

Influence of Mineralogical Nature of Aggregates on Acid Resistance of Mortar

K. P. Ramaswamy

Assistant Professor, Department of Civil Engineering, TKM College of Engineering, Kollam, India.

M Santhanam

Professor, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India.

ABSTRACT

Cement-based materials being alkaline in nature are often subjected to rapid deterioration on exposure to the aggressive acidic environments. Acids penetrate into the cement matrix causing calcium leaching and deterioration of phases leading to alteration in the microstructure. Currently, there are hardly any codes or standards available for evaluating the durability of materials to acid attack. Moreover, the literature addressing the material resistance is quite inconclusive. This paper aims to evaluate the influence of mineralogical nature of aggregates on the degradation kinetics of cement mortar when exposed to inorganic and organic acid solutions by performing a static accelerated leaching test. Cement mortar (1: 3) specimens of size 10 × 10 × 60 mm were prepared using Ordinary Portland Cement (OPC), using limestone (calcareous) aggregates and siliceous aggregates with a water to cement ratio of 0.40. After 28 days of initial curing in saturated lime water, the specimens were exposed to various concentrations of sulphuric (1 % and 3 %) and acetic acid solutions (0.25 M and 0.5 M) for a testing period of 4 months. The acid solution was replenished on a periodic basis to maintain the aggressiveness of the solution. The degradation kinetics was investigated by measuring mass changes, thickness changes, changes in pH of the acid solution and imaging using X-ray micro-tomography. Additionally, periodic abrasive action applied manually (using soft nylon brush) was used to accelerate the degradation process in case of sulphuric acid exposure and its effect was compared with the testing without the abrasive action. An attempt was also made to evaluate the changes in compressive strength and changes in dynamic modulus of elasticity of cylindrical mortar specimens (25 mm diameter and 50 mm height) on exposure to the acid solutions. The test results indicate that the performance of limestone aggregates is better on exposure to sulphuric acid and worse in case of acetic acid when compared to siliceous aggregates.

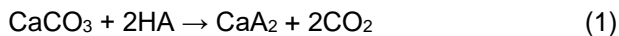
Keywords: acid attack, aggregate, durability, degradation kinetics, cement mortar, micro-tomography

1.0 INTRODUCTION

Concrete structures being alkaline in nature are often subjected to deterioration on exposure to aggressive acidic environments. The range of attacking species is wide and includes accidental spillage and leakage of acids from industries, biogenic acid attack in concrete sewer pipes, agricultural and agro-food effluents, wastewater treatment and biogas plants etc (Allahverdi and Skvara, 2000; Bertron and Duchesne, 2013; Ramaswamy *et al.*, 2017; Ramaswamy and Santhanam, 2017a; Hudon *et al.*, 2011; Larreur-Cayol *et al.*, 2011). Portland cement hydration products are reactive in acids to a great extent. The chemical composition of the hydrated phases (C-S-H, Ca(OH)₂, AF_m and AF_t for hydrated Portland cement) and their proportions inside the matrix – which depend mainly on the composition of the binder (cement and supplementary cementitious materials) – mostly determine the chemical stability of the matrix. Portlandite (Ca(OH)₂) is the most reactive and completely dissociates, while calcium silicates are

less reactive followed by calcium aluminates and calcium aluminoferrites hydrates. A gel layer of mainly acid-insoluble silica (SiO₂.nH₂O) remains on the surface of the cementitious matrix after the departure of calcium from the calcium silicate hydrates. The elements such as Ca, Na, K, Mg leaves the matrix whereas Si, Al and Fe remains, the stability of their bearing phases notably depending on the pH. More precisely, calcium hydroxide dissolves at a pH value of 12.5, followed by ettringite at pH value of 10.7, C-S-H at pH between ~10.5 and 8.8 (according to different authors) and finally calcium aluminate and ferrite hydrates decompose successively until a C-A-S-H gel, in the case of leaching at pH above 7, or a silica gel residue (SiO₂. nH₂O) containing Al and Fe, is obtained at pH between 1 and 6 (Bertron and Duchesne, 2013; Duchesne and Bertron, 2013; Beddoe and Dorner, 2005). These microstructural changes manifest in the form of mass loss, loss in strength and rigidity, loss in elastic modulus, increase in porosity etc. which eventually corrodes the reinforcement in concrete structures.

Degradation of concrete due to acids is influenced by multitude of factors related to acid, cement as well as the test method. This creates a difficulty in finalising the testing method which will address majority of the influencing factors altogether. Moreover, the assessment of cementitious materials is still hindered by the lack of standardised test or at least reference test methods. The response of given cementitious materials to acid attack clearly depends on architecture of tests as well as various other parameters. Further in-depth studies are necessary to investigate and clarify the mechanisms of degradation and kinetics in these conditions by developing new test methods and to design materials that perform well in these environments. Among the influencing factors, the mineralogical nature of the aggregate (calcareous or siliceous) and the binder to aggregate ratio also affects the kinetics of degradation. Limestone (calcareous) and siliceous aggregates behave differently when comes into contact with acidic environment (Alexander and Fourie, 2011). Chang *et al.* (2005) investigated sulphuric acid resistance of concrete made with limestone and siliceous aggregates in combination with supplementary cementing materials. It was found that the use of limestone aggregates along with proper ternary cementitious blend of supplementary cementing materials (SCM) will result in enhanced resistance in sulphuric acid environment. The chemical and microbiological tests conducted by De Belie *et al.* (2004) also showed that the aggregate type had the largest effect on degradation. According to Dyer (2014), when limestone aggregate is brought into contact with an acid (HA), the following reaction occurs (eq. 1).



