Degradation kinetics of alkali-activated mortar in aggressive citric acid environment

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Abstract. Acid attack is a complex phenomenon arising in construction industries worldwide as it is responsible for the deterioration of concrete in acidic environments resulting in premature degradation with regard to mass changes, weakening of mechanical properties, and increase in porosity due to calcium leaching. This paper investigates the citric acid resistance of geopolymer composites (GP) and its comparison with conventional concrete system (OPC) in lower and higher concentrations of acid medium. The GP samples displayed increased resistance to citric acid attack than OPC system in terms of mass and strength loss. It was also found that geopolymer mortar made with a blend of ground granulated blast furnace slag (GGBS) and red mud (RM) offered increased acid resistance based on the parameters studied in the degradation kinetics.

1. Introduction
Concrete has been one of the most versatile materials adopted in the construction of key infrastructural components like sewerage pipes, industrial floors and foundations, water treatment facilities and many more. These infrastructural elements are easily deteriorated over the years when in contact with an acidic environment. Since high alkalinity is mandatory for the stability of the cementitious matrix, concrete is prone to attack by acidic media which affects the pH of the pore solution, that tends to crumble the hydrated cement paste to different levels based on the predominant exposure condition and some mixture design parameters of concrete. Numerous industries still rely on measures that create effluents or wastewater. Such effluents hold a wide variety of inorganic and organic acids whose activity may prompt extreme and quick deterioration of cementitious structures. Understanding the alteration kinetics and mechanisms of degradation of concrete by these aggressive media is a fundamental step towards making a durable concrete, which will then increase the service life of the concrete form.

Organic acids are naturally found in the farming products or as intermediary or final products of the metabolism of microorganisms growing within the effluents. Food and drink industries also produce large amount of organic acids. Alcoholic beverages contain lactic acid, while pharmaceutical industry uses citric acid. Concrete structures in cattle milk sheds degrade because of lactic acid attack combined with abrasive action of animals. Liquid manure also contributes to a wide variety of organic acids, including butyric, propionic, acetic, iso-butyric acids etc. and concrete structures used to store manure are prone to attack by these acids.

Among the agro-food effluents, whey water from the dairy industry contains acetic, lactic and citric acids. Molasses which has malic, lactic, acetic, oxalic, succinic and citric acids are produced by sugar
industry. The fermenting business effluents mainly contain acetic, tartaric and succinic acid. The factors such as the binders used, acid type and test methods seem to influence the degradation of cementitious materials by acids [1]. Underlining the exact mechanism of deterioration is not yet inferred. Therefore, thorough investigations are required to understand the actual mechanisms involved in the deterioration process to propose a durable binder system.

Generally, cementitious materials are said to be in disequilibrium with an acidic environment due to the inherent alkaline nature of its pore solution. Concrete with OPC is reported to be less resistant to these acidic media. Moreover, the use of OPC is discouraged nowadays as its production contributes alarmingly to carbon dioxide emissions and thus global warming [2]. As we strive towards achieving sustainable development, replacement of cement-based systems with alkali activated/ geopolymer (GP) composites can be considered as a viable alternative for cementitious materials exposed to aggressive acidic environments. This also paves the way to utilize industrial wastes as a precursor binder material in the production of alkali activated binder systems. One such unused and untapped waste is red mud which is generated during the production of alumina in aluminium industry.

Around 35-40% of the processed bauxite mineral is deposited as an alkaline red mud slurry comprising 0.8-1.5 tons of red mud and 15-40% solids that are developed per ton of alumina produced [3]. It is assessed that every year, 70 million tons of red mud is manufactured worldwide [4]. Red mud is commonly disposed in mud lakes as slurry impoundment or stacked in ponds as dry mud close to alumina plants or straight headed off into the sea. The disposal of untreated red mud has caused genuine natural issues such as groundwater pollution, soil pollution and fine particles suspension in the sea [5,6]. Therefore, the incorporation of such waste materials as an alternative binder material in concrete could enhance the reduction of pollution level across the globe.

Geopolymer system is an innovative technology that utilizes industrial wastes such as red mud (RM), fly ash and ground granulated blast furnace slag (GGBS) as a binder material to produce a 3D system of cementitious materials under alkaline conditions through polymerization [7]. Individually, alkali activated GGBS and fly ash-based composites have been studied by many authors. However, the behaviour of such materials in aggressive acids such as citric acid has not been researched yet. Presently there are no codes or norms accessible for assessing the resistance of the binder constituents to acid attack. From the review of recent literatures on acid attack on concrete, enormous investigations have been done on the impact of inorganic acids on concrete but only a few investigations have concentrated on the impact of organic acids that could be detrimental to the matrix leading to premature deterioration of concrete structures. Therefore, this paper evaluates the degradation kinetics and the resistance of geopolymer composites in citric acid, an acid that is considered as one of the most aggressive organic acids that is detrimental to cementitious systems.

