

Corrosion Resistance of Calcium Aluminate Cement Concrete Subjected to Sulfuric Acid

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ABSTRACT: Concrete structures in oil and gas industry are often exposed to the highly corrosive sulfuric acid environment. The natural gas production and processing facilities are prone to attack from acidic vapor at high temperature. The waste molten sulfur produced in the SRU's of the gas plants generates sulfurous and sulfuric acid vapors in a sealed reinforced concrete tank. These acids attacks concrete element triggering severe deterioration of concrete, reducing the service life of the structure and causing a steep rise in the maintenance expenses and enhancing the time for bringing the plant online. Several types of concrete mixes have been investigated extensively for enhancing the service life of concrete structures under acid attack. Calcium aluminate cement investigated under biogenic sulfuric acid attack shows higher performance as compared to ordinary Portland cement. This paper presents the results of investigation conducted on calcium aluminate (CA) concrete subjected to 5% sulfuric acid solution at ambient and high temperatures simulating the environment in molten sulfur tank. The effect of acid on physical and mechanical properties of the CA concrete and microstructural characterization of acid exposed using SEM/EDS and XRD is presented. CA concrete gave a superior performance in terms mass loss and strength degradation.

1 INTRODUCTION

A special type of reinforced concrete structure exposed to a different form of sulfate 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 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 $\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
2. Decalcification $\text{C}_3\text{S}_2\text{H}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_2\text{S}_2\text{H}_2$
3. Ettringite Formation
 $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O} + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 14\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

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.

Calcium Aluminate cement (CAC) was initially developed to resist sulfate attack. Unlike Portland cement, the hydration reaction of CAC, does not form calcium hydroxide, providing a better resistance to sulfate and acidic environments and to elevated temperature exposure (Bassouni and Nehdi 2007). The hydration reaction of CAC forms mainly Alumina gel. (Neville 1996). CAC is the product obtained by pulverizing calcium aluminate cement clinker (hydraulic calcium aluminates). It contains monocalcium aluminate (CA) as the principal cementing compound with C12A7, CA, C2AS, C2S, as minor compounds. Al₂O₃ in the range of (50-80%).

Evolution of the hydration reaction and products formed are dependent on both time and temperature, causing a phenomenon that is called “Conversion”, where the CAC hydrates and gains strength which drops again after some period and temperature rise. Initially at a temperature of 20oC it will form CAH10, which converts to C2AH8 between 21 and 30°C, and finally to C3AH6 at higher temperature. Under conditions of elevated temperature C3AH6 will form which is the most stable and least soluble.

Researchers addressing the sulfuric acid effect on concrete have employed accelerated laboratory tests subjecting concrete specimens to various concentration of sulfuric acid represented by H₂SO₄% or its pH. This paper presents the results experimental investigations conducted on CAC concrete subjected to 5% H₂SO₄ at normal and high temperature and testing for various physical and mechanical properties as well as material analysis to investigate the performance. Mass loss, visual appearance, compressive and tensile strength, corrosion depth and microstructural analysis including SEM, EDX, XRD are reported.

2 EXPERIMENTAL INVESTIGATION

In this experimental program, CAC concrete performance was investigated subjected to sulfuric acid attack. Samples were cast and cured for 28 days and tested for initial mechanical properties including compressive and tensile strength, mass loss, water absorption, density, permeable voids. Samples were then placed in 5% sulfuric acid at both normal (23oC) and elevated temperature (100oC) for 12 weeks. Exposed as well as cured samples retrieved at 2, 4, 8 and 12 weeks were tested for physical and mechanical properties as well as material characterization.

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 concentration constant at 5%. The solution-to-specimen volume ratio was kept constant at 2.5.

Experimental setup for the elevated temperature exposure was established after evaluation and testing of several combination of coated carbon steel and polymers. Most of them have failed to withstand the high temperature combined with acidity. A specially manufactured Glass Fiber Reinforced Polymer (GFRP) tank was manufactured for testing samples exposed to acid at elevated temperature (100oC). The GFRP was based on Vinyl ester resin which has the resistance to 5% sulfuric acid. GFRP gratings and support tubes were used to stack the samples. External heating jacket was used to achieve the required temperature.

3 RESULTS AND ANALYSIS

3.1 Density, Absorption and Voids

Density, water absorption and volume of permeable voids (VPV) were measured according to ASTM C-642 (2013). Oven-dry mass was determined after drying specimens at a temperature of 100 to 110 °C for 24h was followed by immersion in water at 21 °C for 48h and then boiling for 5h to find saturated mass. Table 1 shows the computed absorption, density, and VPV.