Limestone aggregates neutralise acids as they dissolve. This will enhance the neutralization capacity of the concrete compared to siliceous aggregates which are considered as inert. The use of calcareous aggregates such as limestone could lead to sacrificial protection as the attack on cement hydrates are shared also with the attack on calcium bearing aggregates. Again, this can have different effects depending on the salt formed and these have to be investigated further. Moreover, depending on the acid involved, the corroded layer can undergo shrinkage. This leads to cracking, which increases the porosity further, thus increasing the rate of deterioration. Limited studies are available on the effect of

mineralogical nature of aggregate on acid attack. Hence, the paper aims to investigate the effect of mineralogical nature of aggregate on the kinetics of degradation of mortar on exposure to various types of acids.

2.0 EXPERIMENTAL PROGRAMME

2.1 Materials

The materials used in the current investigation include Ordinary Portland Cement (OPC) 53 Grade (IS 12269) and distilled water. Ordinary Portland Cement with specific gravity and Blaine's fineness values of 3.15 and 318 m²/kg respectively, and having a minimum 28th day compressive strength (tested using mortar cubes) of 53 MPa was used and the details of oxide composition of the cement are presented in Table 1. Particle size distribution of cement was studied using laser diffraction technique and D₅₀ (average size) of the cement particle was 19.41 µm. Loss on ignition of cement when tested as per IS 4032 was 3.43%.

Two types of fine aggregates (graded to standard size as per IS 650) were used to prepare OPC cement mortar of proportion 1:3; river sand (siliceous) and limestone aggregate (calcareous). The cement mortar mix was prepared using distilled water with water to cement ratio of 0.40. The mixing was done for about 3-4 minutes using a Hobart mixer. The fresh mortar was poured into lubricated acrylic/plastic moulds and prismatic specimens of size 10 × 10 × 60 mm and cylindrical specimens of 25 mm diameter and 50 mm height were demoulded after 24 hours. No chemical admixture was used for the mortar mix investigated in the current study.

The principal phase identified in river sand (designated as RS hereafter) and limestone aggregates (designated as LS hereafter) are quartz and calcite respectively (using X-ray diffraction technique). The elemental composition and oxide composition of aggregates obtained by X-ray fluorescence (XRF) are presented in Table 2 and 3 respectively. The physical properties of aggregates are given in Table 4. Fig. 1 shows the limestone aggregates which are pulverised and used as fine aggregates in the study.

Table 1. Chemical composition of OPC

Chemical composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	P ₂ O ₅
% by mass	64.59	19.01	4.17	3.89	0.89	0.16	0.59	1.70	0.24	0.11

Table 2. Elemental composition of aggregates from XRF

Element (%)	River sand	Limestone sand
O	47.90	29.10
Ca	1.92	68.45
Si	32.18	0.64
Al	8.26	0.24
Mg	0.36	1.06
Fe	2.27	0.25
Na	4.18	0.04
K	2.32	0.04
Ti	0.29	0.00

Table 3. Oxide composition of aggregates

Oxide (%)	River sand	Limestone sand
CaO	2.68	53.60
SiO ₂	68.84	1.37
Al ₂ O ₃	15.61	0.46
Fe ₂ O ₃	3.24	0.36
MgO	0.59	1.75
Na ₂ O	3.12	0.05
K ₂ O	5.03	0.05
TiO ₂	0.48	0.00

Table 4. Physical properties of aggregates

Aggregate type	Specific gravity	Water absorption (%)	Bulk density (kg/m ³)
River sand	2.62	2.20	1680
Limestone sand	2.70	0.35	1600

**Fig. 1.** Limestone aggregates

2.2 Test Method

The test method for acid attack should be accelerated, reliable and easy to implement in the laboratories (De Belie *et al.*, 2002). Hence, a static immersion based, accelerated leaching test was conducted on prismatic cement mortar specimens of size 10 × 10 × 60 mm to investigate the alteration

kinetics. The smaller specimen size was selected so as to have a higher surface area to volume ratio (0.43 mm²/mm³) to enable accelerated testing. The specimens were initially cured in saturated lime water for a period of 28 days to avoid calcium leaching and to gather the required strength before the acid exposure. After the initial curing, saturated mass and initial thickness of specimens were measured after which they were exposed to 1% and 3% sulphuric, 0.25M and 0.5M acetic acid solutions respectively. A volume ratio (i.e. volume of acid solution to volume of specimen) of 5 was used for testing.

Three specimens of the same mortar mix (RS or LS) were kept fully immersed in a beaker containing acid solution and the beaker was then covered tightly with the lid in order to avoid carbonation and exposure to outside environment as much as possible. Acid solutions were renewed every 2 weeks till 8th week and every 4 weeks till 16th week of exposure with the freshly prepared acid solution to maintain aggressiveness of the acid solution.

Brushing of specimens (with soft nylon brush) was done on the specimens exposed to sulphuric acid, just before the acid replenishment to remove the loosely held corroded particles (precipitates) and also to accelerate the testing (by exposing the fresh surface for the attack to proceed). Also, the periodic abrasive action is expected to simulate the action of flowing effluents on cementitious surfaces such as in concrete sewer pipes and waste water treatment plants. The tests were also done without abrasive action to study the action of static effluents. The degradation was stopped (by solvent exchange process using isopropanol) after 16 weeks of exposure and the specimens were stored in sealed zip lock covers inside a vacuum desiccator for imaging using X-ray micro-tomography (μCT). As there is no deposition of precipitates on specimens exposed to acetic acid, the tests were done without any abrasive action only.