2. Action of organic acids
Concrete is highly susceptible to severe deterioration under acid attack. The essential mechanism behind the decay of cement by acid attack is acidolysis. When acid comes into contact with concrete surface, the hydrates of the concrete reacts with the acid protons, decomposing the hydrates. Other two different mechanisms are additionally discovered to be effective in organic acid attack. First is complexolysis, which happens when complex formation occurs by the reaction of acid ions and metal ions, allowing the dissolution of more of the solid phases. It is considered as a significant mechanism only where the metal ions are in solution because of acidolysis.

The subsequent mechanism is the precipitation of reaction products that are expansive in nature. It happens only when the salts formed by the reaction between metal ions (from hydrates) and the acidic species are of low solvency and are precipitated from the solution. Now, this doesn't have a harming impact, as precipitation may not upset the concrete framework on account of low molar volume salts. When the salt has a higher molar volume than the hydrates it replaces, its precipitation leads to the rupture and defragmentation of the cement matrix [8, 9]. Among the organic acids, the most aggressive and the least investigated acid is perhaps citric acid. Citric acid is a weak organic acid that exhibits poly acidity. Due to the citric acid's chemical nature, it can react with hydrates to produce
calcium citrate salts of low solubility. As the acid is neutralized, the solubility decreases, and the calcium citrate precipitates out, which eventually delaminates from the surface owing to weakening in the acid solution. Moreover, as hydrates of conventional cementitious systems offer less resistance, the acid resistance of geopolymer (GP) composites is explored in the current study.

GP are amorphous in nature and are considered to be inorganic polymers. They are viewed as a subset of alkali activated binder systems [10,11]. Geopolymerization is an exothermic reaction where the reaction happens between silica (Si) - alumina (Al) under the alkaline condition which forms three-dimensional polymeric chain of Si-O-Al-O bonds. The soundness of a geopolymer framework depends on alumina-silicate instead of calcium silicate hydrate in conventional systems [12, 13]. On exposure to acid, the ion exchange reaction between the metal cations and hydronium ions are followed by an electrophilic attack of acid protons on Si-O-Al-O bonds, thereby leaching out the sodium ions that act as charge compensation cations of the aluminosilicate framework. Now, the Si-to-Al increases, highlighting the dissolution of the tetrahedral Al from the aluminosilicate framework by breaking the Si-O-Al bond [12, 14, 15]. It has been established that the durability in acids increased with a decrease in CaO content within the hydrates i.e. N-A-S-H > C-A-S-H > C-S-H [16]. These are the proposed mechanisms and the actual resistance could vary with the changes in the chemical composition of binders and formulation of the mixes. Acid attack itself is still an infant area of research. Moreover, the literature investigations on citric acid resistance of geopolymer systems are rather limited and hence these aspects and findings are presented in this paper. New mixture formulations with red mud are also attempted and the citric acid resistance of mixes is evaluated.

3. Experimental program

3.1. Materials
The precursors used in the current investigation include GGBS and RM. Ordinary Portland Cement (OPC) 53 Grade with a specific gravity of 3.15 is taken to be the control mix. Slag having a specific gravity of 2.90 was used. 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. The specific gravity of red mud was 2.63. Alkaline activators, sodium hydroxide (10M) and sodium silicate solution were adopted with alkali silicate/alkali hydroxide ratio as 2.50. The admixture used is Sulphonated Napthalene Formaldehyde (SNF) superplasticizer with 3% by weight of binders for the preparation of geopolymer mixes. The mortar ratio for mix design is taken as 1:1.5 (binder: sand) by weight. Mortar specimen size adopted is cylindrical specimens having 25 mm in diameter and 50 mm in height. The control mix was done using distilled water with a water to cement ratio of 0.50. GP mixes were prepared with Alkali/Binder (a/b) ratio of 0.50. Manufactured sand (finer than 2 mm) was used as fine aggregates in the preparation of mortar specimens.

3.2. Mixing, casting, curing and testing procedures
The mixes adopted are OPC (control mix) and geopolymer mixes (SGP (100% GGBS), RSGP50 (50% GGBS + 50% RM) and RSGP25 (75% GGBS + 25% RM)). The mixing was done using Hobart mortar mixer. The plastic cylindrical moulds were oiled. Filling of mortar 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 prevent any leaching of metal ions from the matrix. A fourteen days air (ambient) curing was done for SGP and RSGP specimens. Chemical admixture was not used for the preparation of the OPC mix.

