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PERFORMANCE EVALUATION OF VARIOUS CONCRETE MIXES SUBJECTED TO SULFURIC ACID

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Concrete is an essential structural material that has long been used for the construction of buildings, bridges, tanks, pavements and variety of the other types of structures. Due to its physical properties and economical use, concrete is used extensively in the country's infrastructure. In the Oil and Gas sector, concrete infrastructures are more challenging structures, which are exposed to a highly aggressive environment. A special type of reinforced concrete structure exposed to different forms of sulfur attack is the sulfur storage structure, typically referred to as "Sulfur Pit". Sulfur Pit is an essential part of oil and gas processing facilities, where the sulfur after extraction from the hydrocarbons in Sulfur Recovery Units is stored and maintained in the liquid phase at temperatures ranging from 130 °C to 160 °C. The gas sweeting process results in the formation of acid gas consisting of H_2S, water vapor in addition to residual sulfuric acid. Reinforced concrete exposed to this environment is subject to deterioration and corrosion of the reinforcing steel. This paper presents the experimental investigation of four different concrete mixes exposed to 5% sulfuric acid at ambient temperature. These mixes include normal OPC, sulfate resistant (Type V) cement, and two mixes with supplementary cementitious materials blast furnace slag (GGBFS) and Class-F fly ash. The investigation is focused on mechanical properties and mass loss of the concrete samples.

Keywords: Sour crudes, Sulfur pit, Corrosion, Service life, GGBFS, Fly ash.

1 INTRODUCTION

Concrete is an essential structural material that has long been used for the construction of buildings, bridges, foundations, tanks, pavements, tunnels, dams and variety of the other types of structures. Concrete is subject to various forms of deterioration mechanisms, which affects its ability for the intended use, and limit its service life. In general, concrete has a low resistance to chemical attacks. The most common forms of chemical attack on concrete are the corrosion of steel reinforcement arising from chloride attack and due to carbonation, sulfate attack, alkali-aggregate reactions, and acid attacks.

Sulfate attacks on the concrete manifest in terms of extensive cracks-based deterioration mechanisms in concrete structures. Sulfates present in soils, underground water, sewage, and seawater ingress through the concrete, react with its components and form expansive compounds.

The reaction leads to an increase in the volume of the products resulting in the disintegration of the concrete matrix. In industrial applications and sewage transport and processing concrete structures, another mechanism of concrete deterioration involving sulfate ions is the sulfuric acid attack. The sulfuric acid has a two-prong attack, with the sulfate ions forming expansive products and the acid reducing the concrete alkalinity, thereby, destroying the concrete passivity which protects steel from corrosion.

A special type of reinforced concrete structure exposed to a different form of sulfate attack is the sulfur storage structure, referred to as "Sulfur Pit", which is an essential part of oil and gas processing facilities, where the sulfur extracted from the hydrocarbons in Sulfur Recovery Units is stored and maintained in the liquid phase at temperatures ranging from 130°C to 160°C.

The reinforced concrete sulfur pits are exposed to a very corrosive environment and subject to frequent deterioration in a short span of time. Corrosion of reinforcing steel and sulfate attack are prominent forms of deterioration leading to delamination spalling of concrete cover in the walls and the roof of the sulfur pit. Heavy deterioration is more prominent in the soffit of the roof slab and the upper part of the walls (vapor zone). The extracted molten sulfur contains some moisture in addition to the ingress of moisture from external sources as well as from the steam coil used to heat the sulfur to maintain the liquid phase. The sulfuric acid and fumes attack the reinforcing steel causing corrosion (Rahman *et al.* 2016).