The parameters used for understanding the degradation kinetics in prismatic specimens include mass changes, thickness changes and changes in the pH of the acid solution. Mass changes of specimen before and after the brushing were noted every week using a weighing balance having a precision of 0.1 mg. The excess superficial water on the specimen was wiped gently with a cotton cloth and the mass was measured in the saturated state immediately after wiping. The thickness of the specimens (after the brushing) was noted using a digital caliper having sensitivity of 1 μm. Average of six readings per specimen was used for the calculation of the thickness changes. The changes in pH of the acid solution were monitored using a digital pH meter (having a sensitivity of 0.01), just before the renewal of the acid. X-ray computed micro-tomography (μCT) test was conducted on selected mortar specimens to get the 3-D and 2-D images of the cut dried specimen of approximate size 10 × 10 ×

10 mm after the degradation in order to study the microstructural changes and to evaluate the depth of decalcification due to acid attack. More details about the tomography and its applications in studying microstructure of cementitious materials can be found in Ramaswamy *et al.* (2015), Ramaswamy and Santhanam (2017a, 2017b).

In addition to tests on prismatic specimens, cylindrical specimens after acid exposure (using the same volume ratio of 5) were tested to evaluate the changes in compressive strength, bulk density (in saturated state), ultrasonic pulse velocity (UPV) and dynamic modulus of elasticity. However, these tests were done without any abrasive action to preserve the corroded zones. The specimens were tested for the compressive strength after 6, 10, 16 weeks of acid exposure. The bulk density of specimens in saturated condition was noted by measuring the average diameter and height of cylinders just before testing the specimens for the compressive strength. Ultrasonic pulse velocity test (UPV) is done using transducers of 25 mm diameter before testing the compressive strength. The test was carried out on specimens in saturated and surface dry condition. A test frequency of 150 kHz, an excitation voltage of 500 V, averaging time and burst transmission mode was used as the test settings. The dynamic modulus of elasticity of the specimen is a measure of the quality of the interior of the specimen. It was calculated based on the values of UPV and bulk density according to IS 13311 (Part I), by assuming a poisson ratio of 0.17 for mortar.

3.0 RESULTS AND DISCUSSIONS

3.1 Visual Observations

The aspect of mortar specimens made using RS and LS before and after the acid exposure is shown in Fig. 2 and 3 respectively. The calcium bearing phases in the cementitious system react with the sulphuric acid to form gypsum salts of low solubility (as shown in Table 5). Hence, the salts precipitate as white soft deposits on the specimen. In case of RS specimens, the aggregates being inert were seen to be exposed. Also, considerable loss of thickness was evident from the visual observations on exposure to high concentration of sulphuric acid (3%). The loss of thickness is attributed to the expansive pressure exerted by the formation of gypsum crystals. However, in case of LS specimens, the aggregates were seen to be less protruded compared to the RS specimens. More precipitate formation was seen on the periphery of the specimens on exposure to sulphuric acid. This could be due to the dissolution of calcium bearing phases from the limestone aggregate acting as sacrificial protection to the dissolution of cement hydrates.

Both RS and LS specimens appeared orange brown in colour on exposure to acetic acid. The surface appeared smoother compared to sulphuric acid as the calcium salts formed were highly soluble (as shown in Table 5). Hence, thickness changes were found to be less. However, LS specimens appeared more porous and degraded when compared to RS specimens.

Table 5. Solubility of calcium and aluminium salts of acids (Bertron and Duchesne, 2013; Dyer, 2014)

Acid	Calcium salt	Solubility at 20°C (g/L)	Aluminium salt	Solubility at 20°C (g/L)
Sulphuric	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.4	$\text{Al}_2(\text{SO}_4)_3$	364
Acetic	$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	347	$\text{Al}(\text{CH}_3\text{COO})_3$	Springly soluble