Table 1. Calculated absorption, density, and voids

Absorption after immersion %	Absorption after Immersion and Boiling	Dry bulk density (kg/m ³)	Bulk density after Immersion (kg/m ³)	Bulk Density after immersion and boiling	Apparent density (kg/m ³)	Volume of permeable voids %
3.55%	4.04%	2.630	2.724	2.737	2.943	7.47%

3.2 Visual Monitoring

Throughout the exposure period, the changes in the appearance of the specimens were monitored visually. Samples retrieved at periods of 2, 4, 8 and 12 weeks were brushed and washed and photographed. Figure 1 shows the changes on surface appearance of all concrete specimens over the 12 weeks period of exposure to sulfuric acid at 23 °C. The CAC did not show signs of color change that are typically found in Ordinary Portland Concrete where white powder material (gypsum) is deposited on the surface. Small amount of soft and easily removable corroded layer in CAC concrete expanded gradually and slowly.



Figure 1. Samples after exposure to sulfuric acid (From left 2, 4, 8 & 12 weeks).

3.3 Mass Reduction

After exposure to 5% sulfuric acid solution at normal and elevated temperatures, mass loss as a percentage of original mass at different exposure periods are shown in Table 2. Cylinder specimen retrieved after exposure for 2, 4, 8 and 12 weeks in sulfuric acid solutions are shown in Figure 1. After 120 days of exposure, the mass loss was 6.1% for CAC specimens exposed to acid at normal temperature and 13.7% for the samples exposed at 100°C temperature. During the first two weeks of exposure mass increased slightly and subsequently started losing mass after 8 weeks of exposure.

Table 2. Calculated absorption, density, and voids

Concrete Mix	2W	4W	8W	12W	4W(100 °C)	12W(100°C)
Calcium aluminate cement	-0.3%	-0.6%	0.7%	6.1%	-2.1	13.7

3.4 Compressive Strength

Compressive strength tests were conducted in accordance with ASTM C39 (2018). Average of 3 cylinders 3” x 6” size was considered. Samples were capped with sulfur to ensure a smooth surface of the acid deteriorated surfaces. Samples were tested for compressive strength at 7 days and 28 days before exposure to sulfuric acid solution. 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 samples in order to make a comparison. Compressive strength results of the water-cured and exposed samples are shown in Figure 2. After 90 days of exposure to sulfuric acid, at normal and high temperatures, the compressive strength of CAC mix decreased by 25% for samples exposed at normal temperature and 39% for the samples exposed at high temperature. This indicates that higher temperature affects the strength substantially in sulfuric acid solution. The high temperature in the sulfur pit and the acid-laden vapors results in deterioration of the soffit of the roof slab inside the pit.

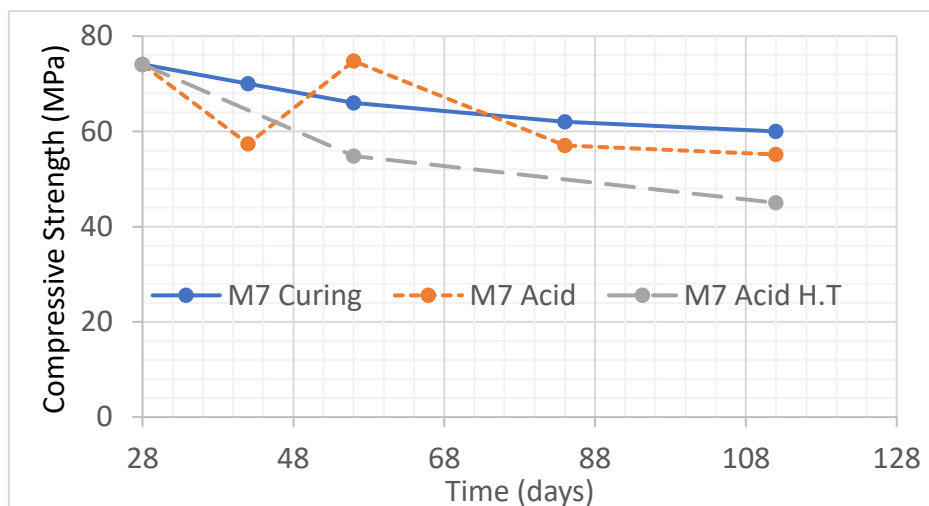


Figure 2. Compressive strength of water-cured and 5% H₂SO₄ samples at 23°C and at 100°C.

