Degradation kinetics of alkali-activated pastes in acetic acid

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Abstract. Growing urban and industrial activities globally are found to be the sources of rising acidic environment. These acidic environments ensue early degradation of concrete in terms of microstructural alteration of phases formulating to mass changes, weakening of mechanical properties, and increase in porosity due to calcium leaching. This paper probes into the acetic acid resistance of geopolymer composites (GP) and its comparison with conventional concrete system (OPC) in 0.125M and 0.25M concentrations of acetic acid medium. The GP samples displayed increased resistance to acetic acid attack in terms of mass and thickness loss. It was also found that blends of ground granulated blast furnace slag (GGBS) and fly ash (class F) (FA) with red mud (RM) offered increased acid resistance due to the nature of the main binder gel produced in GP systems.

1. Introduction

The never-ending hunger of the people for industrial products has directly or indirectly affected the durability aspect of concrete structures by exposing the latter to a vulnerable aggressive environment. Most industries worldwide are built upon processes that produce effluents or waste water. When untreated, the existence of complex acidic compositions within these effluents have led to severe degradation of structures involved in processes such as production, collection, storage and treatment. For example, about 40 billion litres of spent wash are annually generated in India with regard to the production from sugar mills and molasses-based distilleries [1, 2]. Spent wash is acidic in nature and contains a mixture of organic and inorganic acids. The direct disposal of untreated spent wash is considered hazardous as it arrests the growth of vegetation and damages the quality of ground water. Liquid manure, silage effluents, winery wastewaters from the distillery and fermentation industries contain predominant organic acids like acetic, lactic, citric, butyric and tartaric acids where the pH is around 4.5 generally [3]. Table 1 represents the predominant sources of organic acids that could endanger the service life of any reinforced concrete structures.

The acids present in silage effluents cause deterioration of concrete silos. Due to the increased horizontal pressure within the silos, larger silos are more prone to acid deterioration than smaller silos [4]. On placing moist plant material in a silo over a long period, the process releases silage acid mainly lactic and acetic. When the concrete silo walls come in contact with these silage acids, it causes a reduction in the strength, which leads to the buckling of walls and eventually causing failure. Most of the researches were carried out on the degradation of concrete caused by the presence of inorganic acids. Only limited studies are reported on the effect of organic acids. Regardless of organic acids being weak acids due to its partial dissociative nature, it could destruct the concrete matrix which is
alkaline. These acids accelerate the corrosion of embedded reinforcements and disturb the production facilities.

### Table 1. Predominant acids in agro-food industries [5].

| Industry                  | Waste waters     | Acids            | Concentration (mmol/L) | pH |
|---------------------------|------------------|------------------|------------------------|----|
| Wine industry             | Vinasses         | Tartaric         | 3.2–8.73               | 4-6|
|                           |                  | Acetic           | 3.1–5.0                |    |
|                           |                  | Lactic           | 2.2–5.6                |    |
|                           |                  | Succinic         | 0.3–6.8                |    |
|                           |                  | Malic            | 0.5–0.8                |    |
|                           |                  | Total (max.)     | 26.9                   |    |
| Sugar industries          | Sugar cane vinasses | Lactic         | 18–80.4               | 4-7|
|                           |                  | Glycolic         | 12–25                  |    |
|                           |                  | Citric           | 1.7–10.4               |    |
|                           |                  | Trans-Aconitic   | 0.2–4.8                |    |
|                           |                  | Cis-Aconitic     | 0.1–2.8                |    |
|                           |                  | Oxalic           | 0.08–0.8               |    |
|                           |                  | Fumaric          | 0.1–0.4                |    |
|                           |                  | Total (max.)     | 124.2                  |    |
| Dairy industries          | Whey             | Acetic           | 14.0                   | 4-6|
|                           |                  | Citric           | 9.2–9.6                |    |
|                           |                  | Lactic           | 3.4–5.7                |    |
|                           |                  | Propionic        | 1.0                    |    |
|                           |                  | Butyric          | 0.6                    |    |
|                           |                  | Total (max.)     | 30.9                   |    |
| Animal rearing            | Silage juice     | Lactic           | 55.3–63.7              | 4-5|
|                           |                  | Acetic           | 25.3–28.3              |    |
|                           |                  | Butyric          | 43.4                   |    |
|                           |                  | Propionic        | 3.1                    |    |
|                           |                  | Total (max.)     | 99.1                   |    |
| Liquid manure             |                  | Acetic,          | 31.7–213               | 5-8|
|                           |                  | Butyric          | 1.1–28.8               |    |
|                           |                  | Propionic        | 5.4–37.8               |    |
|                           |                  | Total (max.)     | 279.6                  |    |