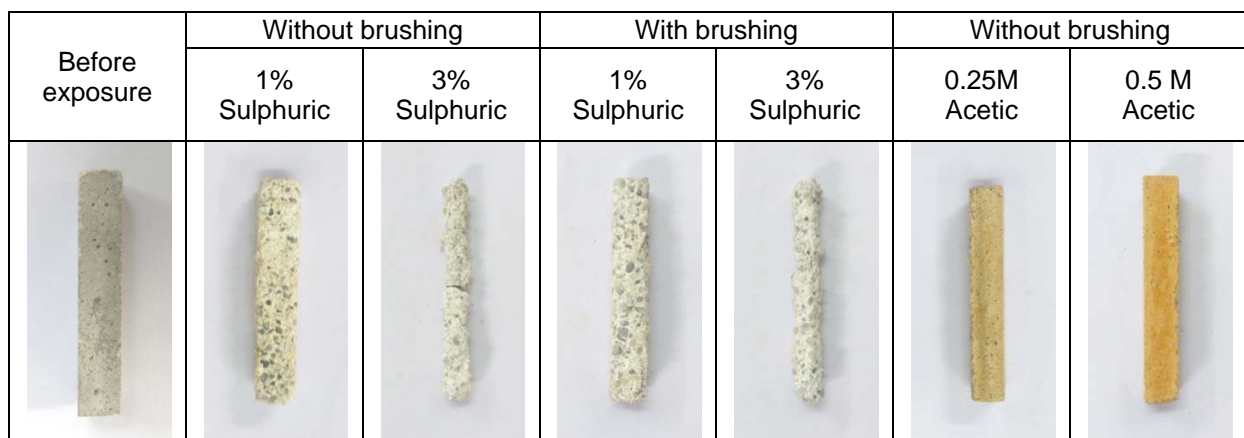


Fig. 2. Aspect of mortar specimens made with river sand

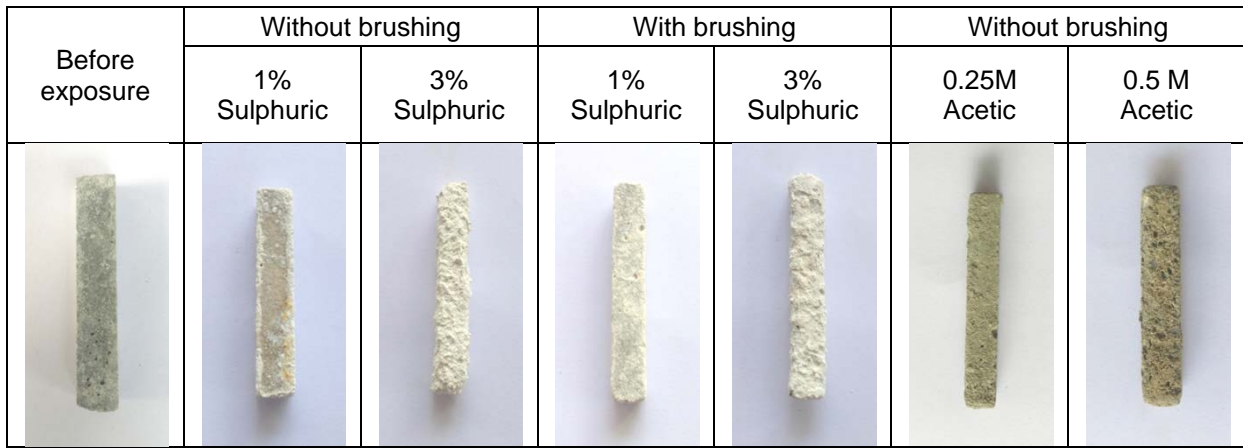


Fig. 3. Aspect of mortar specimens made with limestone sand

3.2 Mass Changes

The mass changes of specimens are calculated based on the initial mass (mass of the specimen before the acid exposure) and these are presented in Figs. 4 to 9. The RS mix suffered mass loss on exposure to sulphuric acid due to direct attack on cement hydrates forming gypsum and silica gel. This renders the matrix weak and the binding ability is affected leading to mass loss. However, the LS mix had mass gain for 1% sulphuric acid (Fig. 4 and 6). This could be ascribed to the increased precipitation of gypsum due to increased calcium content of the system. Also, there could be sacrificial protection effect by the limestone aggregates, protecting the hydrates of the cementitious system. This trend is observed for both test cases (with and without brushing). The mass loss of LS mix exposed to 3% sulphuric acid was significantly lesser than RS mix

(Fig. 5 and 7). Periodic abrasive action in the form of brushing accelerated the process of degradation due to the removal of corroded layer of gypsum which is soft.

Both RS and LS mixes had mass loss on exposure to acetic acid as leaching was the driving process (Fig. 8 and 9). As the calcium salts are soluble, they leach out to the acid solution making the matrix porous. It was observed that the mass losses of LS mixes are higher compared to RS mixes in acetic acid. This increased mass loss may be attributed to the increased calcium content of the mix and the higher solubility of salts. The protective effect of gypsum clogging the pores in sulphuric acid attack was hence not present in acetic acid. Also, it is noted that the variation of mass loss is linear with the acid exposure period and is almost directly proportional to the concentration of acetic acid.

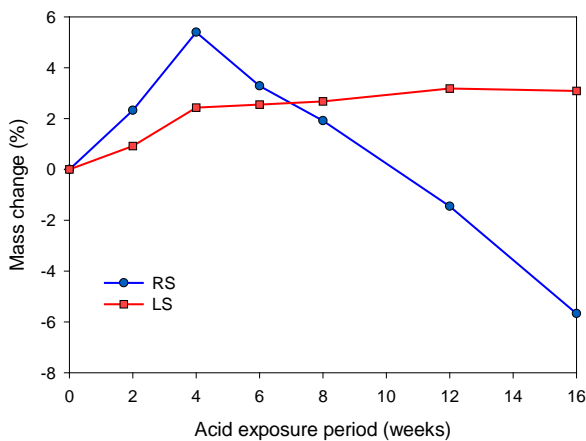


Fig. 4. Mass changes on exposure to 1 % sulphuric acid (without brushing)

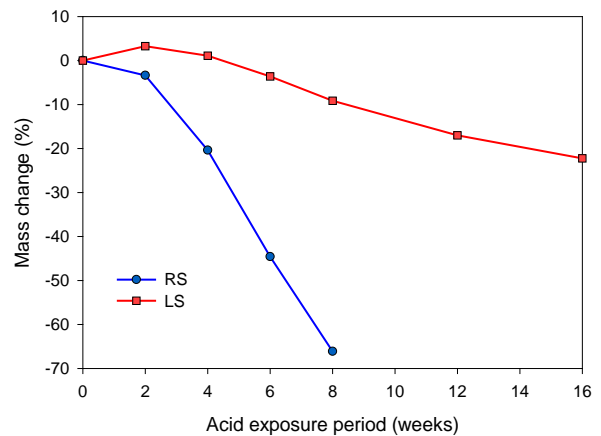


Fig. 5. Mass changes on exposure to 3 % sulphuric acid (without brushing)

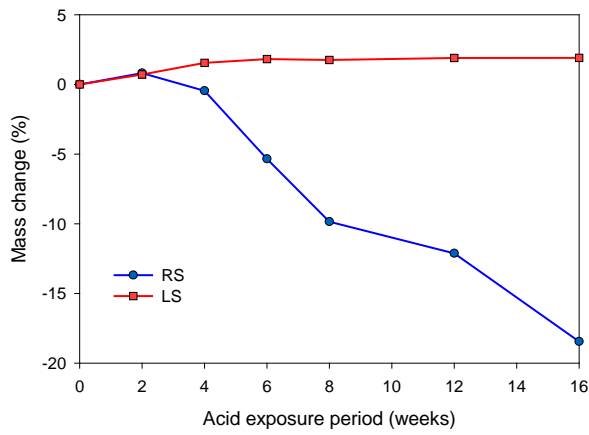


Fig. 6. Mass changes on exposure to 1 % sulphuric acid (with brushing)

