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Study on Concrete Properties under Acid Attacks

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Abstract- **Acidic attack on concrete imparts unique set of injury mechanisms and manifestations compared to other durability problems with concrete. vitriol attack limits the service lifetime of concrete elements and, thus, leads to increased expenditures for the repair or in some cases replacement of the entire structure. To date, there's lack of standardized tests for specifically evaluating the resistance of concrete to vitriol attack, which has caused great variability, for instance in terms of solution concentration, pH level/control, etc., among previous studies during 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 vitriol. Hence, the primary objective of this thesis was to assess the behaviour of an equivalent concretes, prepared with single and blended binders, to incremental levels (mild, severe and really severe) of vitriol solutions over 36 weeks. The test variables included the sort 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 really 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 wasn't a controlling factor, under severe and really severe damage by vitriol attack, whereas the chemical vulnerability of the binder was the dominant factor. Mixtures prepared from PLC performed better than that of counterparts made up of GU. While the quaternary mixtures comprising GU or PLC, fly ash, silica fume and nanosilica showed the very best mass losses after 36 weeks,binarymixturesincorporatingGUorPLCwith ash had rockbottom masslosses. Several studies reported that the improved chemical resistance of alkali-activated materials (AAMs) over concrete supported Portland cements. However, AAMs have technical limitations, which could deter its widespread use in cast-in place applications. These limitations include need for warmth curing, slow setting, and slow strength development, which could be mitigated by further improving the reactivity of AAMs during early-age with nanoparticles; however, this area remains largely unexplored. Hence, the second objective of this thesis was to develop innovative sorts of AAMs-based concrete [alkali activated ash (AAFA), alkali activated slag (AAS) and their blends incorporating nanosilica] and evaluate their resistance to 2 different vitriol exposures over 18 weeks for potential use in repair of concrete elements susceptible to acidic attack. While AAFA specimens, produced without heat curing, experienced rapid ingress of the acidic solution and a big reduction within the bond strength with substrate concrete, ash based AAMs comprising slag and or nanosilica (AAFA-S and AAFA-S-NS) had improved performance thanks to discounting the ingress of acidic solution and continued geopolymerization reactivity. Comparatively, specimens from the slag group exhibited high levels of swelling, internal cracking and mass loss thanks to chemical deterioration. The general results suggest that AAFA-S and AAFA-S-NS mixture, without heat curing, could also be a viable option for repair applications of concrete elements in acidic entrainments, but field trials are still needed to further verify their performance.**

Keywords- **AAFA specimens, AAFA-S and AAFA-S-NS,**

I.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 (Attiogbe 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.

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In 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 (H2S) 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 mega cities. 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 rain falls 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 [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.

1. Need for Research:

In a mild environment with 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.

II. GENERAL FEATURES OF SULFURIC ACID ATTACK

Sulfuric acid [H2 (SO4)] attack on concrete may be characterized by a chemical reaction between the acidic media and cement hydration products and, if soluble, the aggregate particles, results in excessive formation of gypsum (Fig. 2.1).

The nature of attack of sulfuric acid on concrete is manifold. Acid attack can occur under static or flowing conditions at different temperatures and pressures in structures such as containers for liquid manure, silage, deicing agent run-off at airports as well as cooling towers and sewers etc. (Alexander et al., 2013).

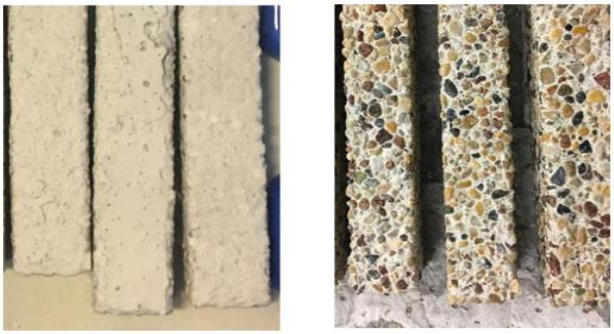

Fig 1. a) Gypsum depositions and b) aggregate disintegration after exposure to 2.5% concentration of sulfuric acid in a laboratory test.

III. MATERIALS AND MIXTURES

General use cement (GU) and Portland limestone cement (PLC) have been used in this study, which meet CSA

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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, a 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 a specific gravity and absorption of 2.65 and 1.6%, respectively. The fine aggregate was well-graded river sand with a specific gravity, absorption, and fineness modulus of 2.53, 1.5% and 2.9, respectively.