3.5 Acid Penetration (Corrosion Depth)

After each period of exposure, the acid affected layer as defined by the layer through which acid penetrated was measured by testing the pH across the depth of the concrete sample (sample from

split tensile test is utilized). Phenolphthalein color indicator was used to evaluate the pH. Phenolphthalein is colorless below 8 and pink above 10. The test confirmed that the affected layer is just the outermost surface and that acid does not penetrate deep into the CAC concrete. Figure 3 shows that only a thin outer shell is affected by the acid exposure. At an age of 12 weeks there increase in the affected area was insignificant, indicating the resistance provided by CAC concrete. The higher temperature also showed a similar trend.

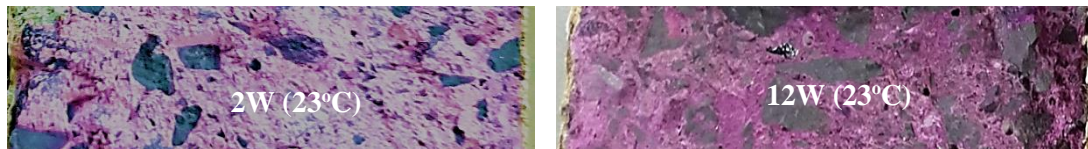
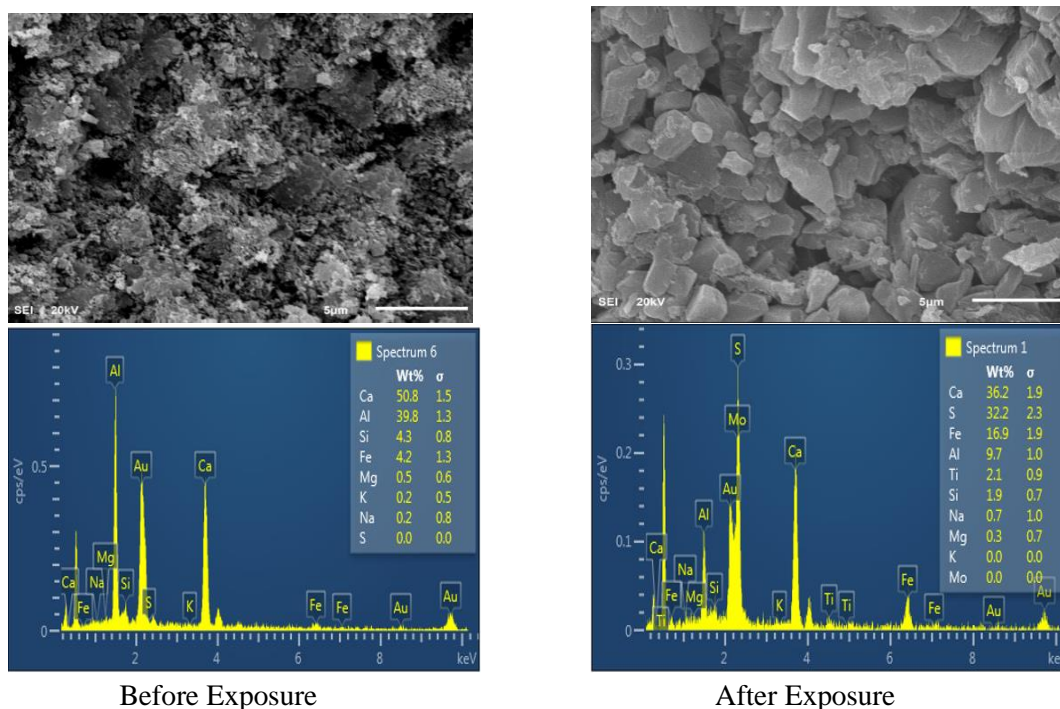


Figure 3. Depth of acid attack in the samples at an age of 8 and 12 weeks at 23°C.

3.6 Material Characterization

Characterization is an essential aspect of materials research that involves the determination of the composition and microstructure of the material. This experimental program involves extensive microstructural studies for CAC samples before and after exposure to 5% sulfuric acid solution, at normal and elevated temperature. These studies are conducted to understand the change in chemical composition of CAC concrete under such environment and consequently its relation to the degradation of the mechanical properties. The techniques used include XRF, XRD, SEM and EDX.

