

# Study of Concrete Properties under Acid Attacks

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## ABSTRACT

Acidic attack on concrete imparts a unique set of damage mechanisms and manifestations compared to other durability issues of concrete. Sulfuric acid attack limits the service life of concrete elements and, thus, results in increased expenditures for the repair or in some cases replacement of the whole structure. To date, there is lack of standardized tests for specifically evaluating the resistance of concrete to sulfuric acid attack, which has caused great variability, for example in terms of solution concentration, pH level/control, etc., among previous studies in this area. Accordingly, there are conflicting data about the role of key constituents of concrete (e.g. supplementary cementitious materials [SCMs]), and uncertainty about building codes' stipulations for concrete exposed to sulfuric acid. Hence, the first objective of this thesis was to assess the behaviour of the same concretes, prepared with single and blended binders, to incremental levels (mild, severe and very severe) of sulfuric acid solutions over 36 weeks. The test variables included the type of cement (general use [GU] or portland limestone cement [PLC]) and SCMs (fly ash, silica fume and nano-silica). The severe (1%, pH of 1) and very severe aggression (2.5%, pH of 0.5) phases caused mass loss of all specimens, with the latter phase providing clear distinction among the performance of concrete mixtures. The results showed that the penetrability of concrete was not a controlling factor, under severe and very severe damage by sulfuric acid attack, whereas the chemical vulnerability of the binder was the dominant factor. Mixtures prepared from PLC performed better than that of counterparts made from GU. While the quaternary mixtures comprising GU or PLC, fly ash, silica fume and nano-silica showed the highest mass losses after 36 weeks, binary mixtures incorporating GU or PLC with fly ash had the lowest mass losses.

**KEYWORDS:** Acid attack, Concrete durability

## INTRODUCTION

Chemical attack of concrete by sulfuric acid is a chief durability concern worldwide, and the recent increase in the reported attacks in industrial zones, wastewater plants, sewage facilities, etc. by acidic media has drawn much attention to this topic (Attigbo and Rizkalla, 1988; Monteny et al., 2000; De Belie et al., 2004; Gutiérrez-Padilla et al., 2010). Sulfuric acid attack limits the service life of concrete elements, which basically are constructed to meet a target life span, and thus it results in increased expenditures on the repair or in some cases replacement of the whole structure. In the USA alone, the Congressional Budget Office estimated annual maintenance costs of \$25 billion for wastewater systems during the period 2000-2019 (Sunshine, 2009). The most commonly known type of sulfuric acid damage occurs in concrete sewer pipes, treatment plants, pumping stations, manholes, junction chambers, etc. This type of corrosion is known by different names, such as microbial induced corrosion (MIC), biogenic sulfuric acid corrosion and hydrogen sulfide (H<sub>2</sub>S) corrosion (Wei et al., 2013; Gutiérrez-Padilla et al., 2010; Leemann et al., 2010). Also, sulfuric acid can originate from industrial wastewater and acid rain (Chen et al., 2013; Xie et al., 2004) due to severe air pollution problems in megacities. For example, in China, it was reported that acid rain falls over about one-third of Chinese territories (Fan et al., 2010). High rise buildings

made of concrete in these areas may be damaged due to exposure to frequent rainfalls with high acidity for a long time (Okochi et al., 2000). In addition, sulfuric acid may be produced in groundwater and soils as a result of the oxidation of iron-sulfide minerals in the form of pyrites (Pye and Miller, 1990). Acid attack of concrete is generally classified as a chemical attack. The sulfuric acid reacts with calcium hydroxide (CH) and calcium silicate hydrate (C-S-H), the main hydration components in the cement paste, resulting in the precipitation of calcium sulfate 1[gypsum] (Alexander, 2011). This reaction ultimately leads to decalcification and disintegration of the cementitious matrix (C-S-H gel, being converted ultimately to amorphous hydrous silica). Sulfuric acid has a combined attack by the proton (an acid) and sulfate attack in which the acid component enhances dissolution and thereby plays a significant role in the damage mechanism.

## Need for Research

In a mild environment with an adequate design, concrete made from ordinary and blended binders can be durable. However, it has been recognized that conventional concrete can suffer from degradation due to the attack from aggressive media such as sulfates and acids. Hence, looking for efficient ways to protect existing sanitary facilities from

further damage or possibly even increase their life span is a more realistic approach. Also, producing concrete which has improved resistance against chemical and sulfuric acid corrosion can also be a solution. This goal may be achieved by the partial replacement of General Use (GU) by active nanoparticles or supplementary cementitious materials (SCMs). Numerous research studies (e.g. Roy et al., 2001; Papadakis, 2000; Elahi et al., 2010; Durning and Hicks, 1991; Mehta 1985; Hewayde et al., 2003; Chang et al., 2005; Tamimi, 1997; Beddoe and Dorner, 2005; Torii and Kawamura, 1994) have proposed the use of SCMs (silica fume, fly ash, slag and nanosilica, and their combinations) to generally improve durability of concrete to chemical attack, without a general agreement on their effectiveness. It should be noted that there have been no North American specific