Mortar samples were submerged completely in citric acid solution of 0.15M and 0.31M concentrations for a period of 4 weeks to examine the resistance of OPC and GP based systems to citric acid attack. The volume of acid solution to the volume of specimens was kept as 5. The samples were observed visually for the changes, and their altered depth, mass change, pH variation of the solution and compressive strength was also recorded periodically. The acid solution was replaced once
in two weeks with a fresh solution to maintain the aggressiveness of the solution and to sustain the reactions.

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 4 weeks of exposure in various concentrations of citric acid solution.

| Binder       | Visual variation                                      |
|--------------|-------------------------------------------------------|
|              | Before immersion                                      |
|              | Citric acid-0.15 M                                   |
|              | Citric acid-0.3 M                                    |
| OPC          |                                                        |
| SGP          |                                                        |
| RSGP50       |                                                        |
| RSGP25       |                                                        |

![Figure 1](image)

Figure 1. Visual observation of specimens immersed in various concentrations of citric acid after 4 weeks of exposure.

When specimens were closely observed, the formation of a white coloured salt in substantial quantities was observed. This salt was confirmed as calcium citrate tetrahydrate by X-ray diffraction in a similar study done by Ramaswamy and Santhanam [1]. The precipitated salt has low solubility (0.95 g/L), and observed to be non-protective, and loosely stuck to 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 0.31M citric acid than 0.15 M solution. The salt formed does not have a shielding effect on the matrix due to the high molar volume of the salt. More precipitate formation and damage effect was observed on OPC specimens when compared to all the geopolymer mixes. It was also noted that the precipitation formation was lesser at lower concentrations of exposure.

4.2 Mass changes

On a weekly basis, the mass of specimens (in saturated but surface dry condition) were noted with a precise digital weighing balance. The average of the mass of three specimens was then calculated. Mass loss is determined with respect to the initial saturated mass taken before the acid exposure and showed in %. The changes in mass of the specimens with age of exposure to different concentration of citric acid medium are shown in Figure 2.
(a) 0.15M  (b) 0.31M

Figure 2. Mass change of mixes in various concentrations of citric acid solution.

From the graph (Figure 2), it can be seen that there is a continuous decrease in the mass of all specimens in citric acid medium irrespective of the medium concentrations due to the dissolution of cementitious material to form the high molar volume precipitates. The rapid and severe mass loss prove that the intensity of degradation was high, deteriorating the inner layers on progressive exposure. Among the various mixes studied, the RSGP50 mix indicated lower mass loss while the OPC mix indicated the least resistance as the mass loss was higher. OPC specimens seem to have the highest mass loss in all acid medium with highest mass loss of about 35% in 0.31M citric acid medium. These observations are in alignment with the visual observations. On the contrary, RSGP50, RSGP25 and SGP mixes have lower mass loss in all acid medium, with a maximum of 13%, 15% and 18% mass loss in 0.31M medium. It was also observed that the mass loss in 0.15M citric acid was much lesser than 0.31M citric acid.

The severe mass loss and the aggressiveness of the attack may be ascribed to a combination of factors such as non-protective nature and high molar volume of the salt, poly acidic nature and buffer action exhibited by the acid and the high concentration being used for obtaining accelerated results in short span of time. Citric acid is polyacidic as it dissociates to give several protons at their corresponding pKa values of 3.14, 4.76 and 6.40 and this could lead to a sustained attack, if the pH of the solution is the range of pKa values.

4.3. Strength changes

The compressive strength was measured for all specimens on a weekly basis using a modified digital compression testing machine having a capacity of 50 kN. The test was conducted with a start load of 1 kN and stop load at 40%. The loading rate was maintained as 0.5 kN/sec. The initial compressive strength for OPC, SGP, RSGP50 and RSGP25 are found to be 44, 53, 36 and 48 N/mm². SGP have higher initial strength than the other mixes. Similar to mass loss, strength loss was computed based on the strength at particular age of exposure and the initial strength, and expressed as %. The strength loss of various mixes with the period of acid exposure is shown in Figure 3. All the mixes incurred a significant loss in strength with time. Notably, OPC specimens showed the highest strength loss in all acid medium in spite of having good initial strength. Loss of strength for OPC varies from 48% in 0.15M to 55% in 0.31M medium. The calcium hydroxide and CSH gel being least stable hydrates in OPC system might have been decalcified by the citric acid causing leaching and dissolution of calcium ions into the solution to effect the formation of expansive salts. The dissolution of calcium hydroxide and formation of silica gel due to decalcification of CSH gel brings about an increase in the porosity and adds to a rapid reduction in compressive strength [17].
Figure 3. Strength change of mixes in various concentration of citric acid solution.

