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# Evaluating acid resistance of Portland cement, calcium aluminate cement, and calcium sulfoaluminate based cement using acid neutralisation

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## ABSTRACT

Cementitious materials are alkaline in nature. As a result, they are prone to neutralisation reaction by acids and possible deterioration. Among the existing binders, the acid resistance of calcium sulfoaluminate (CSA) cement is not well explored. Moreover, the phase composition of CSA cement varies significantly to reflect its expansive and non-expansive characteristics. In this article, the effect of chemical composition on acid resistance is evaluated in terms of acid neutralisation capacity (ANC) or acid consumption, providing a novel approach to evaluate the durability of CSA cements in low pH environment. This research focuses on evaluating citric acid and sulfuric acid resistance of Portland cement (PC), high ye'elinite CSA cement (CSA (HY)), and calcium aluminate cement (CAC). The tests were performed on monolithic specimens as well as powdered hydrated samples using an autotitrator. The acid resistance of three binders could be evaluated from total acid consumption and predicted based on early period of test depending on a binder's acid - pH interaction curve. Furthermore, a procedure was developed to correlate powder and monolithic tests.

## 1. Introduction

Portland Cement (PC) has poor resistance against aggressive acidic environment [1,2]. Acid attack is a commonly-observed phenomenon in sewer structures and is also referred as biogenic acid attack [3–5]. As a result of acid attack, material loss occurs from the surface of a structure, leading to section and strength loss [6]. A sewer structure is subjected to earth and water pressure along with building and traffic loads above it [7]. Loading capacity or structural integrity of a sewer structure depends on its wall thickness. To reduce the section loss (or deterioration), selection of a suitable acid resistant binder is a potential solution. To that end, calcium aluminate cement (CAC) has been used in sewer applications because of its superior biogenic acid resistance [1,8]. However, high cost limits its widespread application [9]. Furthermore, CAC exhibits conversion reactions leading to the loss in strength [10,11]. The acid resistance of high alumina binder can be attributed to its aluminium content [9]. Calcium sulfoaluminate (CSA) cement is an alternative low CO<sub>2</sub> cement containing higher aluminium fraction than that in PC [12–15]. Moreover, the acid attack studies on CSA cement are limited as its composition can vary significantly depending on desired properties such as rapid hardening or shrinkage compensation.

Acid neutralisation capacity (ANC) has been used to assess nitric and

acetic acid resistance at constituent phase level [16,17]. ANC is the amount of acid consumed to neutralise or dissolve 1 g of the material under consideration [1]. The neutralisation capacity of calcite is 20 mol H<sup>+</sup>/kg. Neutralisation capacity of 4 mol H<sup>+</sup>/kg for pH 4–5 itself is very high [18,19], whereas 0.2 mol H<sup>+</sup>/kg can be considered low [20]. The ANC details of some phases and hydrated binders are provided in Table 1.

ANC has been used to characterise solidified wastes such as radioactive wastes and heavy metals [17,25,26]. It can be viewed as the fingerprint of a particular waste product. Before disposing a waste to a site, the ANC must be known. When ANC of solidified waste (in terms of soluble salt-forming acids such as acetic and nitric acid) is high, the buffering capacity will also be high, and it will be effective in preventing the leaching of stabilized heavy metals from it. The solubility of most heavy metal species is high at low pH [23,27]. However, solubility is high at high pH for oxyanions such as selenate. Similar is the case with lead [28]. When the ANC evaluation is performed with acetic acid, complex compounds are formed, affecting the analysis [27]. At same pH, the acetic acid is more damaging than nitric acid [17]. The strength of acid is determined by acid dissociation constant (K<sub>a</sub>) which is expressed as its negative logarithm: pK<sub>a</sub>. The acid dissociation constant is specific for different protons in an acid molecule. Acetic acid has pK<sub>a</sub> of 4.76,

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**Table 1**

ANC details of selected phases and hydrated binders.

Phases / hydrated binders	ANC	References
Portlandite	27 eq/kg	[21]
Calcite	20 eq/kg	[18]
Portland cement (@pH 6)	18 eq/kg	[22]
Portland cement/ slag (1:4) (@pH 6)	10 eq/kg	[22]
Portland cement/ fly ash (10–80 % substitution) (@pH 6)	~ 4.8–5.4 eq/kg	[23]
Portland cement (w/c = 0.4) to pH 9	16 eq/kg (50 % dissolved)	[24]
High alumina cement/lime/gypsum (60:10:30, w/c = 0.4) to pH 9	8.1 eq/kg (1 % dissolved)	[24]

**Table 2**

The pH stability of various phases.

pH	Phases	References
12.4–12.6	Portlandite	[33–35]
12–12.5	C <sub>4</sub> AH <sub>13</sub> <sup>a</sup>	[33]
11.6	Monosulfate	[36]
10.6, 11	Ettringite	[37,38]
10	Hydrogarnet	[36]
8.8, 9	C-S-H	[33,39]
4.5–6	Calcite	[40]
3–4	Aluminium hydroxide	[41,42]
1.5–2	Ferric phases	[41,42]
Only by HF	Silicon oxide	[41]

