgO	1.35	0.66	–	<1.5	<1.5
SO_3	2.58	–	0.57	<0.1	<0.3
LOI	1.67	1.01	2.6	–	–
K_2O	–	1.56	1.06	<0.5	0.4
Na_2O	–	0.48	0.0		–
H_2O	–	–	0.4	–	–
C	–	–	1.09	–	–
TiO_2	–	0.94	–	4.0	<4.0
MnO	–	0.05	–	–	–
P_2O_5	–	0.08	–	–	–
C_3S	49.99	–	–	–	–
C_2S	22.01	–	–	–	–
C_3A	7.89	–	–	–	–
C_4AF	10.41	–	–	–	–

The specimens were first exposed to the acid solution for 73 days. They were then taken out of the solution, washed with potable water, and air-dried before testing. After photographic recording, the specimens were weighed and tested for compressive strength [6]. Diluted water extracts of the powdered mortar samples were tested for alkalinity and sulfate content [7]. The alkalinity was assessed by measuring the pH using a digital ion analyzer manufactured by Orion Research Company. The remaining specimens were kept in the acid solution for another 77 days and then tested as before.

For the field investigation, the proprietary materials were exposed to actual sewage environment in a wastewater lift station in Jubail, Saudi Arabia. Walls and ceiling of the lift station were sand blasted and coated with CC and SC at a thickness of 15 mm. After the application, the coated surfaces of the lift station were exposed to domestic wastewater as usual. The lift station was inspected after 0, 6, 12 and 24 months following the application of the coatings. At each inspection, the condition of the walls and ceiling was recorded. Powder samples were taken, using an electrical drilling machine, at 5, 10, 15 mm depths from the coatings and at 10 and 20 mm depths in the concrete wall underneath. The powder samples were tested for sulfate concentration and alkalinity.

Compressive strength was determined by testing triplicate specimens for each data point. For sulfate and alkalinity, representative powder specimens were used for water extracts. The analysis was repeated at least twice for each data point.

3. Results

3.1. Laboratory test results

3.1.1. Visual inspection

During the accelerated laboratory test where the mortar specimens were exposed to a 2% sulfuric acid solution, deterioration of the mortar specimens was quite severe. The effect of sulfate on the specimens was photographically recorded during the exposure period before testing of the specimens. Fig. 1 shows the mortar specimens after 25 and 150 days of exposure to the acid solution.

3.1.2. Weight change

Fig. 2 shows weight change in mortar specimens in the 2% sulfuric acid compared to their initial weight after 28 days of curing in potable water under labora-

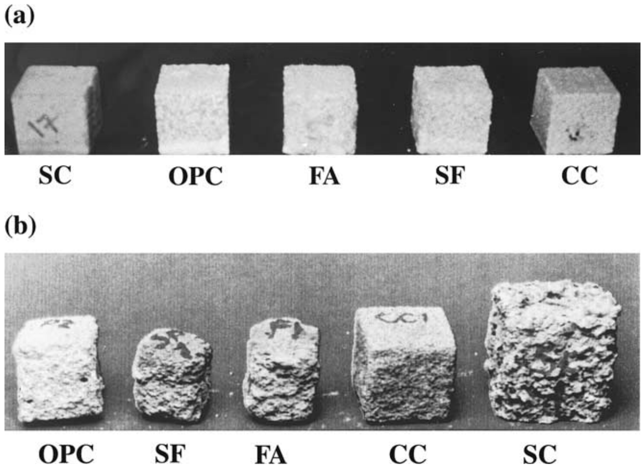

Fig. 1. Mortar specimens after exposure to a 2% sulfuric acid solution: (a) after 25 days of exposure; (b) after 150 days of exposure.