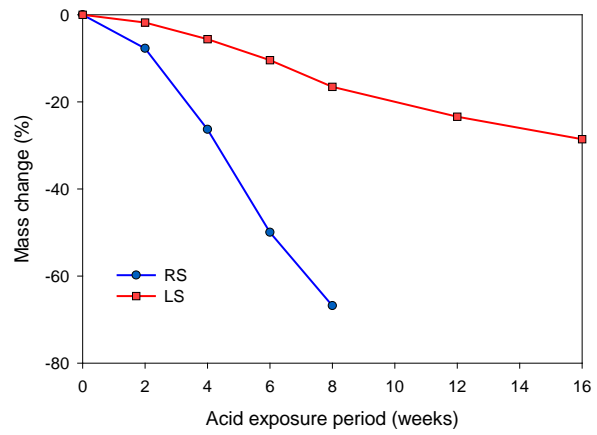


Fig. 7. Mass changes on exposure to 3 % sulphuric acid (with brushing)

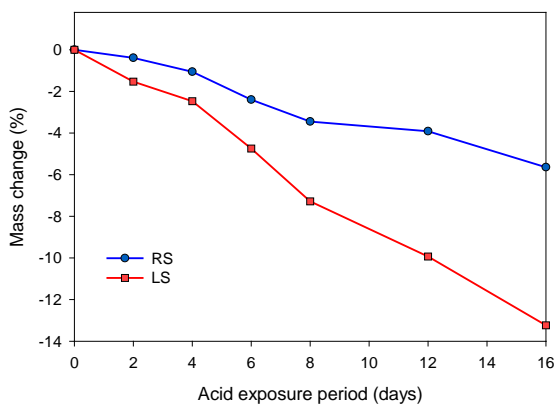


Fig. 8. Mass changes on exposure to 0.25M acetic acid (without brushing)

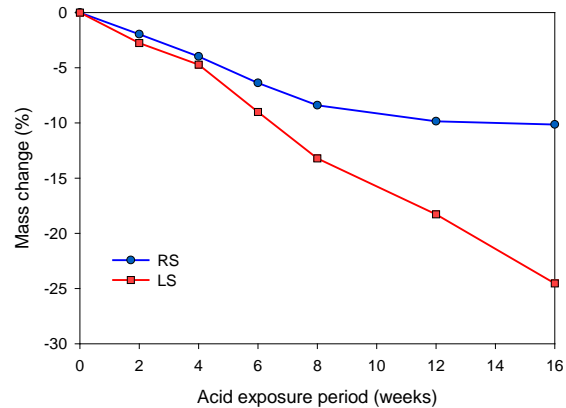


Fig. 9. Mass changes on exposure to 0.5M acetic acid (without brushing)

3.3 Changes in pH

Tables 6 and 7 shows the average pH of the sulphuric and acetic acid solutions measured just before each acid renewal. The terms 'S' and 'A' in the tables hereafter denote sulphuric and acetic acid respectively. As strong acids are completely dissociative, their chemical properties are reflected also in the evolution of pH of the solution. Also, the lower pH of sulphuric acid solution compared to acetic acid may be linked with the solubility of calcium salts. The more the solubility of calcium salts, the higher will be the pH of the acid solution on exposure. It was noted that, despite the higher neutralisation capacity of the LS mix (due to acid soluble calcite), there was no significant difference in the pH of the acid solutions between the RS and LS mixes on exposure to lower concentrations of sulphuric (1%) and acetic acid (0.25M). However, the neutralisation effect of LS mix was prominent in higher concentrations of sulphuric (3%) and acetic acid (0.5M). The higher pH of the solutions for LS mix implies that the acid solution is lesser aggressive and hence leads to lesser mass changes and associated degradation.

Table 6. Changes in pH of sulphuric acid solution

Acid	1 % S	1 % S	3 % S	3 % S
Age (weeks)	RS	LS	RS	LS
0	0.98	0.98	0.51	0.51
2	4.20	6.26	1.32	4.02
4	2.10	2.00	0.87	3.66
6	1.11	1.78	0.55	4.02
8	1.10	1.66	0.55	2.48
12	3.11	1.65	-	2.52
16	2.72	1.56	-	1.70

Table 7. Changes in pH of acetic acid solution

Acid	0.25M A	0.25M A	0.5M A	0.5M A
Age (weeks)	RS	LS	RS	LS
0	2.68	2.68	2.53	2.53
2	7.60	8.03	8.25	7.09
4	8.18	6.97	5.74	6.70
6	7.37	7.07	4.64	6.91
8	5.98	7.06	4.32	6.71
12	7.34	6.87	4.49	6.52
16	5.91	7.72	3.68	6.52

3.4 Thickness Changes

Similar to mass changes, the thickness changes are calculated based on the initial thickness of the specimens. The thickness changes were found to be in alignment with the mass measurements. Based on the thickness measurements, it is observed that the LS mix performed better on exposure to 1% and 3% sulphuric acid. The residual thickness after the acid exposure for the LS mix was higher compared to the RS mix (Fig. 10 and 11). However, on exposure to acetic acid, LS mix incurred considerably higher loss of thickness when compared to RS mix as evident from Fig. 12. It was also observed that the change in thickness is directly proportional to the concentration of acetic acid.

