Durability of Concrete under Acid Attacks

Ch. Veerottam Kumar, N. Susmitha, K. Soma Sekhar, K. Kanakalakshmi and P. Ashok

Dept. of Civil Engineering Ramachandra College of Engineering Vatluru, Eluru, Andhra Pradesh, India

veerottamk143@gmail.com, {susmitha.n, sekhar08674, kanaka.lakshmi93}@rcee.ac.in, and ashokani31@gmail.com

Abstract— Acidic assault on concrete results in a distinct set of damage processes and manifestations in comparison to other concrete durability difficulties. Sulfuric acid attack reduces the service life of concrete components and, thus, increases the cost of repairing or, in certain instances, replacing the whole building. To present, there are no established tests for measuring the particular resistance of concrete to sulfuric acid assault, which has led to a considerable deal of variation, for example, in terms of solution concentration, pH level/control, etc., among prior research in this field. Consequently, there are contradictory facts on the role of essential elements of concrete (e.g., supplementary cementitious materials [SCMs]) and there is a lack of clarity regarding the requirements of building codes for concrete exposed to sulfuric acid. As a result, the primary objective of this thesis was to examine, over the course of a period of three months, how different types of concrete, those made with single binders and those made with blended binders, reacted to progressively higher concentrations of sulfuric acid solutions, ranging from mild to severe to very severe. In order to carry out the experiment, we were required to choose either a portland limestone cement (PLC) or a general-purpose cement (GU) (fly ash, silica fume and nano-silica). All specimens saw mass loss during the severe (1 percent, pH 1) and very severe (2.5 percent, pH 0.5) aggressiveness phases, with the latter phase revealing a clear differentiation between the performance of concrete mixes. Under severe and very severe sulfuric acid assault, the findings demonstrated that the penetrability of concrete was not the governing element; rather than that, the most important factor was the chemical fragility of the binder. Mixtures made with PLC performed far better than their counterparts prepared using GU. After 36 weeks, quaternary combinations including GU or PLC, fly ash, silica fume, and nanosilica exhibited the greatest mass losses, while binary mixtures containing GU or PLC and fly ash exhibited the least.

Keywords-durability of concrete; acid attacks;

I. INTRODUCTION

Chemical assault of concrete by sulfuric acid is a key worry for durability across the globe, and the recent growth in the reported attacks in industrial zones, wastewater plants, sewage facilities, etc. by acidic media has brought considerable attention to this topic. Sulfuric acid assault reduces the service life of concrete components, which are often manufactured to satisfy a predetermined lifespan, resulting in higher costs for maintenance or, in certain instances, replacement of the whole

building. During 2000-2019, the Congressional Budget Office expected yearly maintenance expenses for wastewater systems in the United States to be \$25 billion (Sunshine, 2009). The most prevalent sort of damage caused by sulfuric acid is to concrete sewage pipes, treatment facilities, pumping stations, manholes, and junction chambers. This kind of corrosion is also known as microbially induced corrosion (MIC), biogenic sulfuric acid corrosion, and hydrogen sulphide (H2S) corrosion (Wei et al., 2013; Gutiérrez-Padilla et al., 2010). [Citation needed]; Leemann et al., 2010) are two examples of this. Sulfuric acid may also arise from industrial effluent and acid rain as a consequence of air pollution problems in megacities. It has been stated that acid rain occurs on around one-third of Chinese territory (Fan et al., 2010). Due to prolonged exposure to frequent, highly acidic rain showers, high-rise concrete structures in certain regions may sustain damage (Okochi et al., 2000). As a consequence of the oxidation of iron-sulfide minerals in the form of pyrites, sulfuric acid may also be formed in groundwater and soils (Pye and Miller, 1990). In general, acid attacks against concrete are considered as chemical attacks. The sulfuric acid combines with the primary hydration components of the cement paste, gypsum is formed through the reaction of calcium hydroxide (CH) with calcium silicate hydrate (C-S-H) (Alexander, 2011). Decalcification and degradation of the cementitious matrix are the end results of this process (C-S-H gel, being converted ultimately to amorphous hydrous silica). The acid component of sulfuric acid considerably adds to the damaging process by increasing the solubility of the acid.