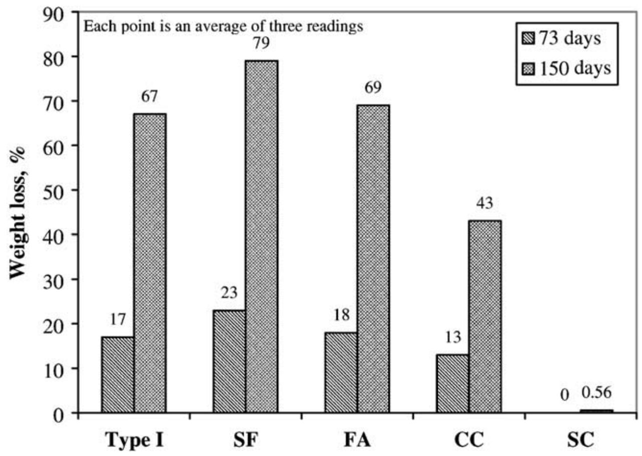

Fig. 2. Weight loss in mortar specimens with exposure period in a 2% sulfuric acid solution.

tory conditions (i.e. at a temperature of 24 °C). The SC mortar samples showed the least weight loss, which was 0% and 0.56% after 73 and 150 days of exposure to the acid, respectively.

3.1.3. Compressive strength

Fig. 3 shows the compressive strength for the specimens in a 2% sulfuric acid compared to their strength in potable water under laboratory conditions. The compressive strength reductions in SC specimens were 17% and 34% after 73 and 150 days of exposures, respectively. For the OPC mortar samples, the compressive strength reduction was 15% and 72%, after 73 and 150 days, respectively. The compressive strength reduction for the other specimens was higher than that for SC after both exposure periods.

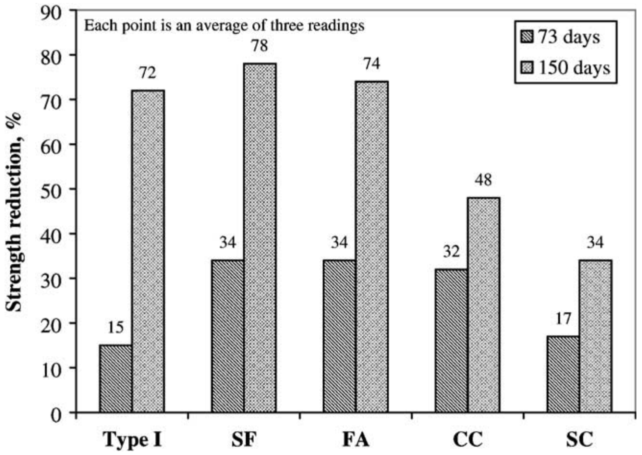

Fig. 3. Compressive strength reduction in mortar specimens with exposure period in a 2% sulfuric acid solution.

3.1.4. Sulfate content

The test results showed that the SC mortar samples exhibited the lowest sulfate penetration at both exposure periods of 73 and 150 days. The sulfate concentration in the SC mortar was 0.37% and 3.77% by weight of mortar, in 0–10 mm depth at 73 and 150 days, respectively. The sulfate concentration increased in almost all of the mortar specimens with longer period of acid exposure. Fig. 4 shows sulfate concentration profile in the mortar specimens after 150 days of exposure to 2% sulfuric acid.

3.1.5. Alkalinity

Fig. 5 shows the pH variation in the mortar specimens after exposure to a 2% sulfuric acid solution for 150 days under laboratory conditions. The SC showed the lowest decrease in pH in the 0–10 mm depth. The pH profile in the SC mortar samples decreased from 10.9 to

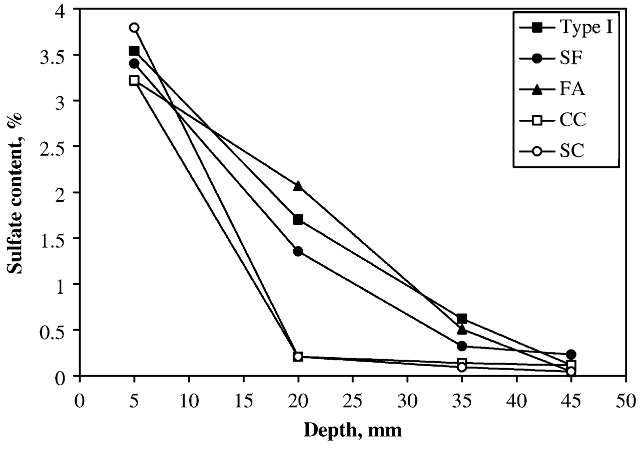

Fig. 4. Variation of sulfate content with depth in the laboratory mortar specimens after 150 days of exposure.

