Mechanical properties of alkali-activated mortar in organic acid environment

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Abstract. Ingression of acid into the concrete results in early degradation by microstructural alteration of phases leading to mass changes, weakening of mechanical properties and increase in porosity due to calcium leaching. This paper discusses the resistance of geopolymer composites (GP) and conventional concrete system (OPC) in 0.125M and 0.25M concentrations of acetic acid medium by investigating the changes in the mechanical properties of mortar. The results of the study reveal that the GP samples display increased resistance to acetic acid attack not only in terms of mass and strength loss but also with reference to the variation in ultrasonic pulse velocity and relative dynamic modulus of elasticity. The results also manifest that blends of ground granulated blast furnace slag (GGBS) and fly ash (class F) (FA) with red mud (RM) offer increased acid resistance due to the nature of the main binder gel produced in GP systems.

1. Introduction
Proliferation of agriculture and food industries like breeding, sugar and dairy industries produce large quantities of effluents that are major sources of organic acids. Concrete, being an extensively used construction material worldwide, often comes in contact with these untreated effluents and the organic acids in the effluents will eventually deteriorate the concrete structures. The interaction of these complex organic acids with the concrete structures leads to serious premature degradation of concrete matrix and thereby affects the durability of the structure.

Effluents such as liquid manure, silage effluents, winery wastewaters from the distillery and fermentation industries contain predominant organic acids like acetic, lactic, citric, butyric and tartaric acids, the pH of which is around 4.5 generally [1,2]. The silage acids namely acetic and lactic acids present in the silage effluents cause deterioration of conventional cast-in-place and precast concrete silos [3]. These acids react with the cement matrix and reduce the strength of the silo wall prompting the buckling of walls and eventually lead to failure. Majority of the previous research has focused on the degradation of concrete in the presence of inorganic acids. Only limited studies have reported the effect of organic acids on concrete structures. Regardless of organic acids being weak acids, its partial dissociative
nature can destroy the alkaline concrete matrix. These acids instigate the corrosion of installed reinforcement demanding maintenance and repair, thereby disrupting the production facilities.

Concrete with Ordinary Portland Cement (OPC) has been reported to be less resistant to 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% [4]. 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.

According to the Brazilian NBR 10004 standards, 66 million tons of red mud (RM) is produced annually across the world and it has been labeled as a hazardous pollutant [5, 6]. 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. Geopolymer composites (GP) system is an innovative technology that adopts the industrial solid wastes such as class F-fly ash (FA), ground granulated blast furnace slag (GGBS) and RM as raw material to form a 3D network of cementitious materials under alkaline conditions through polymerization [7]. Performance of alkali activated GGBS and FA against inorganic acids has been individually assessed by many authors. The organic acid resistance of these two binder types has not received much attention. This paper investigates the resistance of GP materials in acetic acid solution based on the study of degradation kinetics. The degradation kinetics was studied by monitoring the changes in the physico-mechanical properties of mortar specimens.

2. Mechanism of degradation by organic acids
Concrete being highly alkaline in nature has a pH around 12. In contact with acidic environment, the pH of the matrix decreases and the equilibrium of cement matrix get disturbed. The hydration products then undergo decomposition leading to severe degradation in the properties of the material. This basic mechanism of deterioration due to acid attack is acidolysis. In the case of organic acid attack, there is potential of two more mechanisms to happen simultaneously. Of the two other mechanisms, the first one is complexolysis, where the complexes are formed from the reaction between acid ions and metal ions extracted during the acidolysis phase. As a result, more of the solid phase is dissolved within the acid solution. The latter mechanism is the precipitation of expansive reaction products that is prominently significant when the salt product with a higher molar volume replaces the hydration products within the matrix and thus results in expansion and cracking [8, 9].

The rate of degradation of concrete system is influenced by the aggressiveness of the attacking acid which depends on numerous factors like the solubility of the salts, acid dissociation constant (pKa), mono/poly-acidity of the acids and the physical properties of the salts formed. Also, the alteration kinetics is influenced by these salts that may either precipitate or leach out depending on its solubility in the acid solution. While considering organic acids with soluble salts, the relative combativeness of the acids seems to be primarily influenced by the pKa of the acids. However, for organic acids with insoluble salts the relative aggressiveness is dominated by the poly-acidity factor [8, 9, 10]. The reaction of cement-based materials in acetic acid is comparable to that of strong acids like nitric acid or hydrochloric acid. Acetic acid, generally termed as a weak monocarboxylic acid, stimulates the dissolution of the calcium hydroxide present in concrete which gets leached away exposing fresh concrete surface to acid attack [10]. On reaction of acetic acid with C-S-H gel and aluminates, water soluble calcium and aluminum salts are formed, paving the way for increase in porosity of the matrix and reduction of mechanical strength. The rate of degradation by reaction with acetic acid proliferates at a rapid rate as no protective layer is formed on the external surface of specimens. This instates the need to investigate the effect of acetic acid further.
Moreover, as hydrates in conventional cementitious systems offer less resistance, the acid resistance potential of geopolymer (GP) composites as an alternative material is to be explored.