II. NEED OF RESEARCH

Ordinary and mixed concrete binders may be durable in a moderate climate with the proper design. However, it has been acknowledged that typical concrete may deteriorate when subjected to hostile media such as sulphates and acids. Consequently, it is more practical to seek out methods to safeguard existing sanitary facilities from further deterioration and potentially even extend their lifespan. Producing concrete with enhanced resistance to chemical and sulfuric acid corrosion is also a potential option. This objective may be accomplished by partially substituting General Use (GU) with active nanoparticles or other cementitious materials (SCMs). SCMs, also known as silica fume and fly ash, have been the subject of a number of studies, all of which have concluded

that they are effective cancer treatments (Roy et al., 2001; Papadakis, 2000; Elahi et al., 2010, Durning and Hicks, 1991; Mehta 1985, et al. 2003; Chang et al. 2005; Tamimi, 1997; Beddoe and Dorner, 2005). The majority of these studies (e.g. Chang et al., 2005; Rostami and Ahmad-Jangi, 2011; Lotfy et al., 2016; Soroushian et al., 2009) used the ASTM C267 test method, which is a standard test method for the chemical resistance of mortars, grouts, and polymer-modified mortars and grout. There are no North American standards for testing the resistance of concrete to sulfuric acid attack. However, neither a specified concentration nor pH level was supplied (Monteny et al., 2000). It's not yet clear what concentration, pH level and exposure time is needed to do this test on concrete.

A. Materials and Mixtures

In order to fulfil the requirements of CSA A3001, we used both portland limestone cement and general use cement (GU) (PLC). In the creation of 14 different concrete mixes, several alternatives to binder were used. These alternatives included Type F fly ash (abbreviated as FA), silica fume (abbreviated as SF), and nanosilica sol (abbreviated as NS). All of the mixes were improved by adding an admixture that was based on polycarboxylic acid and conformed to ASTM C494/C494M13 Type F (2016). This allowed for the slump ranges of 75mm to 125mm to be attained. The chemical and physical characteristics of cement and SCMs are compared and contrasted in Table 3.1. The specific gravity of the carbonaceous aggregate was 2.65, and its absorption value was 1.6 percent, was used as a coarse aggregate in a well-graded natural gravel (9.5 mm).

Table-1.0: Chemical and physical properties of cement and SCMs

| Chemical | | | | ~~ | 2.70 |
|----------------|-------|-------|-------|-------|---------------------|
| (%) | 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 | 11.81 | 16.56 | 0.15 | 35×10^{-3} |
| Fineness | | | | | |
| (m^2/kg) | 390 | 453 | 290 | 20000 | 80000 |
| Viscosity (Cp) | | | | | 8 |
| pН | | | | | 9.5 |

B. Acid Exposure

Following the curing process, samples of concrete were immersed in sulfuric acid solutions with concentrations of 0.0001, 1.12, and 2.5 percent and initial pH values of 4.5, 0.35, and 0 percent respectively (Phases I through III). There

were a total of 36 weeks spent being exposed, with each phase being spaced out by 12 weeks (Fig. 3.2). The standard time intervals that are indicated in the academic literature were employed for the accelerated research of sulfuric acid assault, and these exposure durations lasted for the appropriate amount of time. Both the European standard EN 206 and the Class DS-1 of the BRE Special Digest 1 (2005) were used in order to estimate the aggression level for Phase I. (2005). Class XA2 of exposure Under some conditions (such as sewage treatment plants), the level of aggressiveness may be more extreme.

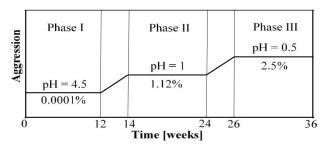


Fig-1.0:Incremental aggression of the sulfuric acid exposure: phase I, II and III

III. TESTS

It was carried out in accordance with ASTM C1202 on discs (10050 mm) from all combinations to measure the physical resistance of the concrete specimens by carrying out a quick chloride permeability test on them. This test was carried out in order to measure the physical resistance of the concrete specimens (2015). Using Bassuoni et al. (2005)'s approach for calculating chloride ions/front penetration depth into concrete, the electrolysis bias of this methodology was reduced. After the RCPT, the discs were sprayed with a solution of 0.1 M silver nitrate, which upon reaction becomes white silver chloride. This was done in order to illustrate the depth of penetration. Small samples, known as "chucks," were taken from concrete cylinders and analysed using mercury intrusion porosimetry so that the porosity of various concrete mixes could be calculated (MIP). In order to prevent big aggregates, these samples were carefully selected from 4 to 7 mm in diameter. In order to reduce the likelihood of drying shrinkage fractures occurring at higher temperatures, about 5 grammes of these fragments were dried in an oven at 452 degrees Celsius until they became one solid mass. This was done for each combination. At the conclusion of each week, the MLt value for each specimen's change in relative mass was determined.