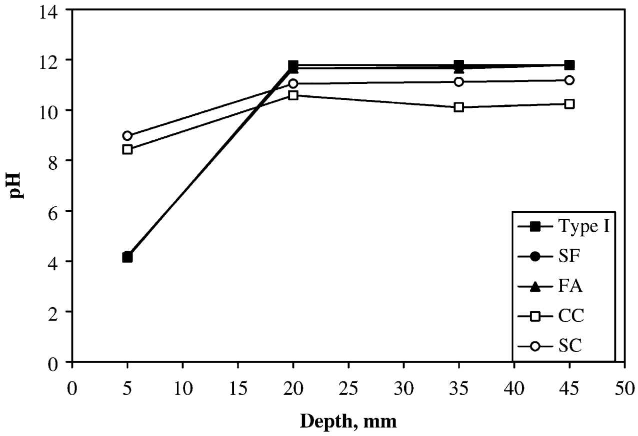

Fig. 5. pH variation with depth in the laboratory mortar specimens after 150 days of exposure.

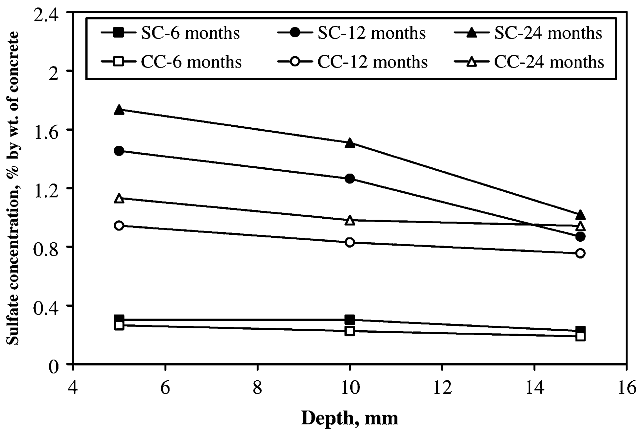

Fig. 6. Variation of sulfate with depth in liner materials on the wall of wastewater manhole during 24 months.

8.9, in 0–10 mm thickness of the mortar cubes after 150 days.

3.2. Field test results

3.2.1. Visual inspection

During the two-year exposure and monitoring period, there was no noticeable change in the appearance of the walls of the wastewater manhole. Although in severe cases the pH of condensate on sewer walls becomes as low as 1.0 [1], no measurement of pH on the walls was done in this study.

3.2.2. Sulfate content

Generally, the sulfate content in all the surfaces and in all the coatings decreased with depth and increased with duration of exposure, as expected. The results showed that CC performed better than SC on the walls at the end of the 24-month exposure period. On the ceiling of the manhole, however, the performance of CC and SC was about the same. Fig. 6 shows the sulfate analysis results of the field powder samples retrieved from the walls of the manhole. As shown on the figure, the performance of CC and SC are about the same after six months, however, CC shows better performance than SC with increasing exposure period.

3.2.3. Alkalinity

Generally, the pH of the coatings decreased with exposure period. The pH results showed that the SC performed better than the CC on the walls at the end of the 24-month exposure period. The performance of SC and CC on the ceiling of the manhole was similar. Fig. 7 shows the pH of the field powder samples retrieved from the walls of the manhole.

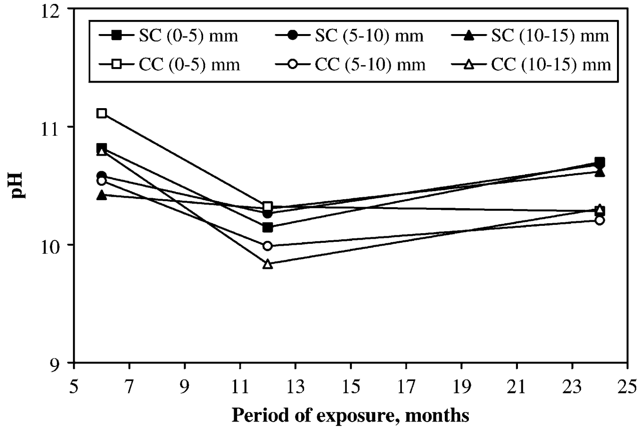

Fig. 7. Variation of alkalinity with period of exposure in liner materials on the wall of wastewater manhole.