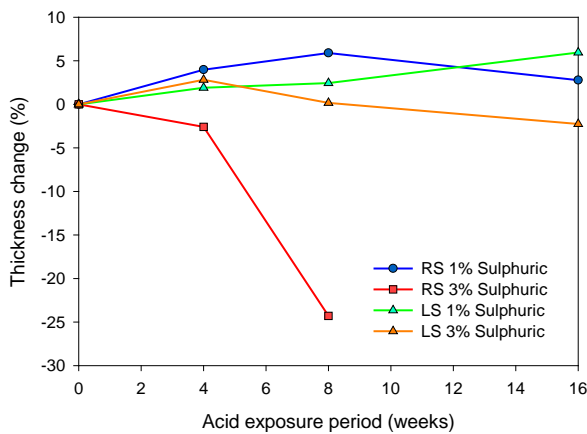


Fig. 10. Changes in thickness on exposure to sulphuric acid (without brushing)

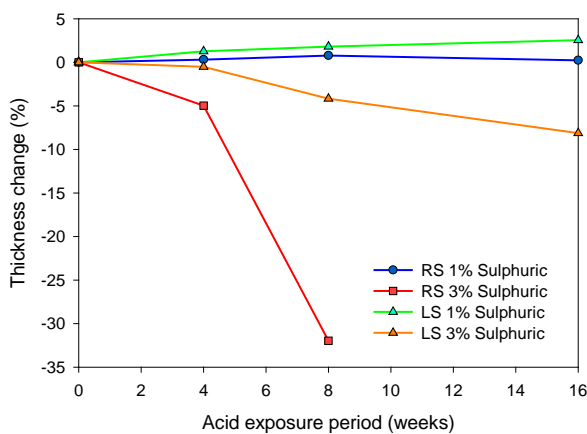


Fig. 11. Changes in thickness on exposure to sulphuric acid (with brushing)

3.5 Strength Changes

The compressive strength of specimens was found to reduce on acid exposure due to degradation. Figure 13 to 16 shows the variation of compressive strength on acid exposure. The drop in the strength values were more pronounced in case of specimens

exposed to acetic acid. This may be ascribed to the high porosity and altered depth of the degraded

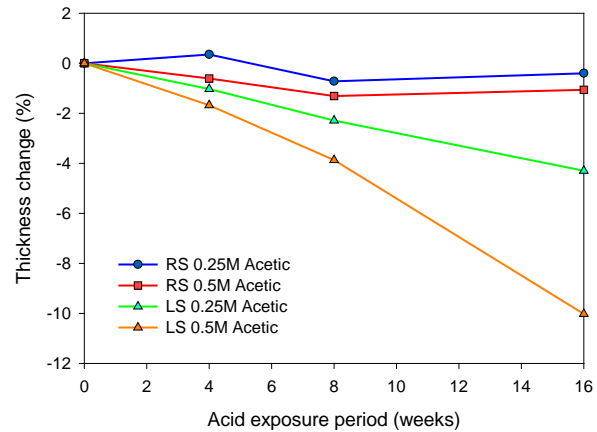


Fig. 12. Changes in thickness on exposure to acetic acid (without brushing)

layers due to the higher aggressiveness of acetic acid and higher solubility of calcium salts. It was observed that the residual strength after exposure was higher for LS mix compared to RS mix for 1% sulphuric acid (Fig. 13). This could be due to the combined effect of gypsum clogging the pores left behind the decalcification of calcium bearing phases and the sacrificial protection offered by the limestone aggregates. However, the residual strengths were comparable at higher concentrations of sulphuric acid (3%), evident from Fig. 14. On exposure to acetic acid, it was noted that OPC mixes with RS suffered higher degradation of strength on prolonged exposure. Despite the higher mass loss of LS mixes, the residual strength of LS mix at 16 weeks of exposure was found to be slightly higher when compared to RS mixes (Figs. 15 and 16). It is hypothesised that this effect is due to neutralisation of limestone aggregates. The sacrificial loss of calcium from aggregates mean that there is less dissolution of hydrates especially C-S-H gel, thus resulting in higher mass loss but increased strength at prolonged ages of exposure.

3.6 Changes in Ultrasonic Pulse Velocity

The variation in UPV with acid exposure is presented in Table 8. UPV measurements indicate that the LS mixes always show higher velocity values compared to RS mixes. This behaviour may be attributed to increased density of limestone compared to river sand aggregates (higher specific gravity). The loss in UPV due to deterioration was evident for all mixes. However, the loss was significantly higher for acetic acid, indicating serious deterioration of microstructure compared to sulphuric acid. The trend observed in strength measurements was evident in UPV measurements also. The residual UPV (after the acid exposure) was higher for LS mixes for all concentrations of both acids investigated.