standards for assessing the resistance of concrete to sulfuric acid attack and most of these studies (e.g. Chang et al., 2005; Rostami and Ahmad-Jangi, 2011; Lotfy et al., 2016; Soroushian et al., 2009) applied the test method prescribed in ASTM C267, which is a standard test method for the chemical resistance of mortars, grouts and polymer concrete, as a general basis for evaluating the behavior of concrete exposed to sulfuric acid. In this test, the acidic medium should be replaced with a new one as often as necessary in order to maintain the original chemical composition and concentration; however, neither a specific concentration nor a pH level was mentioned (Monteny et al., 2000). So far, there has been no consensus on the concentration, the pH level and the time of exposure that should be used to perform this test on concrete.

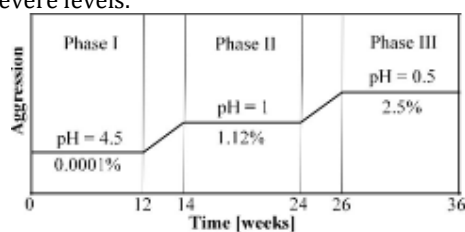
### Materials and Mixtures

General use cement (GU) and portland limestone cement (PLC) have been used in this study, which meets CSA A3001 (CAN/CSA-A3001, 2013) specifications. SCMs including Type F fly ash (abbreviated as FA), silica fume (abbreviated as SF) conforming to CSA A3001 (2013) and nanosilica sol (abbreviated as NS), were used as replacements of the total binder to prepare 14 concrete mixtures. In order to improve the workability, high-range water-reducing admixture, based on polycarboxylic acid and complying with ASTM C494/C494M13 Type F (2016) was added to all mixtures to achieve a slump range between 75 and 125 mm. **Table 3.1** shows the chemical and physical properties of the cement and SCMs. The coarse aggregate was well-graded natural gravel (9.5 mm) containing a small fraction (about 10% by mass) of carbonaceous aggregate with specific gravity and absorption of 2.65 and 1.6%, respectively.

Chemical Composition (%)	GU	PLC	FA	SF	NS
SiO <sub>2</sub> %	19.8	19.2	55.2	92.0	99.17
Al <sub>2</sub> O <sub>3</sub> %	5.0	4.4	23.1	1.0	0.38
Fe <sub>2</sub> O <sub>3</sub> %	2.4	2.6	3.6	1.0	0.02
CaO %	63.2	61.5	10.8	0.3	--
MgO %	3.3	2.4	1.1	0.6	0.21
SO <sub>3</sub> %	3.0	3.4	0.2	0.2	--
Na <sub>2</sub> O <sub>eq</sub> %	0.1	0.2	3.2	0.2	0.20
Specific Gravity	3.17	3.11	2.12	2.22	1.40
Mean Particle Size (μm)	13.15	11.81	16.56	0.15	35×10 <sup>-3</sup>
Fineness (m <sup>2</sup> /kg)	390	453	290	20000	80000
Viscosity (Cp)	--	--	--	--	8
pH	--	--	--	--	9.5

### Chemical and physical properties of cement and SCMs Acid Exposure

After curing, the concrete specimens were immersed into consecutive levels of aggression in sulfuric acid solutions, as shown in **Fig. 3.1**, with concentrations of 0.0001, 1.12 and 2.5% and corresponding initial pH of 4.5, 0.35 and 0, respectively (Phases I, II and III). The time interval was 12 weeks for each phase, i.e. a total exposure period of 36 weeks (**Fig. 3.2**). These exposure periods conformed to the common time intervals reported in the literature on accelerated tests of sulfuric acid attack. The aggression level of Phase I was selected in compliance with the exposure classes in BRE Special Digest 1 (2005) (class of exposure DS-1) and European code EN 206 (2005) (class of exposure XA2). However, in many applications (e.g. wastewater and sewage facilities) the level of aggression level may yield more severe levels.