GP are prominently known to be the subset of alkali activated binder system which are amorphous in nature rather than crystalline [11, 12]. Geopolymerization is the sole reaction taking place within the geopolymer system unlike other alkali activated systems. This process is an exothermic reaction where reaction takes place between silica (Si)-alumina (Al) under alkaline condition which subsequently create three-dimensional polymeric chain of Si-O-Al-O bonds. The aluminium silicate bond influences the structural integrity of GP systems unlike the calcium silicate hydrate bond [13, 14]. 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 calcium aluminium silicate hydrate (N-C-A-S-H) gel are the main reaction products of the alkali-activated aluminosilicates [15]. On exposure to acid, an electrophilic attack of acid protons on Si-O-Al-O bonds is found. The sodium ions that act as charge compensation cations of the aluminosilicate framework, are leached out in exchange with hydronium ions from the solution. The atomic ratio of Si-to-Al is then found to increase, evidently indicating that the tetrahedral Al from the aluminosilicate framework is dissolved completely by breaking the Si-O-Al bond [13, 15, 16]. The acid resistance is found to increase with a decrease in CaO content, i.e., the resistance of C-S-H < C-A-S-H < N-A-S-H [17]. Acid attack itself is still an infant area of research. Moreover, the investigations on the effect of organic acids such as acetic acid resistance of geopolymer systems are rather limited and hence these aspects are explored in the present study.

3. Experimental program

3.1. Materials

The precursors used in the current investigation include FA (class F), GGBS and RM. Ordinary Portland Cement (OPC) 53 Grade is used in the control mix. RM, procured as wet sludge from HINDALCO, Belgaum, was oven dried at 100°C for 24 hours. Later, the oven dried RM was subjected to 1000 revolutions in the Los-Angeles abrasion machine 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. Sulphonated Napthalene Formaldehyde (SNF) superplasticizer with 3% by weight of binders was used for the geopolymer mixes. Mortar ratio for mix design is maintained as 1:1.5 (binder: sand). Cylindrical moulds having 25 mm diameter and 50 mm height were used to prepare the specimens. The control mix was prepared using distilled water with water to cement ratio of 0.50. GP mix was prepared with Alkali/Binder ratio of 0.50. Manufactured sand (finer than 2 mm) was used in the mortar specimens as fine aggregates.

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 and filling of mortar into the moulds were done manually with tamping. After casting, specimens were kept for 24 hours in atmospheric conditions for the initial set. 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. 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, the mortar samples prepared were submerged completely in acetic acid solution of 0.125M and 0.25M concentrations for 8 weeks. The samples were monitored visually and their mass change, compressive strength, altered depth
and ultrasonic pulse velocity variation were 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. No formation or deposition of insoluble precipitate/products on the surface of the specimen was observed. 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 solution. This behaviour may be attributed to the fact that aggressiveness increases due to the increase in concentration. Again, on comparing the binders, extreme colour variation is found to be more predominant in OPC specimen. 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 causing brown colour formation and thereby causing disintegration of the internal microstructure. Visual examination of RSGP and RFGP specimens is difficult because these are rich red in colour even before the onset of exposure. Notably, FGP and FSGP specimens did not depict extreme colour variations even after 8 weeks of exposure.

| Visual appearance | Binder system |
|-------------------|--------------|
| Before immersion  | OPC | FGP | SGP | FSGP | RFGP | RSGP |
| Acetic acid 0.125M| OPC | FGP | SGP | FSGP | RFGP | RSGP |
| (after immersion) | Acetic acid 0.250M | OPC | FGP | SGP | FSGP | RFGP | RSGP |

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

4.2 Mass changes

On a weekly basis, mass changes (in saturated but surface dry condition) with respect to the initial saturated mass (noted before the acid exposure) was determined. The average of the mass changes of three specimens was calculated. The change in mass of the specimens with age of exposure in acid solution is
shown in Figure 2. Typical graphs of the six mixes, i.e., OPC, FGP, SGP, FSGP, RFGP and RSGP on exposure to different concentration of acetic acid medium is represented in Figure 2.