<sup>a</sup> Cement chemistry notation: C = CaO; A = Al<sub>2</sub>O<sub>3</sub>; S = SiO<sub>2</sub>;  $\hat{S}$  = SO<sub>3</sub>; F = Fe<sub>2</sub>O<sub>3</sub>; H = H<sub>2</sub>O.

whereas citric acid has pKa of 3.13, 4.76, and 6.4 associated with each proton. Therefore, when the dissociation of acid molecule is poor, it leads to higher pH despite having a higher concentration of acid. This is observed in the case of organic acids [29,30]. As a result, the large amount of organic acid anions can react with calcium-bearing phases such as portlandite to form the corresponding calcium anion salt and other cation complexes. These organic acid anions act as ligands to the cations such as calcium, iron, and aluminium and the mechanism is called complexolysis [31]. The acid consumption for phases such as C-S-H may vary according to parent binders, and hence, the overall acid consumption for a particular cement is a function of its phase composition and ANC of individual phases [32].

Table 2 shows the pH stability of various phases. First hydrated phase to be attacked in PC is portlandite, followed by monosulfate, ettringite, C-S-H, and AH<sub>3</sub>. It can be interpreted that C-S-H degradation initially begins with transformation into a lower Ca/Si ratio C-S-H [22,23,35] and eventual formation of amorphous silica [39]. The acid resistance of CAC has been attributed to its higher neutralisation capacity contributed by AH<sub>3</sub> [43–45] and the stability of calcium aluminate hydrate phases [46]. After acid attack of aluminium bearing phases, a cohesive pore-filling alumina gel that offers protective action is formed. Aluminium has been suggested to have bacteriocidal property [47,48], but it has not been verified [49,50]. The reaction (1) below [9,51] shows that 1 mol of aluminium hydroxide consumes 6 mol of H<sup>+</sup> ions, indicating higher ANC of the phase.



This indicates that for the same amount of CAC and PC, the former requires higher amount of H<sup>+</sup> ions for overcoming the buffer capacity leading to its better nitric acid resistance as per [51]. Acid neutralisation capacity and chemical resistance could be related when the neutralisation capacity of a binder was fully realised (i.e., the phases should dissolve completely not allowing partial neutralisation) in the acetic and butyric acid attack study [52].

In acid attack experiments, specimens are often immersed in dilute acid solution. The pH of this exposure solution increases with time

depending on the neutralisation capacity of the binders [53,54]. The pH increment needs to be controlled to obtain sustained acid attack. This can be done by replacing exposure solution or by titrating with the acid of higher concentration along with proper stirring. The titration time and amount of acid titrated are measured to calculate the average acid consumption rate [55]. This type of constant pH method can be automated with the help of an autotitrator as reported by [56], where replacement of exposure solution was also adopted. In a study on hydrated PC paste, constant pH of 2, 3, and 4 were maintained for 28 days using the titrant 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in an autotitrator [57]. In this experiment, 3 mm thick 30 mm diameter discs were exposed to 150 ml acid solution constantly stirred by magnetic stirrer. Similarly, sulfuric acid attack on PC-Slag paste was studied at constant pH 1 and 2 [58]. A 5-day test with constant pH of 2, maintained by dosing 1 M HNO<sub>3</sub>, was performed on 10 × 10 × 60 mm prisms of various binders [59]. Constant pH 2 tests were performed on concrete slice of 150 × 150 × 40 mm as well, by dosing 2 M sulfuric acid into 12 l exposure solution [56]. The mass loss due to acid attack was correlated to acid consumed in maintaining constant pH [55–59]. It was reported that the H<sup>+</sup> ion consumption could be correlated to mass loss or they were directly proportional [60]. The soluble salt-forming acid consumption (nitric or acetic) can be predicted from the ANC of the binders [1,17]. The advantage of acid attack tests using an autotitrator is that constant pH and constant stirring can potentially prevent the precipitation of secondary acid attack products, without limiting the study to soluble salt-forming acids such as acetic and nitric acids [16]. The acid consumption and deterioration may not correlate well if the deterioration mechanism is not dissolution (e.g., expansion, cracking, or crumbling) as observed in Portland cement-silica fume blend. The anomaly can also occur when there is a barrier formation of dense and less-soluble silica gel over the specimen in case of certain binders [16]. This urges the need for exploring a relation between acid consumption and acid resistance in case of insoluble salt-forming acids such as sulfuric and citric acids.

The pH response of C-S-H based matrix in hydrated Portland cement is different from that of ettringite based matrix in hydrated CSA cement [24]. Based on the available literature [24,61,62], a technique can be developed for powder, similar to [59] for distinguishing the chemical nature of binders. Titration curve for the binder suspension can be obtained to determine ANC. That involves certain plateaus corresponding to degradation of various phases [34,63]. This method will be used to study the effect of phases on the acid resistance. Even though the former test on monolithic specimens reveals the combined effect of porosity, permeability, and phase (chemical) composition on acid resistance, chemical composition is the critical factor in acid resistance [17]. These novel methods are particularly important for CSA based binders whose composition is not fixed, as acid resistance can be evaluated at constituent phase level.