**Incremental aggression of the sulfuric acid exposure:  
phase I, II and III**

### Tests

The rapid chloride permeability test (RCPT) was conducted to determine the penetrability (physical resistance) of the concrete specimens according to ASTM C1202 (2015) on discs (100×50 mm) from all mixtures. To minimize the electrolysis bias of this method, the penetration depth of chloride ions/front into concrete was determined according to the procedure described by Bassuoni et al. (2005) since it better correlates to the physical characteristics of the pore structure. Following the RCPT, the discs were axially split into two symmetrical halves and then sprayed with 0.1 M silver nitrate solution which converts to white silver chloride, representing the penetration depth. To determine the porosity of concrete mixtures, the mercury intrusion porosimetry (MIP) was conducted, on small samples (chucks) extracted from concrete cylinders of each mixture. These samples were approximately 4 to 7 mm in size and were carefully selected so that large aggregates were avoided. Before conducting the MIP, approximately 5 g of these chunks from each mixture were oven-dried at 45±2°C until reaching a constant mass to reduce the potential of drying shrinkage cracks associated with higher temperatures. For each specimen, the relative mass change at the end of each week (*MLt*) was calculated.



**Drying the specimens in laboratory conditions after taking them out of the solution**

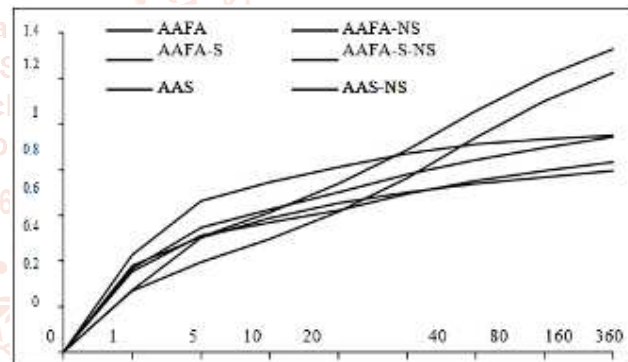
### Materials and Mixtures

Class F fly ash (FA), ground granulated blast-furnace slag (S) Grade 100 and their blends were used as the main binder components for concrete tested in this study. Commercial nanosilica (NS) sol (50% solid content of SiO<sub>2</sub> dispersed in an aqueous solution) with an average particle diameter of 35 nm were used as an additive with a dosage of 6%. The chemical composition and physical properties of the fly ash, slag and nanosilica are presented in **Table. 3.3**. Locally available coarse aggregate (natural gravel with a maximum size of 9.5 mm) and fine aggregate (well-graded river sand with a fineness modulus of 2.9) were used. The specific gravity and absorption were 2.65 and 2%, respectively, for gravel, and 2.53 and 1.5%, respectively, for sand. A high-range water-reducing admixture (HRWRA) based on polycarboxylic acid and complying with ASTM C494/C494M13 (2016) Type F was added to maintain a slump range of 50 to 75 mm. In addition, an air-entraining admixture was used to provide a fresh air content of 6±1%.

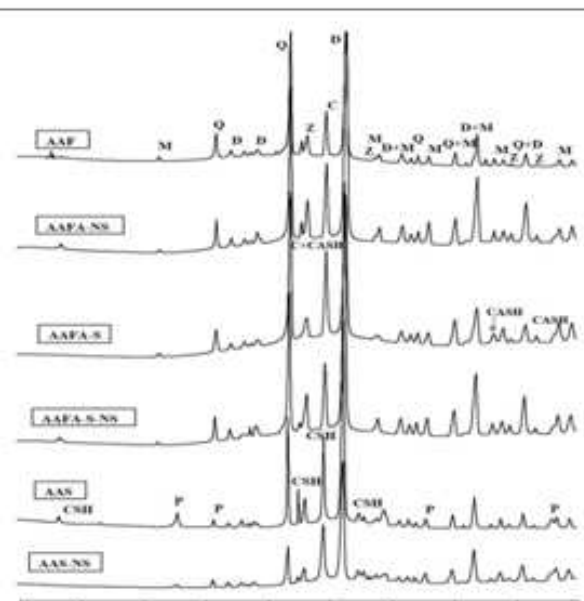
### Acid Exposure

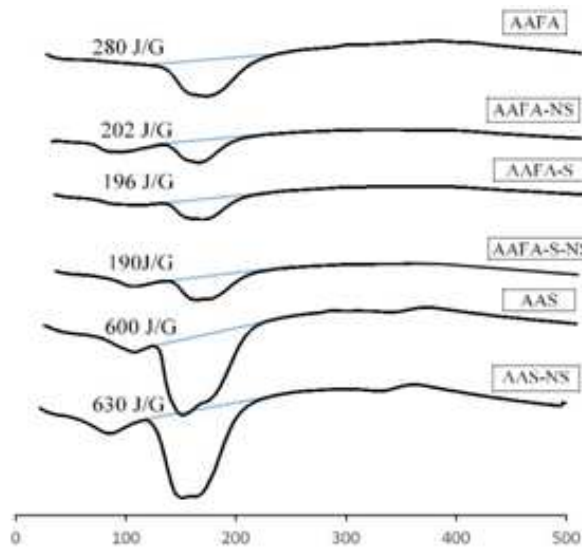
After 28 days, the cubic specimens were fully immersed in 10% sulfuric acid solution with a corresponding initial pH of -0.6 for 18 weeks to monitor the corrosion/penetration depth in specimens with time. Only one surface (treated with curing compound) was exposed to the acidic solution while the other surfaces were sealed with epoxy coating. Such concentration (10%) was applied to induce very severe exposure conditions, which is twice the high concentration (5%) typically used in previous studies for conventional concrete (e.g. Lee and Lee, 2016; Bassuoni et al., 2007; Song et al., 2005). The solution-to-specimens' volume ratio was kept constant at two and solutions were renewed with fresh ones after nine weeks. After 28 days, the top surface of each slab was brushed to remove the curing compound. Subsequently, the slabs were exposed to 18 weeks of aggressive acidic environments: four weeks of