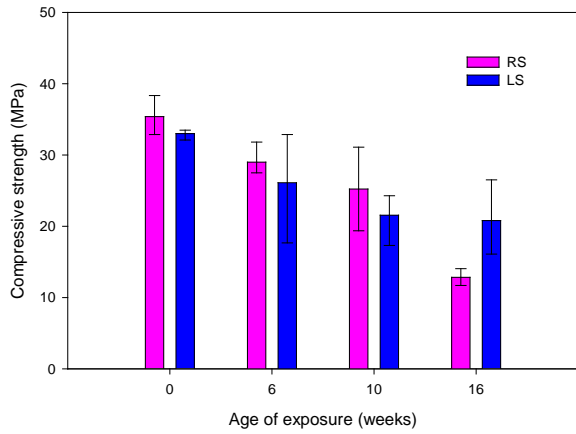


Fig. 13. Strength changes on exposure to 1% sulphuric acid

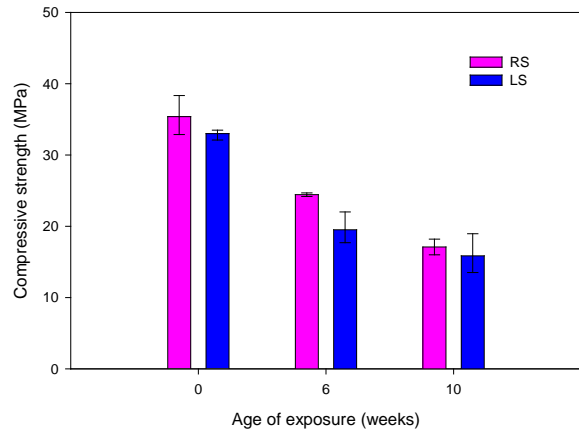


Fig. 14. Strength changes on exposure to 3% sulphuric acid

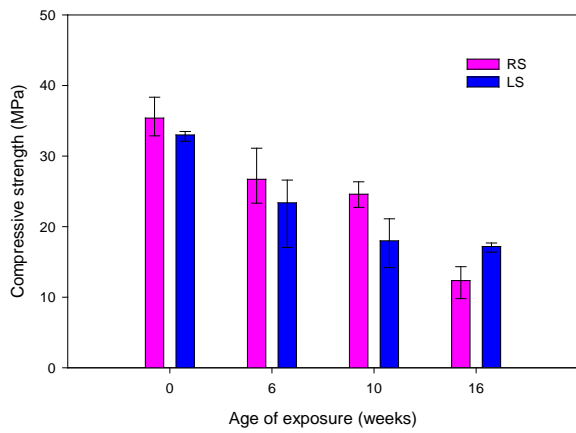


Fig. 15. Strength changes on exposure to 0.25M acetic acid

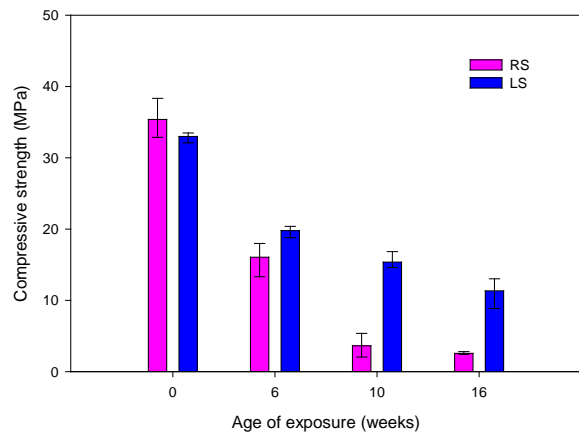


Fig. 16. Strength changes on exposure to 0.5M acetic acid

Table 8. Changes in UPV of specimens on acid exposure

Acid	1% S	1% S	0.25M A	0.25M A	0.5M A	0.5M A
Age (weeks)	RS	LS	RS	LS	RS	LS
0	4739	5038	4739	5038	4739	5038
6	4612	4980	4431	4794	4059	4432
10	3881	4817	4374	4558	3929	4167
16	3423	4824	3634	4076	2305	3873

3.7 Changes in Bulk Density

Density of specimens in saturated condition was noted by measuring the average diameter and height of cylinders just before testing the specimens for the compressive strength. In general, it was noticed that bulk density of specimens reduces with acid attack as shown in Table 9. The reduction in density was marginal for both the mixes on exposure to 1% sulphuric acid while it was considerable for 3% sulphuric acid. It is observed that the bulk density at the end of exposure period for the LS mix was slightly lesser than RS mix for 0.5M acetic acid. This is in alignment with the mass and thickness measurements. The loss of more calcium from the LS

aggregates led to mass loss and hence the reduction in bulk density. This increased porosity of LS mix on exposure to 0.5M acetic acid was also evident on visual observations.

Table 9. Changes in bulk density of specimens on acid exposure

Acid	1% S	3% S	0.25 M A	0.5M A	1% S	3% S	0.25 M A	0.5M A
Age (weeks)	RS	RS	RS	RS	LS	LS	LS	LS
0	2.15	2.1	2.15	2.1	2.2	2.2	2.24	2.2
6	2.1	2.0	2.17	2.0	2.1	2.1	2.22	2.1
10	2.1	1.9	2.15	2.0	2.1	2.0	2.16	2.0
16	2.1	-	2.07	2.0	2.2	-	2.17	1.9

3.7 Changes in Dynamic Modulus of Elasticity

An attempt to evaluate the changes in dynamic modulus of elasticity 'E' was carried out based on the UPV and bulk density measurements. Figures 17 to 19 shows the variation of E value of specimens on exposure to 1% sulphuric, 0.25M acetic and 0.5M acetic acid respectively. The drop in E value was

evident with acid exposure period due to reduction in bulk density and reduction in UPV values. It is noted that E value for LS mix was higher for all the acids at all ages of exposure. As the smoothness of the surface was affected at 3% exposure, UPV measurements were not possible and hence E values could not be obtained. Also, the poisson's ratio of the affected mix needs to be evaluated in order to get actual meaningful estimate of E value.