Concrete with Ordinary Portland Cement (OPC) is reported to be less resistant in acidic media. Moreover, the use of OPC is discouraged nowadays as its production contributes alarmingly to carbon dioxide emissions and thus global warming. Contribution of CO₂ emissions worldwide by cement industry is approximated to be around 7% [6]. As we strive towards achieving sustainable development, the complete replacement of cement with alkali activated/ geopolymer composites can be considered as a viable alternative for cementitious materials exposed to aggressive acidic environments. Also, it has been estimated that 66 million tons of red mud is produced annually across the world and it is considered to be hazardous pollutant according to the Brazilian NBR 10004 standards [7, 8]. Therefore, the incorporation of such waste materials as an alternative binder material in alkali activated systems could lead to reduction of pollution level across the globe. GP system is an innovative technology that utilizes industrial solid wastes such as class F-fly ash (FA), ground granulated blast furnace slag (GGBS) and red mud (RM) as raw material to form a 3D network of cementitious materials under alkaline conditions through polymerization [9]. Individually, alkali activated GGBS and alkali activated FA has been studied by many authors. The organic acid resistance of these two alkali activated binder systems has not received much attention. Therefore, this paper investigates the resistance of GP materials in acetic acid solution by studying the degradation kinetics.
2. Mechanism of organic acid attack

Concrete, particularly the cement paste matrix is highly vulnerable under acid attack. The basic described mechanism of deterioration due to acid attack is acidolysis. In this process, the hydration products developed reacts with the incoming acid thereby releasing metal ions from the hydrates into the solution forming salts of varying characteristics and ultimately reducing the mass and integrity of the matrix. In the case of organic acid attack, complexolysis and precipitation of reaction products mechanisms are also involved. Complexolysis is a process where the metal ions extracted in the initial acidolysis phase reacts with acid ions and formulates complexes thereby dissolving the solid phase in the solution. The latter mechanism (i.e. precipitation) becomes significant based on the character of the salt formed i.e. when the salt formed has a higher molar volume than the originally formed hydration products, expansion and cracking of the matrix seems to accelerate then [2,10]. Table 2 represents the solubility data of salts formed as a result of the reaction of hardened cement paste with an organic acid. The belligerent nature of acids into the cementitious matrix depends on the acid dissociation constant, their solubility in water, mono/poly acidity of acids and the physical properties of salts they form.

| Acid    | Acid dissociation constant (25°C) | Aggressiveness | Major Calcium salts                                                | Solubility (g/L)                  |
|---------|----------------------------------|----------------|------------------------------------------------------------------|----------------------------------|
| Acetic  | 4.76                             | Moderate       | Calcium acetate monohydrate {Ca(CH₃COO)₂·H₂O}                     | 436 (0°C) / Highly soluble        |
| Citric  | 3.14/4.77/6.3                    | Very high      | Calcium citrate tetrahydrate {Ca₃(C₆H₅O₇)₂·4H₂O}                  | 0.095 (25°C) / Slightly soluble   |
| Tartaric| 3.04/4.37                        | Moderately low | Calcium tartrate tetrahydrate {CaC₃H₇O₆·4H₂O}                    | Insoluble                        |
| Lactic  | 3.86                             | Moderate       | Calcium lactate pentahydrate                                     | 0.97 (25°C) / Soluble            |
| Succinic| 4.16/5.61                        | High           | Calcium succinate trihydrate                                     | 0.193 (0°C) / Slightly soluble   |
| Oxalic  | 1.23/4.19                        | Very Low       | Calcium oxalate monohydrate {CaC₂O₄/CaC₂O. H₂O}                  | Insoluble                        |
| Butyric | 4.82                             | Moderate       | Calcium butyrate monohydrate {Ca(CH₂CH₂CH₂CO₂)₂·H₂O}              | 0.04 (25°C) / Slightly soluble   |

Table 2. Calcium and aluminium salts solubility data of various organic acids [2, 10, 11].