wetting/drying (W/D) cycles, four weeks of wetting (W), four weeks of freezing/thawing (F/T) cycles, and a six weeks of alternating W/D and F/T cycles (three weeks each). This customized procedure may simulate aggressive exposures in wastewater facilities, where concrete is subjected to acidic media and changing environmental conditions. For the W/D cycles, the slabs were subjected to wetting by ponding (3 to 5 mm) the surface of specimens with 10% sulfuric acid solution followed by drying. A W/D cycle (five days) consisted of wetting for three days, followed by drying at 40±2°C and 55±5% RH for two days in an environmental chamber. The W/D cycles can be initiated, for instance, by the fluctuation of the wastewater level which might exacerbate the degradation effects of acid attack through ease the ingress of the acid and other synergistic effects. Also, the hot drying cycle might mimic the practical environmental conditions for wastewater facilities during periods of low flows (e.g. in sewer pipelines and acid storage tanks) and elevated ambient temperatures in hot months. The wetting stage was for four weeks at 22±2°C and 98% RH, while ponding the surface constantly with the sulfuric acid solution. The F/T cycles were applied according to the general procedures of ASTM C666 (2015) test procedure A, except that the 10% sulfuric acid solution was used instead of water and the frequency of F/T cycles per day was less to allow for chemical reactions. The duration of one F/T cycle was 12 hours: freezing at -18±1°C for 7 h and thawing at 4±1°C for 3.5 h, and 45 min. to ramp to the minimum freezing temperature or the maximum thawing temperature.



**Absorption trends of all mixtures.**





**DSC curves of all mixtures showing quantities of gypsum formed after the combined exposure.**

### Conclusions:

Considering the materials, mixture designs, and incremental test protocol implemented in this study, the following conclusions can be drawn:

- The results showed that all the GU and PLC specimens exposed to continuous immersion in the mildly acidic environment (Phase I) remained intact without visible features of damage. However, during Phases II and III, progressive precipitation of gypsum was observed and the damage of specimens was sharply escalated. Phase III (very severe acidic exposure) gave the clearest distinction among the performance of concrete mixtures, as expressed by surface degradation and mass loss results.
- Specimens from the PLC group had lower mass losses (average of 24% and 15% reduction after Phases II and III, respectively) than that of corresponding specimens from the GU group due to the neutralization effect offered by the limestone component (chemical resistance).
- The visual assessment showed that all specimens from the fly ash group exposed to continuous immersion in a very severe acidic solution underwent moderate deterioration without distinguishable features among mixtures. Comparatively, specimens from the slag group experienced progressive precipitation of gypsum (blocking effect) on the surface with notable swelling.
- All slabs from the fly ash and slag groups exposed to the cyclic environments combined with sulfuric acid solution showed significant deterioration (surface softening and scaling), reflecting the high level of aggressing of this exposure.
- In comparison to AAFA, the pull-off test results showed that the bond strength of the AAFA-NS, AAFA-S, AAFA-S-NS increased after the combined exposure, due to the limited penetrability of the acid in the repair zone and continual polymerization activity at the interface with substrate concrete. Failure of specimens from slag group

was mainly in the repair zone reflecting a higher level of deterioration with time.

### Recommendations for Future Work

The results and discussion presented in this thesis provide many useful insights for the extension of this research work. The following are recommendations for further investigations:

- Repeating the same incremental sulfuric acid exposure on mixtures composed of fly ash with different substitutions of slag and nanoparticles.
- Investigating the effect of different acidic concentrations and environmental conditions on the mechanisms of deterioration using similar mixtures.
- Calculating the diffusion coefficients of acidic solutions in alkali-activated fly ash or slag based systems.
- Performing a field trial for the repair of concrete elements affected by an acidic attack using AAMs incorporating fly ash and slag without and with nanosilica and monitoring its performance.

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