Corrosion of concrete due to sulfuric acid can generally be characterized by the following reactions, (Salek *et al.* 2016, Vincke *et al*. 2002):

1. Gypsum Formation $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O$
2. Decalcification $C_3S_2H_3 + H_2SO_4 \rightarrow CaSO_4.2H_2O + C_2S_2H_2$
3. Ettringite Formation $3CaO.Al_2O_3.12H_2O+3(CaSO_4.2H_2O)+14H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$

For improving the chemical resistance of concrete to sulfuric acid, many researchers have studied the effect of cement type, cement content, water-to-cementitious materials ratio (w/cm) (Ehrich *et al.* 1999, Fattuhi and Hughes 1988), supplementary cementitious materials (SCMs) (Torii and Kawamura 1994, Roy *et. al* 2001), and polymeric materials (Monteny *et. al* 2003, Vincke *et. al* 2002) on improving the resistance of mortar or concrete to sulfuric acid attack.

In a series of chemical tests with different sulfuric acid concentrations of 1–3%, Fattuhi and Hughes (1988) showed that sulfate resistant portland cement (SRPC) did not offer marked improvement compared to that of ordinary portland cement (OPC) in reducing the mass loss of mortar or concrete specimens.

There is a lack of a consensus concerning the effectiveness of substituting cements with supplementary cementitious materials (SCMs) and nanoparticles in resisting attack caused by acidic media. For instance, Durning and Hicks (1991) and Mehta (1985) reported that the incorporation of silica fume increased the resistance of concrete to 1% sulfuric acid attack due to reduced calcium hydroxide content and lower permeability. Conversely, Monteny *et al.* (2003) reported a negative effect of silica fume incorporation in concrete specimens exposed to 0.5% sulfuric acid. Monteny *et al.* (2003) reported that the highest resistance to a 0.5% sulfuric acid solution was achieved by a binary binder mixture comprising more than 60% ground granulated blast furnace slag. Chang *et al.* (2005) reported that binary binder concrete mixtures prepared with 60% slag and ternary binder mixtures with 56% slag and 7% silica fume had inferior performance compared to that of a 100% OPC mixture when immersed in a 1% sulfuric acid solution with a Ph of 1.27.

Bassuoni and Nehdi (2007) in their study explained the beneficial impacts of SCMs in resisting acid attacks and attributed the better performance of SCMs to the reduction of calcium hydroxides and increase in C-S-H. They explained further that the secondary C-S-H has lower

C/S ratio, less reactive to acid attack and forms a protective layer by reducing the diffusion of acids. Girardi and Di Maggio (2011) concluded that in general, all the beneficial effects of SCMs in resisting aggressive acidic attack are supposed to be diminished with an increase in the severity of the chemical attack.

2 EXPERIMENTAL INVESTIGATION

In this experimental program, four concrete mixes were investigated subjected to sulfuric acid attack. These include concrete mixes with (1) ordinary portland cement (M1), (2) Sulfate resistant portland cement (M2), (3) Glass Granulated Blast Furnace Slag (GGBFS) (M3), and (4) Fly Ash and Silica Fume (M4). Table 1 illustrate the mix design proportions. To evaluate the performance of various concrete mixes to sulfuric acid, samples representing 4 different mixes were placed in 5% by volume sulfuric acid for 12 weeks. Samples were cast and cured for 28 days and tested for initial mechanical properties including compressive and tensile strength, mass, absorption, density, air voids. Exposed as well as cured samples retrieved at 2, 4, 8 and 12 weeks were tested for compressive and tensile strength and mass was measured.

The concentration of the sulfuric acid was monitored through pH measurements as well as through titration with a base (NaOH). The titration process is based on the chemical reaction between an acid (H2So4) and a base (NaOH) in the presence of a colour indicator (phenolphthalein). The base is added to the acid until colour change to pink indicating a neutralized solution. Acid was added regularly to keep the sulfuric acid concertation constant at 5%. The solution-to-specimen volume ratio was kept constant at 2.5.

Table 1. Mix proportions (kg/m^3).