The total binder content and water-to-binder ratio (w/b) for all mixtures were kept constant at 390 kg/m3 and 0.40, respectively. Single binder (control) mixtures were prepared from 100% GU or PLC. The binary binders incorporated GU or PLC with 30% fly ash, 5% 35 nanosilica or 5% silica fume. Ternary binders were prepared from 65% GU or PLC with 30% fly ash and either 5% nanosilica or silica fume. Quaternary binders consisted of 60% GU or PLC with 30% fly ash, 5% nanosilica and 5% silica fume.

Table 1 shows the mix proportions for all mixtures. Concrete was mixed in a mechanical mixer to prepare three replicates of prismatic (50×50×285 mm) and cylindrical (100×200 mm) specimens, which were cured at standard conditions (22±2°C and 98% RH) for 28 days according to ASTM C192 (2016).

Table 1 mix proportions

Chemical Composition (%)	GU	PLC	FA	SF	NS
SiO2 %	19.8	19.2	55.2	92.0	99.17
Al2O3 %	5.0	4.4	23.1	1.0	0.38
Fe2O3 %	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
SO3 %	3.0	3.4	0.2	0.2	--
Na2Oeq %.	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	11.8 1	16.56	0.15	35×10^{-3}
Fineness (m^2/kg)	390	453	290	20000	80000
Viscosity (Cp)	--	--	--	--	8
pH	--	--	--	--	9.5

IV. RESULTS AND DISCUSSIONS

Table 2. Results from RCPT and MIP.

Mixture ID.	Penetration Depth (mm)	Standard Error of penetration Depth	Chloride Ions Penetrability Class (ASTMC1202)	Average Porosity %
GU group				
GU	17.6	0.89	Moderate	15.8
GUF	9.0	0.64	Low	12.8
GUSF	5.3	0.37	Very Low	9.5
GUNS	4.2	0.53	Very Low	9.2
GUFSF	6.8	0.74	Very Low	11.4
GUFNS	3.5	0.32	Very Low	9.0
GUFSFNS	2.7	0.92	Very Low	8.7
PLC group				
PLC	12.7	1.02	Moderate	14.3
PLCF	11.9	0.92	Low	14.0
PLCSF	5.0	0.45	Low	9.4
PLCNS	4.0	1.06	Very Low	9.1
PLCFSF	6.8	0.76	Very Low	11.4
PLCFS	3.2	0.37	Very Low	8.9
PLCFSFNS	3.0	0.21	Very Low	8.8

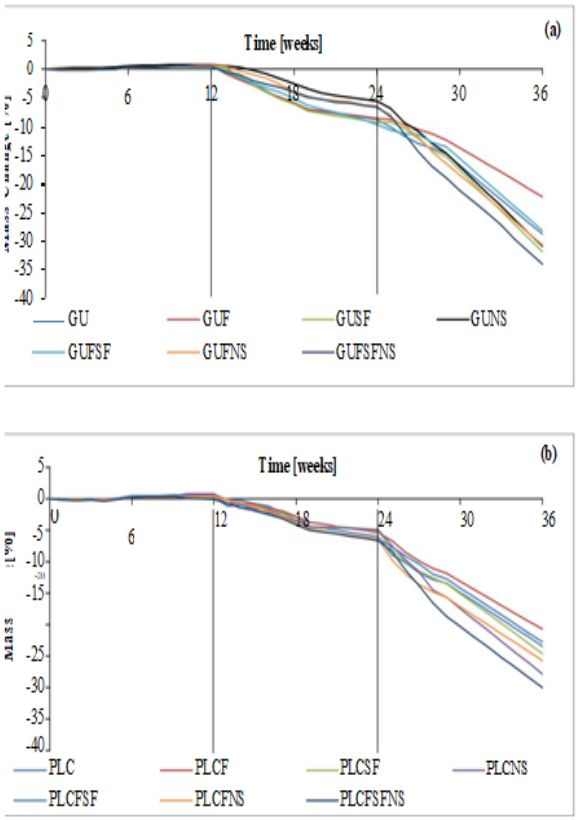

Fig 2. Average mass loss with time for specimens from groups: a) GU, and b) PLC.