From the literatures, it is seen that acetic acid is an important organic acid predominantly present in waste waters. They are popularly known as weak acids but seem to be very aggressive when it comes into contact with cementitious systems. Acetic acid is a monocarboxylic acid that initiates the dissolution of calcium hydroxide present in the concrete and produces highly soluble calcium salts [11]. Since these calcium salts are very soluble, they are leached away exposing the fresh concrete surface to acid attack. Acetic acid also counters with the other hydrates like C-S-H gel and hydrated aluminates within the cement paste to form water soluble calcium and aluminium salts, enhancing the porosity and leads to reduction in the mechanical strength. As the salts formed are highly soluble, there are no protective cover formed on to the surface of the specimen to prevent further ingress of acid into the matrix and this quickens the degradation process. This reinstates the need to investigate the effect of acetic acid further. Moreover, as hydrates in conventional cementitious systems offer less resistance, the acid resistance of geopolymer (GP) composites is explored in the current study.

GP are inorganic polymers that are recognized as an alternative for conventional OPC system with regard to reducing CO₂ emissions. They are generally considered as a subset of alkali activated binder system and are amorphous in nature rather than crystalline. In alkali activated binder systems, alkali activation of a solid aluminosilicate produces a hardened binder which is based on a combination of hydrous alkali-aluminosilicate and/or alkali-alkaline earth-aluminosilicate phases [12, 13]. On the other
hand, Geopolymerization is the reaction taking place within the GP systems. It is an exothermic reaction between silica (Si)-alumina (Al) under alkaline condition thereby subsequently creating three-dimensional polymeric chain of Si-O-Al-O bonds. The structural integrity of GP systems relies on alumina-silicate rather than calcium silicate hydrate bond in traditional OPC based systems [14, 15]. Sodium aluminosilicate hydrate (N-A-S-H) (FA based system) or calcium aluminate hydrate silicate (C-A-S-H) (GGBS based system) or a combination sodium calcium aluminium silicate hydrate (N-C-A-S-H) gel are the main reaction products of the alkali-activated aluminosilicates [16]. When there is a disequilibrium in a geopolymer - acid environment, the ion exchange reaction proceeds in between the cations and hydronium ions and are then consecutively followed by an electrophilic attack of acid protons on Si-O-Al-O bonds. The sodium ions on exposure to acid, act as charge compensation cations for the aluminosilicate framework, are leached out and exchanged by hydronium ions from the solution. Also, the atomic ratio of Si-to-Al peaks up, designating the dissolution of tetrahedral Al from the aluminosilicate framework by breaking the Si-O-Al bond [14, 16, 17]. Again, with a decrease in CaO content, the acid resistance of the binder gel is found to increase i.e. C-S-H < C-A-S-H < N-A-S-H [18]. Acid attack itself is still an infant area of research. Moreover, the literature investigations highlighting the post effects of organic acids such as acetic acid on geopolymer systems are rather limited and hence these aspects are explored in the findings reported in this paper.

3. Experimental program
3.1. Materials
The precursors utilized in the current investigation include Class F fly ash (FA), Slag (GGBS) and red mud (RM). Ordinary Portland Cement (OPC) 53 Grade is taken to be the control mix. RM was procured as wet sludge from HINDALCO, Belgaum. It was then oven dried at 100°C for 24 hours. Later the oven dried RM was put into Los-Angeles abrasion machine for 1000 revolutions to attain the required fineness. Alkaline activators, sodium hydroxide (10M) and sodium silicate solution were adopted with Alkali silicate/Alkali hydroxide ratio as 2.5. The admixture utilized is Sulphonated Napthalene Formaldehyde (SNF) superplasticizer with 3% by weight of binders for the geopolymer mixes. Paste sample size adopted is cylindrical having 25 mm in diameter and 50 mm in height. The control mix was prepared using distilled water with water to cement ratio of 0.50. GP mixes were prepared with alkali/binder ratio of 0.50.