Mix No.	Cement	GGBSF	FA	SF	W/C ratio	Sand	Aggregate	Superplasticiser (L)
M1	370				0.4	776	1121	3.7
M2	370 Type V				0.4	776	1121	3.7
M3	165	340		45	0.3	696	1006	5.5
M4	335		160	37	0.3	629	1119	6

3 RESULTS AND ANALYSIS

3.1 Density, Absorption and Voids

Density, water absorption and volume of permeable voids were measured according to ASTM C-642 (2013). Oven-dry mass was determined after drying specimens at a temperature of 100°C to 110°C for 24 hrs. Saturated mass was determined after immersing the specimen in water at approximately 21°C for 48 h. Saturated mass after boiling was then determined after placing the specimen in water and boil for 5 h. Apparent mass of concrete specimens was measured for samples immersed in water. Table 2 shows the computed values for the four mixes.

3.2 Mass Reduction

Mass was measured for samples before and after exposure to sulfuric acid. Mass loss as a percentage of original mass at different exposure time for specimens from all mixtures exposed to the 5% sulfuric acid solutions are calculated and presented in Table 3. A sample representing the different mixes after exposure for 90 days are shown in Figure 1. After 90 days of exposure, the mass loss was 21% for OPC and SRPC mixes, 22% for the GGBFS and SF mix and 28% for Fly

Ash and SF mix. During the first two weeks of exposure, a notable mass loss of about 6% was observed for all the specimens, except for the GGBFS mix, which showed an increase in mass by 3%. The rate of mass loss mass loss was slower over the period between 2-4 weeks due to neutralization of solution and the increase of the pH in the solution up to 2.0 (Acid is added after titration every 4 weeks). The rate of mass loss continued from the fourth week up to the end of the exposure.

Table 2. Calculated absorption, density, and voids.

Mix	Absorption after immersion, %	Absorption after Immersion and Boiling	Bulk Density, Dry kg/m^3	Bulk Density After Immersion kg/m^3	Bulk Density after immersion and boiling	Apparent density kg/m^3	Volume of permeable pore space (voids), %
M1	4.25%	4.50%	2.292	2.390	2.396	2.556	6.51%
M2	3.81%	4.55%	2.338	2.427	2.444	2.616	7.23%
M3	2.12%	2.37%	2.369	2.419	2.425	2.510	3.61%
M4	3.09%	3.27%	2.341	2.413	2.418	2.535	4.81%

Table 3. Mass reduction after 2, 4, 8 and 12 weeks of exposure.

Mix No.	% mass reduction 2W	% mass reduction 4W	% mass reduction 8W	% mass reduction 12W
M1	6.47%	6.17%	12%	21%
M2	5.80%	5.88%	12%	21%
M3	-3.14%	3.28%	11%	22%
M4	6.35%	6.46%	15%	28%

Figure 1. Samples after exposure to sulfuric acid (From left M1, M2, M3 and M4).

3.3 Compressive Strength

Compressive strength tests were conducted in accordance with ASTM C39 (2018). Average of 3 cylinders 3” x 6” size were considered. Samples were capped with sulfur to ensure a smooth surface of the acid deteriorated surfaces. Samples tested for 7 days, 28 days before starting the exposure to sulfuric acid. Exposed samples were retrieved and tested for periods of 2, 4, 8 and 12 weeks. Each retrieved sample includes both water cured and acid exposed in order to make a comparison. Compressive strength results of the water cured and exposed samples are shown in Figure 2.