4. Discussion of results

Overall evaluation of the laboratory and field results showed that SC performs better than CC in a sulfate environment. In the laboratory, after 150 days of exposure to a 2% sulfuric acid, the materials tested ranked in the following order:

$$\mathrm{SC} > \mathrm{CC} > \text{Type I} + 20\%\ \mathrm{FA} > \text{Type I} > \text{Type I} + 10\%\ \mathrm{SF}$$

In the field, after 24 months of exposure in a wastewater manhole, performance of the proprietary lining materials was in the following order:

CC > SC (from sulfate content point of view), and

SC > CC (from alkalinity point of view).

Portland cement is mainly composed of four main minerals: tricalcium silicate, $3CaO \cdot SiO_2$, dicalcium silicate, $2CaO \cdot SiO_2$, tricalcium aluminate, $3CaO \cdot Al_2O_3$, and tetracalcium ferro aluminate, $4CaO \cdot Fe_2O_3 \cdot Al_2O_3$. These mineral products react with water to form a number of hydrated products, including high amounts of calcium hydroxide, $Ca(OH)_2$. Sulfate ions react with the hydration products of cement or cementitious material in two main forms [8].

One common form of sulfate attack on concrete is the reaction of sulfate ions with calcium hydroxide, $Ca(OH)_2$ which results in the formation of calcium sulfate ($CaSO_4 \cdot 2H_2O$), gypsum. Gypsum formation decreases the pH in concrete, and causes softening of the concrete and loss of strength and mass [8].

The other common form of sulfate attack occurs by reaction of sulfate ions with alumina-bearing compounds of cement. In the presence of calcium hydroxide, sulfate ions react with tricalcium aluminate, $3CaO \cdot Al_2O_3$ (C_3A), and convert them into ettringite, $6CaO \cdot Al_2O_3 \cdot 3SO_4 \cdot 32H_2O$ and monosulfoaluminate. Ettringite formation also causes expansion and loss of strength of concrete [9,10].

Further, gypsum can react with calcium carbonate, a carbonation product of cement, and with calcium silica hydrate (CSH) to form thaumasite, $CaSO_4 \cdot CaCO_3 \cdot CaSiO_3 \cdot 15H_2O$. Thaumasite formation transforms hardened concrete into a pulpy mass and results in very severe damage [9].

Therefore, realizing the role of C_3A on the promotion of sulfate attack, cements of low C_3A content or sulfate resistant cements (SRCs) are recommended in environments where concrete structures are exposed to sulfate ions. However, cements with low C_3A have a higher ratio of tricalcium silicate to dicalcium silicate. An increase in the tricalcium silicate content of cement causes the formation of significantly higher amounts of calcium hydroxide during hydration of cement. This increases the risk of gypsum formation, as explained above.

It was, however pointed out that performance of concrete in alkaline and acidic sulfate environments can be different. Investigations carried out in a sodium sulfate (Na_2SO_4) environment showed that concrete specimens made with cement of a higher C_3A content exhibited a higher deterioration than those prepared with cement of a lower C_3A content [10]. The addition of pozzolanic materials, such as silica fume or fly ash by 15% and 20% as replacement of cement, respectively, improved the sulfate resistance of concrete in a sodium sulfate solution [10,11]. Magnesium sulfate solution was, however, more aggressive in attacking blended cement mortars containing silica fume or blast furnace slag than it was against unblended mortars. This was due most probably to the low amount of $Ca(OH)_2$ in blended cement mortars and the direct reaction of magnesium ions with cementitious C–S–H to form gypsum and non-cementitious magnesium silicate hydrate [12].

The sulfate resistance of concrete in sulfuric acid is, however, different than that reported above. Fattuhi and Hughes [13] reported that at the end of 81 days of exposure of mortar and concrete cubes to a 3% solution of flowing sulfuric acid showed the following order of performance: Densit (a proprietary material based on OPC + silica fume) > OPC + fly-ash > OPC = SRC. The SRC did not show any superiority over ordinary Portland cement under the test conditions. Another study by Attiogbe and Rizkalla [8] exposed ASTM Type I and Type V cement concrete mixes to a 1% sulfuric acid solution at a pH of 1 for 71 days. The results showed that, in the long run, Type V cement concrete was less resistant to sulfate attack under acidic conditions than Type I cement concrete. Similar results were also reported by others [14]. This is explained by the fact that sulfate attack is only one aspect of sulfuric acid attack on concrete [8].