3.2. Mixing, casting, curing and testing procedures
The mixes adopted are OPC, FGP (100% FA), SGP (100% GGBS), FSGP (50% GGBS + 50% FA), RFGP (50% FA+ 50% RM) and RSGP (50% GGBS + 50% RM). The mixing was done using Hobart mixer. The plastic moulds were oiled. Filling of the paste into the moulds were done manually with tamping. After casting, specimens were kept for 24 hours in atmospheric conditions for initial set before demoulding. For OPC mix, lime solution curing was done for 14 days to maintain the alkalinity and to ensure that no degradation reaction takes place with an alteration in the pH level. A 14 days air (ambient) curing was done for SGP, FSGP and RSGP specimens. FGP and RFGP specimens were oven cured at 70°C for 24 hours and then air cured for 14 days. No chemical admixture was used for the preparation of OPC mix investigated in the current study. To investigate the resistance of GP and OPC based systems to acetic acid attack, paste samples prepared are submerged completely in acetic acid solution of 0.125M and 0.25M concentrations for 8 weeks. The samples were visually monitored and their mass change, thickness change and pH variation of the solution was also recorded periodically. The acid solution was replaced once in two weeks to maintain the aggressiveness of the solution and to sustain the attack.

4. Results and discussions
4.1. Visual appearance
The extent of deterioration can be visually explored by taking digital photographs on a regular basis. Figure 1 showcases the photographs of specimens after 8 weeks of exposure in various concentrations of acetic acid solution. When specimens were closely observed, there is no formation or deposition of insoluble precipitate/products on the surface of the specimen. On comparing the intensity of
degradation with the concentrations of acids for all the binders, more damage was observed in the case of 0.25M acetic acid than 0.125M acid solution.

| Visual appearance | OPC | FGP | SGP | FSGP | RFGP | RSGP |
|-------------------|-----|-----|-----|------|------|------|
| Before immersion  | ![OPC image] | ![FGP image] | ![SGP image] | ![FSGP image] | ![RFGP image] | ![RSGP image] |
| Acetic acid 0.125M| ![OPC image] | ![FGP image] | ![SGP image] | ![FSGP image] | ![RFGP image] | ![RSGP image] |
| Acetic acid 0.250M| ![OPC image] | ![FGP image] | ![SGP image] | ![FSGP image] | ![RFGP image] | ![RSGP image] |

**Figure 1.** Visual observation of specimens immersed in various concentrations of acetic acid after 8 weeks of exposure.

This behaviour may be attributed to the fact that aggressiveness increases due to the increase in concentration. Again, on comparing the various mixes, extreme colour variation is found to be more predominant in OPC specimen on comparison with other mixes. This may be due to the reaction of acetic acid with Portlandite and C-S-H gel to form water soluble calcium acetate monohydrate which leaches to the solution leaving amorphous silica gel on the specimen, thereby causing disintegration of the internal microstructure and brown colour formation on the specimen. Visual examination of RSGP and RFGP specimens is difficult because these are originally rich red in colour even before the onset of exposure. Again, FGP and FSGP specimens did not depict extreme colour variations even after 8 weeks exposure.

### 4.2 Mass changes

On a weekly basis, mass changes (in saturated but surface dry condition) are calculated with respect to the initial saturated mass (noted before the acid exposure). The average of the mass changes of three specimens were calculated. The change in mass of the specimens with age of exposure in acid solution is shown in Figure 2. From the graph, it can be seen that there is a continuous decrease in the mass of all specimen in acetic acid medium irrespective of the medium concentrations. The continuous mass loss may be due to leaching of soluble salts formed as the reaction product. The mass loss prove that the intensity of degradation was high, deteriorating the inner layers by penetration of acid through the pores of the specimens.
Figure 2. Mass change of mixes in various concentrations of acetic acid solution.