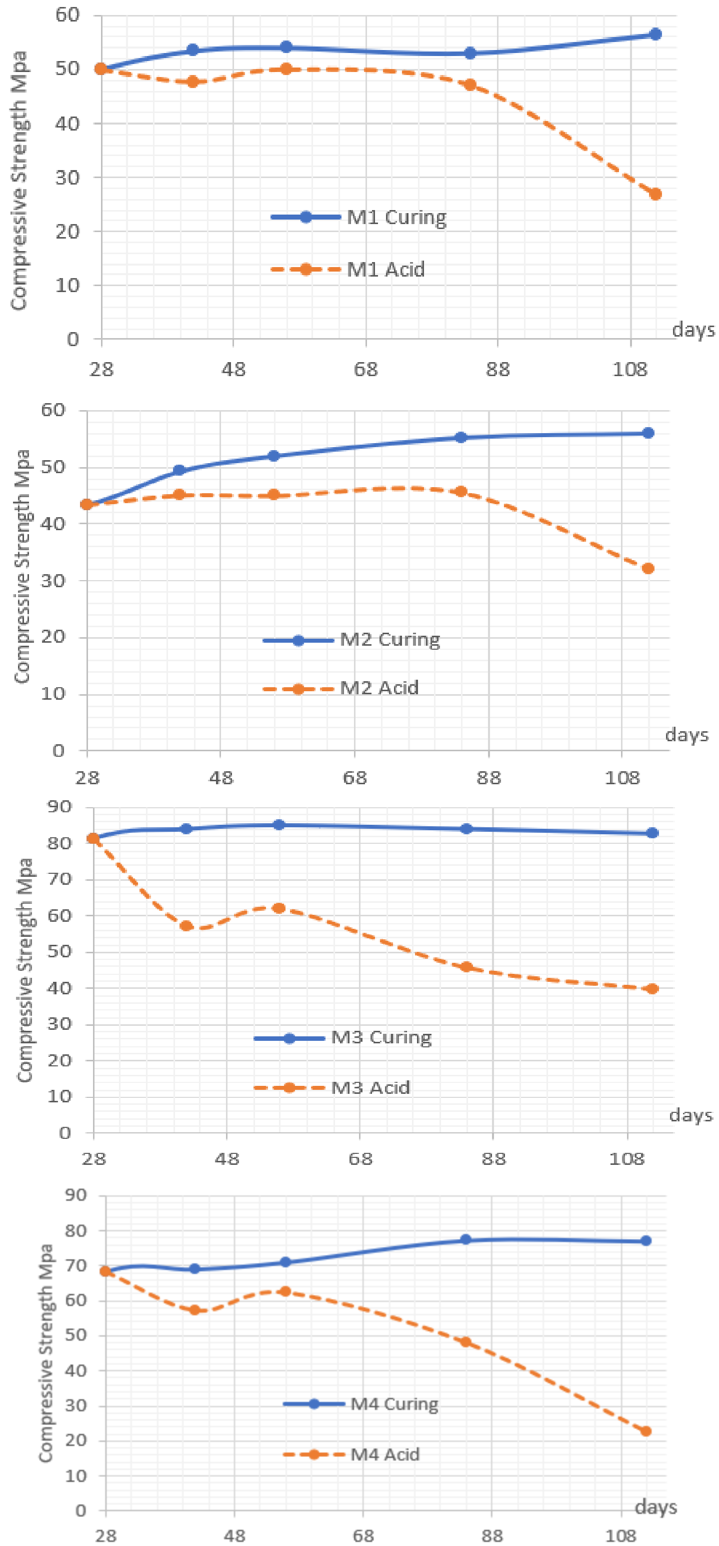

Figure 2. Compressive strength of water cured and acid exposed samples for M1, M2, M3, and M4.

4 CONCLUSION

Sulfuric acid reacts with calcium-bearing phases (portlandite and CSH in absence of portlandite) in hydrated cement paste to form expansive gypsum, resulting in gradual disintegration of paste matrix, consequential loosening of aggregate, and precipitation of outer paste.

After 90 days of exposure to sulfuric acid, the compressive strength OPC mix decreased by 51% as compared to 39% for SRPC. The SCM mixes on the other hand show similar or higher loss of strength compared to OPC. The strength of GGBFS+SF mix decreased by 52%. For FA+SF mix the reduction was 67%. Prominent reduction in compressive strength started after 8 and 12 weeks of exposure. The mass loss for OPC and SRPC mixes and the GGBFS+SF mix were both at about 21-22%, whereas, the FA+SF mix lost about 28%, reflecting in lower strength.

The mass stability and compressive strength of concrete mixes subjected to sulfuric acid attack depend on the chemical composition of the cementitious materials as well as the pH of the acid under consideration. In this research addition of SCMs didn’t help improve the performance of the concrete as has been reported by many researchers. The SRPC mix did offer marked improvement compared to that of OPC mix in reducing the mass loss of concrete specimens.

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