![Figure 2. Mass loss of mixes in various concentrations of acetic acid solution.](image)

From Figure 2, 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 proves that the intensity of degradation was high, the inner layers getting deteriorated by penetration of acid through the pores of the specimens. The decrease in mass is due to the formation of water-soluble calcium acetate which leaches out, leading to increase in the inherent porosity within the specimen and thus leading to mass loss. OPC specimens seems to have the highest mass loss in all acid medium with highest mass loss of about 5.90% in 0.25M and 1.85% in 0.125M acetic acid medium. On the contrary, FGP mixes have lowest mass loss in all acid medium, with a maximum of 1.41% and 0.48% mass loss in 0.25M and 0.125M medium respectively. This is due to presence of enhanced N-A-S-H gel and low calcium content within the FGP mix. Clearly RFGP mix showed improved resistance than RSGP and FSGP mix. The chemistry of GP system is different as there are no less stable hydrates such as Portlandite and CSH gel. Mass loss is found to increase in higher concentrations of acid medium. 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. Moreover, the variation of mass loss could be approximated to be linearly varying with the age of exposure.

4.3. Strength changes

The compressive strength was measured for all specimens on a weekly basis using a modified digital compression testing machine with a specially fabricated test rig. Initial compressive strength for OPC, FGP, SGP, FSGP, RFGP and RSGP are found to be 45.06, 20.50, 48.68, 26.70, 18.60 and 37.05 N/mm². SGP specimens are found to have higher strength than all mixes. The strength loss of mixes with respect to age of exposure in two acetic acid medium concentrations is presented in Figure 3.
After 8 weeks of immersion, all mixes showed a significant loss in strength with time. However, OPC specimens showed the highest strength loss in all acid medium in spite of having good initial strength. Loss of strength for OPC mix varies from 33.60% in 0.125M medium to 48.86% in 0.25M medium. The calcium hydroxide being least stable in OPC system has been attacked by the acetic acid causing dissolution and leaching of calcium into solution. The dissolution of calcium hydroxide results in an increased porosity and contributes to a rapid decrease in compressive strength [18]. The FGP mix showed the lowest strength loss for both concentrations ranging from 21.3% in 0.125M acetic acid medium to 32% in 0.25M acetic acid solution. Although, the initial strength showcased by FGP is the lowest, its retainment of strength (residual strength) with regard to time and concentration seems to be more profound than all other mixes. These observations are in agreement with the mass loss where the OPC specimens also suffered larger mass losses when compared to GP mixes.

4.4. Altered depth

Altered depth is defined as the depth directly affected due to acid attack and is considered as a prime indicator of degradation kinetics. This can be estimated as the sum of depth of erosion and depth of reaction. The depth of reaction can be determined by spraying phenolphthalein solution to a freshly fractured surface of mortar specimens, and by measuring the depth of colorless layer in the specimen. Phenolphthalein changes from colorless to pink in the pH range of 8.2 to 10.0 [19]. The depth of erosion is deduced from the difference of diameter of specimens before and after exposure (at specific ages of exposure). The cross-section of specimens before and after acid attack is shown in Figure 4. The pink colour region after application of phenolphthalein solution shows the regions unaffected by acid exposure.

![Figure 3. Strength change of mixes in various concentration of acetic acid solution.](image)
Figure 4. Altered depth variation of mixes after 8 weeks of exposure in acetic acid medium.

From Figure 4, on keen observation, it can be concluded that the altered depth increased at a higher rate on exposure to 0.25M acid medium. For an elaborate understanding, a plot of altered depth of mixes in various concentrations with respect to the exposure age is plotted and shown in Figure 5. The depth of penetration is seen to be higher for FGP mix when compared to OPC and other GP mixes.

Figure 5. Altered depth variation of mixes with age of exposure in different concentrations of acetic acid solution.
The FGP mix depicted the maximum depth of 10.62 mm in 0.25M and 5.93 mm in 0.125M acetic acid medium. On the contrary, the altered depth of OPC is determined to be the least, i.e., 5.57 mm in 0.25M and 3.13 mm in 0.125M acetic acid medium. Out of all GP mixes, the SGP mix showed the least altered depth in both concentrations of acetic acid solution. The lower altered depth in OPC may be ascribed to the additional calcium buffer available in OPC systems. Nevertheless, the relationship between the rate of advancement of the depth and time had a nonlinear nature [18]. It is concluded that the altered depths in geopolymer systems are higher despite the mass and strength losses being on the lower side when compared to OPC.