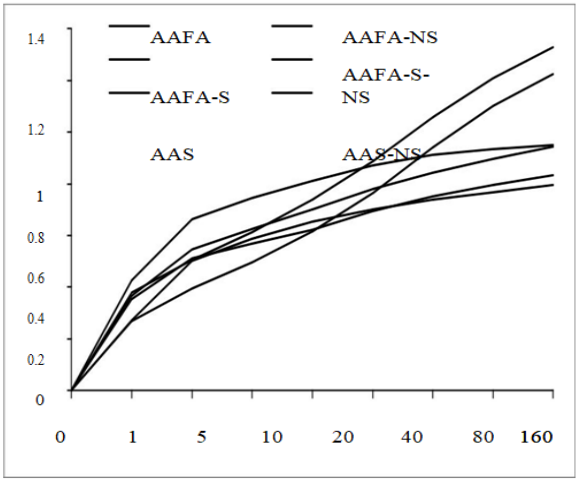

Fig 3. Absorption trends of all mixtures.

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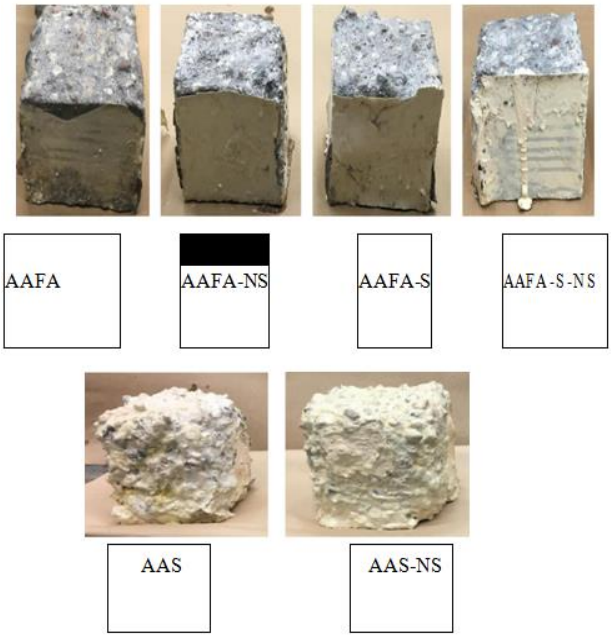

Fig 4. Appearance of concrete specimens after 18 weeks of immersion in 10% sulfuric acid:(a) fly ash based AAMs, and b) slag based AAMs.

V. CONCLUSIONS

1. Incremental Acidic Attack:

Considering the materials, mixture designs, and incremental test protocol implemented during this study, thesubsequent conclusions areoften drawn:

The results showed that each one the GU and PLC specimens exposed to continuous immersion within the mild acidic environment (Phase I) remained intact without visible features of injury . However, during Phases II and III, progressive precipitation of gypsum was observed and therefore the damage of specimens was sharply escalated. Phase III clinical trial (very severe acidic exposure) gave the clearest distinction among the performance of concrete mixtures, as expressed by surface degradation and mass loss results.

The relationship between the penetrability of specimens and their cumulative mass losses after Phases II and III was mixed and discordant. In phase II clinical trial, mixtures from blended binders with lower penetration depths (e.g. GUFSF, PLCFSF) had comparable mass losses to the control specimens from single binders. Also, some concrete mixtures (e.g. GUFSFNS and PLCFSFNS) with very low penetration depths exhibited the very best mass losses after phase III clinical trial, while others (e.g. GUF and PLCF) with higher penetration depths yielded rock bottom mass losses.

This shows that the notion adopted by building codes to enhance the acidic resistance of concrete mainly by discounting its physical penetrability should be reconsidered. 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 thanks to the neutralization effect offered by the limestone component (chemical resistance).

During phase II clinical trial (severe acidic attack), only systems with nanosilica, particularly within the GU group, led to relative improvement of the acidic resistance of concrete compared to regulate specimens; however, no such improvement was achieved for blended binary or ternary binders comprising silica fume and ash . This was ascribed to the further refinement of pore structure in systems containing nanosilica as gypsum formation, which may cause crystallization pressure and thus damage, attended precipitate faster in coarser pore structures (systems with other SCMs).

Chemical vulnerability of binders at this stage, irrespective of the physical features of pore structure (physical resistance). This was due to the increased volume of cementitious gel exposed to deterioration in the sulfuric acid solution at this stage, as indicated by the increased gypsum formation in these specimens. Comparatively, GUF and PLCF binders exhibited the lowest mass losses due to occurrence fly ash particles within the surface of concrete, which acted as inert filler limiting the surface of paste susceptible to the acid-base reaction.

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