Examinations made by SEM and EDX were conducted on small pieces cut from the specimens before and after exposure to acid. For the exposed specimens, the pieces were taken from the corroded layer at regions very close to the acid-exposed surface. SEM and EDX of the specimens are presented in Figure 4.



Before Exposure
After Exposure
Figure 4: SEM of CAC specimens before (left) and after exposure to 5% H₂SO₄ (right) at normal temperature at an age of 12 weeks.

Similar finding was reported by (Allahverdi and Skvara, 2005) confirming that all the sulfur and calcium in the corroded layer are present in the form of gypsum. Ca^{++} reduced from 50.8 to 36.2, while sulfur increased from 0 to 32.2 confirming the ions exchange and bleaching of Ca^{++} ions to react and form gypsum. This was demonstrated by the studies conducted by (Hewayde et al 2007, Arrifin 2013, Aydin et al 2005). Salek et al. (2016) attributed this to decalcification.

The X-ray diffractogram (XRD) of the material before exposure to acid indicates peaks corresponding to CSH, portlandite (P), quartz (Q), Calcite (C) and gypsum (G) phases. Gypsum phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dominated the diffractogram of exposed specimens both at low and at high temperature as well as paste samples. These peaks are identified at 11.5, 29.2, 33.3, 37.2 2-theta. Gypsum was seen as the key reaction product between the sulfuric acid solution and hydrated cement paste (Girardi and Maggio 2011).

XRD diffractogram of the CAC on the other hand indicated presence of calcium aluminate and calcium aluminate hydrate phases. After exposure to acid the main phase identified in XRD is gypsum with small low intensity peaks of quartz.

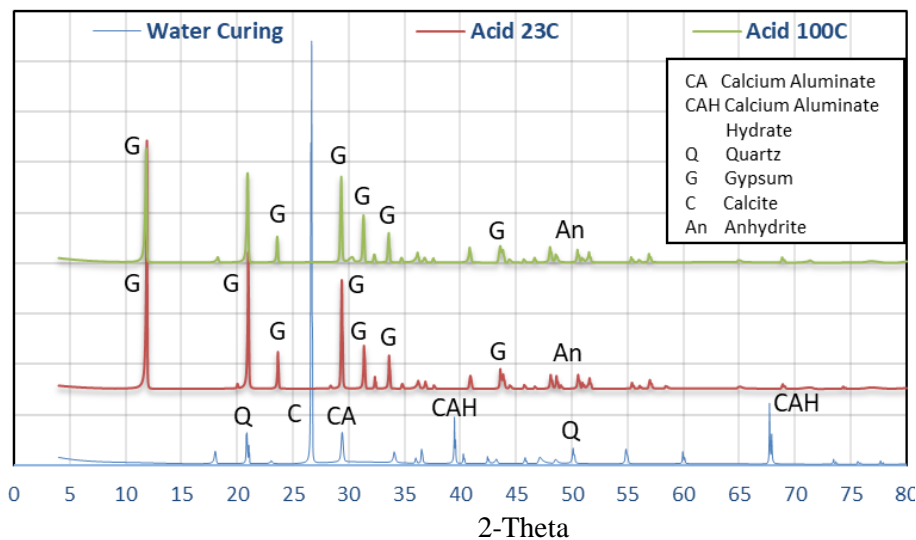


Figure 4: XRD of CAC specimens (a) unexposed sample, (b) sample exposed to 5% H_2SO_4 at normal temperature, and (c) sample exposed to 5% H_2SO_4 at high temperature.

4 CONCLUSIONS

Sulfuric acid reacts with the calcium-bearing phases (primarily portlandite and C-S-H, 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. Due to absence of these phases and due to the higher bonds in CA and CAH phases the calcium aluminate cement concrete demonstrates a higher resistance to dissolution and formation of gypsum when exposed to 5% H_2SO_4 .

After 90 days of exposure to sulfuric acid, the compressive strength of CAC mix decreased by 25% for samples exposed at normal temperature whereas a reduction of 39% was observed in the samples exposed at high temperature. High temperature that exists in sulfur pits accelerates the deterioration of concrete, The concentration of the acid is however, low in the vapors due to which these structures. 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

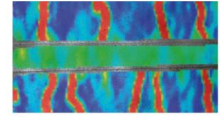
the pH of the acid under consideration and temperature. In this research CAC demonstrated a relatively better performance in resistance to sulfuric acid as compared to ordinary Portland cement reported by many researchers. Material characterization techniques provided a good diagnostic of the reactions taking place under acid attack resulting ultimately in the formation of gypsum.

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