The RSGP50 showed the lowest mass loss of about 34% in 0.15M and 40% in 0.31M citric acid medium. Although, the initial strength showcased by RSGP50 is the lowest, its retainment of strength with regard to time of exposure and acid concentration seems to be better than OPC, SGP and RSGP25. This is in concurrence with the mass loss where the OPC specimen shows the larger mass losses than all the GP mixes. It is noted that SGP mix also suffered strength loss. This is probably because the microstructure consists also of CASH and/or CSH gel which could be attacked by the acid ions at lower pH.

4.4. Altered depth

Altered depth is defined as the depth directly affected due to acid attack and is considered as a primary indicator of degradation kinetics. This can be estimated as the sum of depth of leaching/erosion and depth of reaction. The depth of reaction was determined by sprinkling phenolphthalein solution to a freshly cut surface of mortar specimens, and by measuring the depth (thickness) of colorless layer in the specimen. The depth of erosion is deduced from the difference of diameter of specimens before and after exposure, noted using a digital vernier caliper. Figure 4 shows the cross-section of specimens before and after citric acid attack. The pink shaded region shows the area which remain unaffected when exposed to acids after the application of phenolphthalein solution whereas the colourless or white regions show the deteriorated zone consisting of silica gel and/or calcium citrate salt.

For an elaborate understanding, altered depth of mortar specimens in various concentrations with respect to the exposure age is plotted and shown in Figure 5. The altered depth is seen to be higher for RSGP50 mix with a depth of 2.16mm when compared to other mixes. The altered depth of OPC in 0.15M medium was 1.78mm and is the least on comparing SGP and RSGP mixes. On the contrary, in the higher concentration i.e. 0.31M medium – OPC mix depicted a depth of 1.82mm. The lower depth in OPC may be ascribed to the additional calcium buffer available in OPC systems. In the case of GP systems, acid may be attacking directly the alumino-silicate gel and the penetration proceeds at a faster rate as measured by the application of phenolphthalein.
Altered depth variation

Before immersion

Citric acid 0.15 M

Citric acid 0.31 M

OPC

SGP

RSGP50

RSGP25

Figure 4. Visual examination of altered depth of specimens in different concentrations of citric acid.

Figure 5. Altered depth variation of mixes with age of exposure in different concentrations of citric acid.

4.5. Changes in pH

Acid attack is a classic example of acid-base reaction to form salt and water. In this neutralization process, ions such as calcium, aluminium from the cementitious framework gets into the reaction with the acid solution. Acid protons are consumed and to maintain the equilibrium, hydroxyl ions are released into the solution causing a rise in pH of the acid solution. Hence, estimating pH on consistent basis could be another measure of the degradation kinetics as it gives a reflection about the hydrogen ion utilization rate or in other words, the neutralization capacity of the system. Here, the initial pH of the 0.15M citric and 0.31M citric acid solutions were 2.06 and 1.97 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 6. There is a rapid increase in pH for the first week compared to the initial pH for the acid. This must be due to the rapid neutralization process when the specimen comes into contact with acid solution. The pH increase of acid medium of OPC mix is found to be higher on comparison with SGP and RSGP mixes. The increased pH could also be one of the reasons for the lowered altered depth in the case of OPC mix. The pH rise was observed to be lowermost for RSGP50 mix suggesting that the attack is possibly lower, and this connects well with the mass loss and visual observations.

![Graphs showing pH change](image)

**Figure 6.** Change in pH of different concentrations of citric acid solution with age of exposure.

### 5. Conclusions

Concrete structures are often exposed to aggressive environments due to growing production of acidic industrial effluents in urban areas. This has led to severe degradation of concrete structures made with OPC in contact with the acidic solutions. There is a need to think of a suitable alternative to OPC system and geopolymer technology utilizing industrial wastes is considered to be a potential solution. This paper has exhibited the results and discussion of an accelerated laboratory study conducted to examine and compare the resistance of geopolymer and OPC mortar systems to deterioration by citric acid. The mass loss for both slag and red mud blended slag geopolymer mixes is lesser than OPC during 4 weeks of exposure to different concentrations of citric acid.

The compressive strength of OPC specimens was found to reduce by 55% after 4 weeks of exposure to 0.31M citric acid solution when compared to 47%, 45% and 40% for the SGP, RSGP25 and RSGP50 samples. However, the altered depth (depth of penetration) was higher for SGP and RSGP mortar specimens in 0.15M and 0.31M acid medium unlike OPC which had the least altered depth. Based on the visual observations, mass loss, and strength loss, the performance of geopolymer mixes were better compared to OPC. Among the geopolymer mixes, the mortar mix containing 50% slag and 50% red mud exhibited superior acid resistance. However, when altered depth is considered, OPC showed greater resistance to attack compared to the geopolymer mixes. More studies with prolonged duration of exposure must be conducted to come up with geopolymer mixture formulations which will have better acid resistance with respect to mass changes, strength loss and altered depth.
6. References

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