The decrement in mass is due to the formation of water-soluble calcium acetate which leaches to outside solution, leading to increase in the inherent porosity within the specimen and thus leading to mass loss. OPC specimens appears to have the highest mass loss in both acid medium with highest loss of about 2.17% in 0.125M and 6.12% in 0.25M acetic acid medium. Clearly RFGP mix showed improved resistance than RSGP and FSGP mix too. This is due to the presence of enhanced N-A-S-H gel and low calcium content within the RFGP mix. GP systems exhibited lower mass loss than OPC mix in acetic acid medium for both concentrations. This is as a result of the difference in the chemistry of GP system, as there are no less stable hydrates such as Portlandite and CSH gel in GP systems. Mass loss has a profound increase with regard to higher concentrations of acid medium i.e. from 0.125M to 0.25M. This is due to the increased concentration gradient that exists between the acid solution and the pore solution of the matrix causing higher rate of diffusion of acid ions into the matrix at higher concentrations of acid.

4.3. Thickness changes

The diameter changes were recorded with a digital Vernier caliper to understand the kinetics of degradation. Readings were taken at every 7 days interval. Figure 3 shows the thickness loss of mixes with respect to time in 0.125M and 0.25M acetic acid solution.

Figure 3. Thickness loss of mixes in various concentration of acetic acid solution.
There is a continuous decrease in the diameter of all specimens in acetic acid medium irrespective of the medium concentrations. This coincides with the mass loss findings. OPC specimens seem to have the highest thickness loss in both acid medium with highest loss of about 1.54% in 0.125M and 2.24% in 0.25M acetic acid medium. Furthermore, FGP mixes have lower loss in both acid media i.e. 0.68% in 0.125M and 0.87% in 0.25M acetic acid medium. Among the GP mixes SGP is found to have the highest loss due to the presence of larger calcium content in its C-A-S-H gel unlike the other GP systems that consist of N-A-S-H or N-C-A-S-H gel that are found to be more stable in lower pH environment.

4.4. Changes in pH
Measuring pH of the solution gives an idea about the hydrogen ion consumption of a particular binder system. The reaction of acid solution with various phases of cementitious system tends to release Ca$^{2+}$ and OH$^{-}$ ions to the solution, thereby increasing the pH of the acid solution with age. Here, the initial pH of 0.125M and 0.25M acetic acid medium are 3.26 and 2.72 respectively. The cyclic plots depicting increase in pH after every 14 days of exposure each time back to pH values of fresh acid solution are shown in Figure 4. There is a rapid increase in pH for the first week on contrast to the initial pH for all the acid medium due to the rapid neutralization process. The pH increase of acid medium of OPC mix is found to be higher on comparison with the GP mixes. This is due to leaching of calcium from the hydrates and subsequent release of hydroxyl ions to the solution. The pH rise was found to be lowest for FGP mix and this is in alignment with the mass loss measurements. As concentration of acid increases, the kinetics of degradation was found to increase in a rapid rate.

![Figure 4. Changes in pH of acetic acid solution of different concentrations with age of exposure.](image)

5. Conclusions
The increased proliferation of industries has led to the large-scale generation of untreated effluents being acidic in nature. This has led to severe degradation of concrete structures made with OPC on contact with the acidic solutions and this demands a study on the acid resistance of alternative materials and composites. This paper has presented the results and discussion of an accelerated leaching study carried out to investigate and compare the resistance of GP and OPC paste systems to silage effluent attack caused primarily by acetic acid for an exposure period of 8 weeks.

OPC paste specimens appears to have the highest mass loss (6.12% in 0.25M) and thickness loss (2.24% in 0.25M) even in higher concentration of acetic acid medium. RFGP mix manifested improved acetic acid resistance than RSGP and FSGP mix. Accordingly, red mud (RM) material can
be adopted as a binder or partial replacement for OPC as it promises both durability and sustainability from the preliminary results. The leaching of soluble salts formed as the reaction product are held accountable for the continuous mass loss and thickness loss in all the mixes. FGP delineated enhanced performance on resisting acetic acid attack. Thereby, from the overall assessment GP paste samples have increased acetic acid resistance when compared with OPC paste samples. Nevertheless, evaluating degradation kinetics based on only mass change/thickness change parameter are not admissible. Microstructure studies are recommended to explore the actual degradation mechanisms to understand the phenomena better.