Fig-2.0 Drying the specimens in laboratory conditions after taking them out of the solution.

A. Materials and Mixtures

In this particular investigation, the primary components of the concrete employed were FA and S Grade 100 fly ash, as well as their respective mixtures. Nanosilica (NS) sol, which has a solid composition of fifty percent SiO2 and is distributed in an aqueous solution, was used as a six percent addition. The average particle diameter of the NS sol was thirty-five nanometers. In the following table, the chemical and physical characteristics of fly ash, slag, and nanosilica are laid forth for your perusal. Table 1. For the purpose of this project, it was essential to make use of coarse aggregate (which consisted of natural gravel with a particle size of 9.5 millimetres) and fine aggregate (which consisted of well-graded river sand with a fineness modulus of 2.9). When compared to sand, gravel had a specific gravity of 2.65 and an absorption percentage of 2%. while sand had a specific gravity of 2.53 and an absorption percentage of 1.5. In order to keep the slump within the range of 50 to 75 millimetres, a high-range water-reducing conforms that admixture (HRWRA) C494/C494M13 (2016) Type F was used. In addition to this, an air-entraining additive was used in order to achieve the desired air content of 61%.

B. Acid Exposure

After 28 days, a solution of 10 percent sulfuric acid with an initial pH of -0.6 was added to the cube-shaped specimens so that the corrosion and penetration depth could be determined over time. The acidic solution was only applied to one surface, which had been treated with curing component. All other surfaces were protected by epoxy. In this investigation, a very high concentration of 10 percent was used, which is twice the concentration of 5 percent that was utilised in earlier experiments for regular concrete (e.g. Lee and Lee, 2016; Bassuoni et al., 2007; Song et al., 2005). All solutions were changed out on a nine-week cycle with a fresh one, and the volume ratio was maintained at 2:1. The curing material was scraped from the top surface of each slab after 28 days. Four weeks of wetting and drying (W/D), four weeks of thawing and refreezing (F/T), and six more weeks of alternating cycles of the two states were part of the acidic conditions (three weeks each). This individualised technique might be utilised in wastewater treatment facilities to simulate the difficult conditions that concrete is subjected to, which include the presence of acidic chemicals and a wide range of environmental temperatures. During the W/D cycles, the specimens were first dried after being immersed in a solution containing 10 percent sulfuric acid for 3 to 5 millimetres. At a temperature of 40.2 degrees Celsius and a relative humidity of 55.5 percent, a W/D cycle, which lasts for five days, consists of three days of wetting followed by two days of drying. The degrading effects of acid attack may be enhanced by the W/D cycles, which may be triggered for a number of causes, one of which is fluctuations in the volume of wastewater. It is also possible to use a hot drying cycle to imitate the true environmental conditions of wastewater facilities during periods of low flow (for example, in sewage tunnels and acid storage tanks) and high ambient temperatures throughout the summer. This can be done to simulate the conditions that exist

in real-world wastewater treatment plants. At a temperature of 22.2 degrees Celsius and a relative humidity of 98 percent, the sulfuric acid solution pooled on the surface continuously for four weeks. ASTM C666 (2015) test method A was utilised to administer the F/T cycles, with the exception that a solution of sulfuric acid containing 10% rather than water was used, and the number of F/T cycles administered each day was decreased to allow for chemical interactions. There was an additional 45 minutes of ramp time for each F/T cycle, which included 7 hours of freezing at 181°C and 3.5 hours of thawing at 41°C.

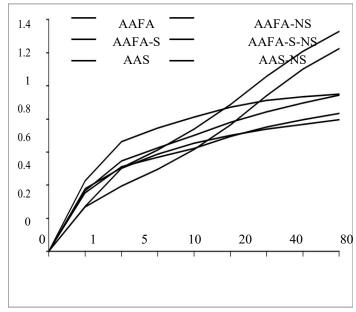


Fig-3.0: Absorption trends of all mixtures.