4.5. Ultrasonic Pulse Velocity (UPV) test

UPV test is a non-destructive test conducted to check the strength and microstructural quality of cementitious systems. This test enables us to determine the concrete uniformity, the presence of internal flaws and voids within the concrete specimens [19]. In the current study, the test was conducted once in two weeks with regard to the concentration of the acid medium. The difference in the UPV of specimens before and after exposure (8 weeks) in acetic acid solution is shown in Table 1. Among all mixes, the initial pulse velocity (measured just before exposure) was highest for SGP mix. But the initial pulse velocities of remaining GP mixes are lower compared to OPC mix. Higher velocities indicate good quality and continuity of the material, unlike lower velocities that indicates the presence of cracks or voids within the concrete. There is a significant decrease in pulse velocities of all mixes with exposure in both concentrations of acetic acid (0.125M and 0.25M). This indicates the progression of microstructural degradation within the concrete thereby increasing the voids or micro cracks within the structure. The outer zone is degraded probably owing to the formation of silica gel which has weak mechanical properties. The rate of decrease of pulse velocity increases for all mixes in higher concentration (0.25M) than in lower concentration (0.125M) of acetic acid.

| Mix   | Ultrasonic Pulse Velocity (km/sec) | Before immersion | Acetic acid 0.125M | Acetic acid 0.25M |
|-------|-----------------------------------|-----------------|-------------------|------------------|
| OPC   | 4.12                              | 3.59            | 3.07              |
| FGP   | 3.34                              | 2.98            | 2.76              |
| SGP   | 4.39                              | 3.73            | 3.35              |
| FSGP  | 3.36                              | 2.89            | 2.67              |
| RFGP  | 3.20                              | 2.84            | 2.64              |
| RSGP  | 3.69                              | 3.25            | 2.99              |

Based on the UPV values, the dynamic modulus of elasticity of specimens can be determined as per IS 13311 (Part 1): 1992 codal provisions. As the Poisson’s ratio of the individual specimens is not known, the variation is expressed in terms of relative dynamic modulus of elasticity (E_{RD}) and is showcased in Figure 6. The relative dynamic modulus of elasticity is computed as the ratio of the dynamic modulus of elasticity of specimens at a particular age of exposure to the dynamic modulus of elasticity measured just before the exposure.
The $E_{RD}$ of OPC mix after 8 weeks of exposure was found to be 0.52 in 0.25M and 0.65 in 0.125M. The drop in the relative dynamic modulus of elasticity indicates the severity of degradation. The results indicate that the loss in dynamic modulus was highest in OPC mix. This correlates well with the strength and mass loss measurements. For FGP mix, the $E_{RD}$ was 0.67 in 0.25M and 0.78 in 0.125M. Again, from the RM based GP mix, RFGP mix shows enhanced performance than RSGP mix. Thereby, with reference to the variation in UPV and $E_{RD}$, GP systems depicted superior performance in resisting acetic acid attack than OPC system in both concentrations of acetic acid.

5. Conclusions
A comprehensive experimental study was conducted to investigate the degradation kinetics and compare the resistance of GP and PC systems to silage effluent attack caused primarily by acetic acid for an exposure period of 8 weeks. Accelerated leaching test method was adopted for the study by selecting smaller sized specimens and frequent replenishment of acid solutions. There is a continuous decrease in mass, strength and dynamic modulus of elasticity due to the formation of water-soluble calcium acetate which leaches out, leading to increase in the inherent porosity within the specimen. OPC system has the highest mass loss (5.9%), strength loss (48.6%), and lowest relative dynamic modulus of elasticity (0.52) at higher concentration (0.25M) of acetic acid.

After 8 weeks of exposure to 0.25M and 0.125M acetic acid solution, FGP mix showed the least mass loss and strength loss. However, the altered depth was higher for FGP mortar samples in 0.125M and 0.25M acid medium unlike OPC which had the least altered depth. Therefore, evaluating degradation kinetics based on only one parameter i.e. either mass loss or altered depth is not suggested. New parameters are to be defined which captures both changes in the physio-mechanical properties and deterioration in microstructure. RFGP mix showed improved acetic acid resistance than RSGP and FSGP mix. Accordingly, RM material can be adopted as a binder or partial replacement for OPC as it promises both durability and sustainability for exposure to lower concentrations of acid solutions. Similarly, with
regard to the variation in UPV and $E_{\text{RD}}$, GP systems delineate enhanced performance in resisting acetic acid attack than OPC system in both concentrations. Thereby, from the overall assessment, GP mortars have increased acetic acid resistance when compared with OPC samples.

The kinetics of degradation was more profound in the case of higher concentration of acids and the long-term effects can be observed by conducting an accelerated leaching test. The rate of degradation is found to be dependent on the concentration of acid, chemical composition of binders, and solubility and characteristics of the salts formed. The difference in behaviour between paste, mortar, and concrete has to be studied further, focusing on the role of interfacial transition zone in the durability of binder systems, in aggressive acidic environments.

6. References

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