Sand et al. [15] argued that, in sewage systems, the microbiological aspect of sulfuric acid attack should also be taken into consideration, and experiments should be conducted in a test chamber where actual sewage conditions were simulated and concrete materials were exposed to biogenic sulfuric acid. Their results, consistent with earlier reports by Wiering [16] and by an ASCE report [17], showed that calcium aluminate based cementitious materials have a high resistance against biogenic sulfuric acid attack.

The sulfuric acid environment used in the laboratory tests does not exactly represent the acidic conditions that are created on the aerobic surfaces of sewer systems. The 2% sulfuric acid used in the laboratory tests is far more corrosive than the conditions in the sewer systems. In sewer systems, the environment is exposed to biogenic sulfuric acid, which forms when hydrogen sulfide is converted into sulfuric acid, in the presence of moisture and oxygen, as a result of a biological process that is the metabolism of the bacteria thiobacilli [15].

The present study showed that, the deterioration of concrete due to acidic sulfate attack progressed inwards from the exposure surface with the duration of exposure. Development of sulfate and pH profiles with depth from the surface of the mortar cube specimens also confirmed this point. Furthermore, as shown by the laboratory specimens, sulfuric acid destroyed the binding material in the specimens layer by layer such that the deteriorated mortar layer lost its strength completely and crumbled into a non-cohesive mass under its own weight at the bottom of the exposure tank. Consequently, the original 50 mm cubic mortar specimens decreased in size and weight depending on the resistance of the binding material to acidic sulfate attack. At the same time, the compressive strength of the specimens decreased with the exposure period.

In the present study, SC and CC are high calcium alumina proprietary materials. Incorporated with coarse silica sand, they showed high resistance to 2% sulfuric acid attack in the lab tests. The present results obtained with pozzolanic and OPC mortars are similar to those reported by Fattuhi and Hughes [13]. The higher sulfate resistance of OPC (Type I) mortar than that of a 10% silica fume cement mortar is attributable to reduced calcium hydroxide in the later specimens, similar to silica fume cement mortars in magnesium sulfate solution [12]. Whereas, the improvement, observed in this study, in the sulfate resistance in 20% fly ash cement mortars can be attributed to a reduction in permeability in fly ash mortar specimens, as well as to a high concentration of alumina (Al_2O_3) in the fly ash (23%) compared to Type I cement (5.25%) and silica fume (1.4%) used.

In the field test, SC and CC were exposed to an actual sewage and biogenic sulfuric acid environment for 24 months. The visual inspection of the proprietary mortars did not reveal any deterioration. They performed equally well in actual sewer conditions, in both aerobic and anaerobic surfaces of the sewer, where the conditions are relatively milder than the sulfuric acid environment used in the laboratory tests. The results showed that SC exhibited a higher alkalinity and at the same time higher sulfate ion penetration than CC. This could be due to the composition of SC which is a combination of calcium aluminate and special aggregate [18] as well as the biogenic nature of sulfate in the sewer environment.

5. Conclusions and recommendations

Conclusions of the study are summarized below:

1. The mortar specimens had very significant deterioration and disintegration during exposure to 2% sulfuric acid in the laboratory. Sulfate attack on the walls of the manhole in the field, however, showed no visible change of the coated surfaces after 24 months.
2. The SC specimens underwent the least amount of weight change and the least percentage of strength reduction after 2% sulfuric acid exposure for 150 days in the laboratory.
3. In the laboratory, SC performed better than CC in terms of both sulfate penetration and alkalinity reduction.
4. In the field, CC showed a slightly higher resistance to sulfate penetration than SC. However, in terms of reduction of alkalinity, SC was superior to CC.
5. The materials tested in this study for sulfuric acid resistance can be ranked in the following order:

$$\mathrm{SC} > \mathrm{CC} > \text{Type I} + 20\%\ \mathrm{FA} > \text{Type I(OPC)} > \text{Type I} + 10\%\ \mathrm{SF}.$$

Overall, SC performed better than CC. It is, however, recommended that the field investigation should be pursued beyond the two-year period because sulfate attack in a wastewater manhole is a slow process.

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