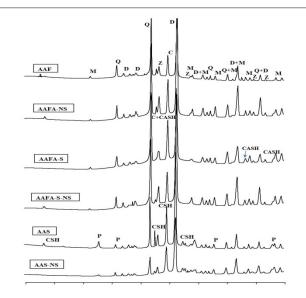


Fig-4.0:X-Ray Diffraction of specimen

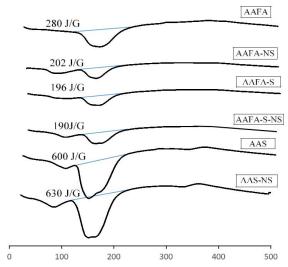


Fig-5.0: DSC curves of all mixtures showing quantities of gypsum formed after the combined exposure.

IV. CONCLUSION

The following conclusions may be taken from the study's materials, mixture designs, and incremental testing method:

- GU and PLC samples exposed to a moderately acidic environment (Phase I) were found to be unharmed and free of visible damage, according to the results. On the other hand, gypsum precipitation increased and specimen deterioration increased dramatically in Phases II and III. Phase III (extreme acidic exposure) was the most noticeable in terms of concrete mix performance in terms of surface degradation and mass loss.
- PLC specimens saw less mass loss (24 percent and 15 percent, respectively, following Phases II and III) than GU specimens because of the neutralising impact of the limestone component (chemical resistance).
- When exposed to a highly acidic solution for an extended period of time, all of the fly ash samples showed considerable degradation, but there were differentiating features among the various mixtures. Specimens from the slag group, on the other hand, demonstrated a rising amount of gypsum precipitation (a blocking effect) on the surface, along with a large amount of expansion.
- Sulfuric acid solution in combination with cyclic settings caused considerable deterioration (softening and scaling) in all fly-ash and slag slabs, showing the high abrasion associated with this exposure.
- Due to the restricted acid penetrability in the repair zone and the ongoing geopolymerization activity at the interface with the concrete substrate, pull-off tests

revealed that the bond strength of AAFA-NS, AAFA-S, and AAFA-S-NS increased after combined exposure. The repair zone had the highest percentage of failed slag specimens, showing that deterioration occurs more rapidly over time.

V. RECOMMENDATIONS AND FUTURE WORK

The observations and analyses that are reported in this thesis offer a number of important insights for the study that will be done in the future. Further investigation might include the following ideas:

- Using different slag and nanoparticle substitutes in lieu
 of the original progressive sulfuric acid exposure on fly
 ash blends.
- Comparison of deterioration processes of similar combinations under varied acidity concentrations and environmental conditions.
- Figuring out how acidic solutions move through alkaliactivated fly ash or slag-based systems and calculating their diffusion coefficients.
- Repairing acid-damaged concrete components using fly ash and slag (both without and with nanosilica) and observing how well these materials work in a field experiment.

REFERENCES

- [1] ACI 201.2R. (2016). Guide to durable concrete. Report by ACI Committee 201, MI. *AmericanConcrete Institute*, Farmington Hills, USA.
- [2] ACI 515.1R. (1985). Guide to the use of waterproofing, damp proofing, protective, and decorative barrier systems for concrete. Report by ACI Committee 515, MI. American Concrete Institute, Farmington Hills, USA.
- [3] Adak, D., Sarkar, M., and Mandal, S. (2014). Effect of nano-silica on strength and durability of fly ash based geopolymer mortar. *Construction and Building Materials*, 70, 453-459.
- [4] Adam, A. (2009). Strength and durability properties of alkali activated slag and fly ash-based geopolymer concrete, Environment and Chemical Engineering. *RMIT University*, Melbourne, Australia.
- [5] Al Bakri Abdullah, M. M., Kamarudin, H., KhairulNizar, I., Bnhussain, M., Zarina, Y., and Rafiza, A. R. (2012). Correlation between Na2SiO3/NaOH ratio and fly ash/alkaline activator ratio to the strength of geopolymer. Advanced Materials Research, 341, 189-193..
- [6] Alexander M, Bertron A, De Belie N. (2013) Performance of cement-based materials in aggressive aqueous environments. RILEM TC 211-PAE.Springer, Berlin.
- [7] Alexander MG, and Fourie C. (2011). Performance of sewer pipe concrete mixtures with Portland and calcium aluminate cements subject to mineral and biogenic acid attack. *Materials and Structures*, 44(1), 313–30.
- [8] Aliques-Granero, J., Tognonvi, T. M., and Tagnit-Hamou, A. (2017). Durability test methods and their application to AAMs: case of sulfuricacid resistance. *Materials and Structures*, 50(1), 36.