The kinetics of degradation was more profound in the case of higher concentration of acids and the long-term effects can be observed from it. The degradation rate seems to rely on the concentration of acid, chemical composition of binders, solubility and characteristics of the salts formed. Again, this study is recommended to be carried on mortar and concrete specimens for a superior understanding of the real-life scenario. Evolution of test methods, studying the mechanism of acid attack, modelling of kinetics and examining the out turn of mixture of acids are some of the further research works that needs to be delved for the broader understanding of acid attack.

6. References

[1] Ramaswamy K P and Santhanam M 2017 Durability of cementitious materials in acidic environments: Evaluation of degradation kinetics 14th International Conference on Durability of Building Materials and Components (DBMC), University of Ghent, Belgium, 1–14

[2] Ramaswamy K P, Bertron A and Santhanam M 2017 Additional insights on the influencing factors and mechanism of degradation due to acid attack: Special case of acids forming soluble salts Proceedings of International Conference on Advances in Construction Materials and Systems (ICACMS), Chennai 4 279–290

[3] Bertron A, Alexander M G and De Belie N 2013 Performance of Cement-Based Materials in Aggressive Aqueous Environments State-of-the-Art Report RILEM TC 211 – PAE 131-173

[4] Dogangun A, Karaca Z, Durmus A and S ezen H 2009 Cause of Damage and Failures in Silo Structures Journal of Performance of Constructed Facilities 23(2) 65-71

[5] Larreur-Cayol S, Bertron A and Escadeillas G 2011 Degradation of cement-based materials by various organic acids in agroindustrial waste-waters Cement and Concrete Research 41 882-892

[6] Pacheco-Torgal F, Abdollahnejad Z, Camoes A F, Jamshidi M and Ding Y 2012 Durability of alkali-activated binders: a clear advantage over Portland cement or an unproven issue? Constr. Build. Mater. 30 400–405

[7] Arhina P D, Nuamah R A, Tuffoura B A, Obadac D O and Awaso A Y 2017 Bauxite red mud-Cement based composites: Characterisation for pavement applications Case Studies in Construction Materials 7 45–55

[8] Deb P S, Nath P, Sarker P K 2014 The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature Mater. Des. 62, 32–39

[9] Li Y, Min X, Ke Y, Liu D and Tang C 2019 Preparation of red mud-based geopolymer materials from MSWI fly ash and red mud by mechanical activation Waste Management 83 202–208

[10] Dyer T 2016 Influence of cement type on resistance to organic acids Magazine of Concrete Research 69(4) 175-200
[11] Bertron A, Larreur-Cayol S and Escadeillas G 2009 Degradation of cementitious materials by some organic acids found in agro industrial effluents *Proceedings of the RILEM TC 211-PAE Final Conference* Toulouse France 1 96-107

[12] Provis J L 2018 Alkali-activated materials *Cement and Concrete Research* 114 40-48

[13] Provis J L and Deventer S J V 2009 Geopolymers Structure, processing, properties and industrial applications *Woodhead Publishing Limited and CRC Press LLC.*

[14] Stephan D, Firdous R, Noël J and Djobo Y 2018 Natural pozzolan based geopolymers: A review on mechanical, microstructural and durability characteristics *Construction and Building Materials* 190 1251-1263

[15] Lodeiro G, Palomo A, Fernández-Jiménez A and Macphee D E 2011 Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na$_2$O–CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O *Cement and Concrete Research* 41 923–931

[16] Aiken T A, Sha W, Kwasny J and Soutsos M N 2017 Resistance of geopolymer and Portland cement-based systems to silage effluent attack *Cement and Concrete Research* 92 52-65

[17] Gu L, Bennett T and Visintin P 2018 Evaluation of accelerated degradation test methods for cementitious composites subject to sulphuric acid attack; application to conventional and alkali activated concretes *Cement and Concrete Composites* 87 187-204

[18] Gu L, Bennett T and Visintin P 2019 Sulphuric acid exposure of conventional concrete and alkali activated concrete: Assessment of test methodologies *Construction and Building Materials* 197 681-692