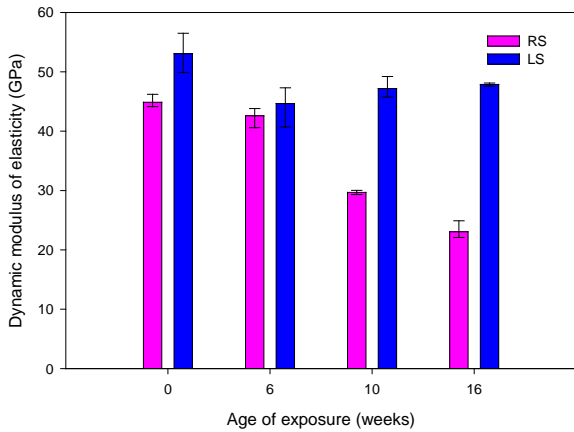


Fig. 17. Changes in E value of specimens on exposure to 1% sulphuric acid

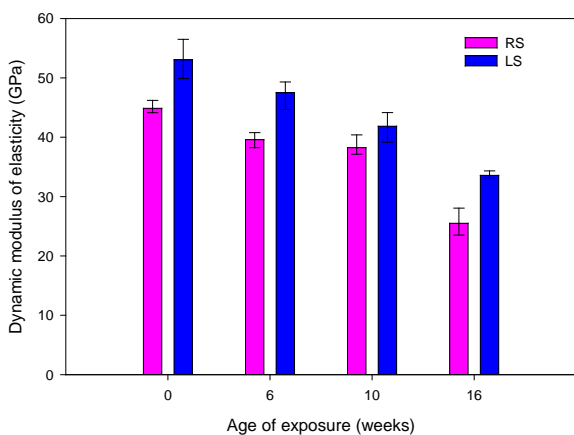


Fig. 18. Changes in E value of specimens on exposure to 0.25M acetic acid

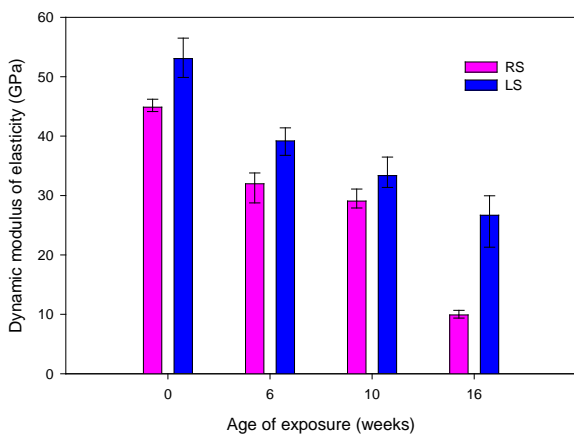


Fig. 19. Changes in E value of specimens on exposure to 0.5M acetic acid

3.8 X-ray Micro-tomography

The microstructural deterioration due to acid attack was evident from the CT slice images shown in Fig. 20. On exposure to 1% sulphuric acid, RS mix undergoes deterioration. The removal of soft gypsum on prolonged exposure led to popping out of aggregates. Severe cracking around the interfacial transition zone of the aggregate was evident. The cracking is due to the expansive pressure generated due to the precipitation of gypsum which has higher molar volume compared to the cement hydrates (portlandite and C-S-H). However, minimal deterioration was observed in LS mix. A thin layer of gypsum was observed around the periphery of the specimen. This behaviour may due to the sacrificial protection already explained in the previous discussions. The altered depth of RS mix on exposure to 0.25M acetic acid was found to be higher. The increased penetration of acid may be due to factors such as higher solubility of calcium salt, buffer action capacity exhibited by acetic acid. However, it is interesting to note that the altered depth could not be measured from the CT images of LS mix. It was observed that the entire cross-section of RS mix is deteriorated on exposure to 0.5M acetic acid. However, the altered depth was not much traceable from the CT images of LS mix. It appears that the paste has been decalcified though (as the paste appeared dark; lesser grayscale value of pixels may be attributed to the formation of silica gel from the decalcification of C-S-H gel).

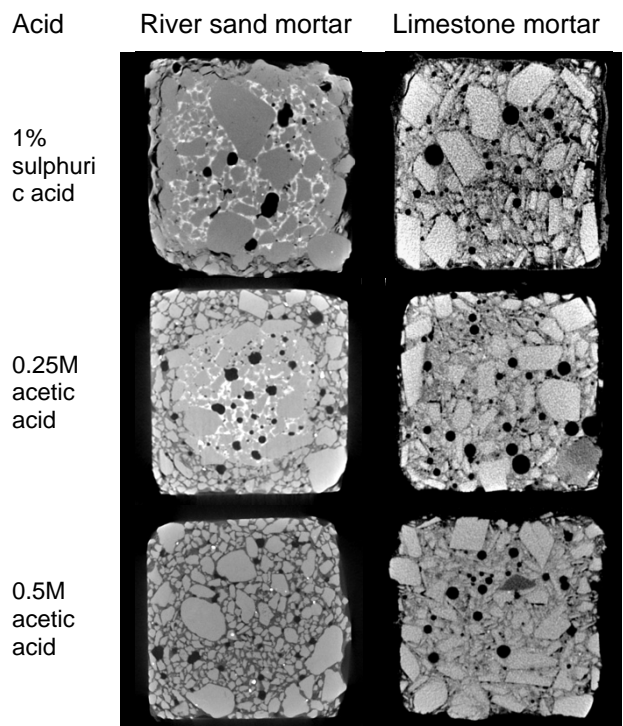


Fig. 20. X-ray tomography images of specimens after 16 weeks of acid exposure

4.0 CONCLUSIONS

Acid attack is a chemical phenomenon resulting in rapid degradation of cement-based materials, thus affecting the durability of concrete structures. The kinetics of degradation is affected by a multitude of factors related to acid, binders, aggregate and the architecture of the test method. The influence of mineralogical nature of aggregates on acid attack has been investigated in the current paper by studying the alteration kinetics of cement mortar solution, strength changes, changes in bulk density, ultrasonic pulse velocity and dynamic modulus of elasticity. The imaging using X-ray micro-tomography was done to understand the changes in microstructure.

It was found that the aggregate type had an effect on the degradation kinetics. The mortar with limestone aggregates showed a lesser degradation depth than did the mortar with inert (siliceous river sand) aggregates. The limestone aggregates locally created a buffering environment due to acid soluble calcium thus rendering a sacrificial protective effect, protecting the cement paste from the acid dissolution. However, this more pronounced neutralisation was not noticed in the pH change of the acid solution, especially on exposure to lower concentrations of sulphuric and acetic acid. Based on the parameters investigated, it was found that the limestone aggregates perform better on exposure to sulphuric acid environment when compared to siliceous aggregates. However, mass loss for limestone aggregates on exposure to acetic acid was found to be significantly higher when compared to siliceous aggregates owing to the solubility of calcium salts. Despite higher mass loss, the residual properties measured by compressive strength and dynamic modulus of elasticity were found to be marginally higher for limestone aggregates. It may be concluded that limestone aggregates could be a better option on exposure to those acids which form less soluble salt as in the case of sulphuric acid. Limestone aggregates may not be a better option for exposure to acids which form highly soluble salts as in case of acetic acid. More studies shall be carried out to investigate the alteration kinetics when limestone aggregates are used along with various blends of supplementary cementing materials so as to evaluate the potential of such materials in resisting aggressive aqueous environments.

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