Ettringite based binder obtained from high alumina cement decomposed more in acetic acid (pH 3 and 5) and nitric acid (pH 3): the corrosion depth and the acid consumption to maintain the pH were higher than other Portland based binders [17]. The hydration of CSA binders gives ettringite along with monosulfate, aluminium hydroxide, strätlingite, and C-S-H; the presence and proportion of these phases depends on the composition of CSA binder used [64,65]. The presence of ettringite and absence of portlandite of this system motivates to carry out acid resistance study. There are very limited studies on the acid attack of CSA cements. In a study, CSA cement (ye'elime: 29 %, belite: 55.2 %, calcium sulfate: 5.3 %) had slightly lower hydrochloric acid resistance than PC [66]. The authors attributed the higher resistance of PC to its high alkalinity. In another study, CSA cement (CaO: 42.25 %, SO<sub>3</sub>: 8.82 %, Al<sub>2</sub>O<sub>3</sub>: 36.46 %, SiO<sub>2</sub>: 6.86 %) and its PC blend had increased sulfuric acid resistance than PC [67]. While the decalcified zone of PC paste consisted of silica gel, in the case of PC-CSA composites it consisted of silica gel and an aluminium-rich phase containing significant quantities of gibbsite. The deterioration of CSA cement (ye'elime: 52.85 %, sulfate: 2.96 %) was reported to be inversely proportional

**Table 3**  
Oxide composition of binders.

Binders	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	SrO	Na <sub>2</sub> O	LOI*
PC	21.2	58.1	6.9	2.8	5.1	1.0	0.8	0.5	0.0	0.1	3.1
CSA (HY)	14.0	39.8	20.9	14.5	3.6	2.8	0.5	1.1	0.1	0.2	1.8
CAC	8.3	32.5	43.6	4.3	2.4	0.7	0.0	3.8	0.1	0.3	3.4

LOI\*: Loss on ignition.

**Table 4**  
Phase composition (%) of raw materials.

Phases/binder	PC	CSA (HY)	CAC
Ye'elimite	0.0	35.5	5.9
Anhydrite	0.0	15.5	2.6
Gypsum/Bassanite	4.1	1.5	0.8
Lime	0.0	3.9	0.0
Dicalcium silicate	21.9	28.7	0.0
Dolomite	0.0	7.6	0.0
Brownmillerite	5.9	3.5	1.1
Mayenite	0.0	2.1	5.0
Quartz	1.8	1.7	0.0
Tricalcium silicate	54.8	0.0	0.0
Tricalcium aluminate	4.7	0.0	0.0
Calcium monoaluminate (CA)	0.0	0.0	20.4
Grossite (CA <sub>2</sub> )	0.0	0.0	13.9
Perovskite	0.0	0.0	7.7
Gibbsite	0.0	0.0	3.5
Aluminium oxide	0.0	0.0	0.6
Calcite	6.9	0.0	7.0
Gehlenite	0.0	0.0	31.4

to the pH of exposure solution irrespective of chemical or biogenic sulfuric acid attack [68]. In a previous study by the authors, CSA cement (CaO: 39.8 %, SO<sub>3</sub>: 14.5 %, Al<sub>2</sub>O<sub>3</sub>: 20.9 %, SiO<sub>2</sub>: 14 %) was outperformed by PC in 1 % sulfuric acid solution. However, in case of citric acid attack, CSA cement outperformed PC because of the higher amount of tri-calcium di-citrate hexahydrate (expansive in nature) formation from calcium hydroxide in PC [69]. When normalized mass and unaffected core area fraction were considered, the organic acid performance of CSA cement (CaO: 44.4 %, SO<sub>3</sub>: 8.7 %, Al<sub>2</sub>O<sub>3</sub>: 31.75 %, SiO<sub>2</sub>: 10.7 %) seemed to be different in case of lactic, citric, acetic, and butyric acids [31,52]. Hence, there is the need for multiple criteria to evaluate acid resistance. In this paper, acid neutralisation or consumption is introduced as an additional criterion to evaluate acid resistance. The neutralisation capacity-based acid resistance evaluation has been extended to insoluble salt-forming acids such as sulfuric and citric acid through this work.

## 2. Materials and methods

Portland Cement (PC) of grade 53 as per IS 12269: 2013 and commercially available CSAB cement – which is labelled as CSA(HY), and CAC were used in this work. The oxide compositions of the three binders are shown in the Table 3.

PC, CSA-HY and CAC binders had specific gravity of 3.15, 2.86 and 3.2 respectively. The phase compositions of the raw binders (100 % crystalline) determined by XRD analysis are shown in the Table 4.

### 2.1. Specimen preparation

Prismatic specimens of dimensions 10 × 10 × 60 mm were cast at water-to-cement (w/c) ratio of 0.4 (by wt.) and cured for 28 days at 25 °C and 65 % relative humidity environment. The mixing was performed using a high shear paste mixer. The binder was added into measured volume of water and stirred for 2 min and then it was transferred into moulds.

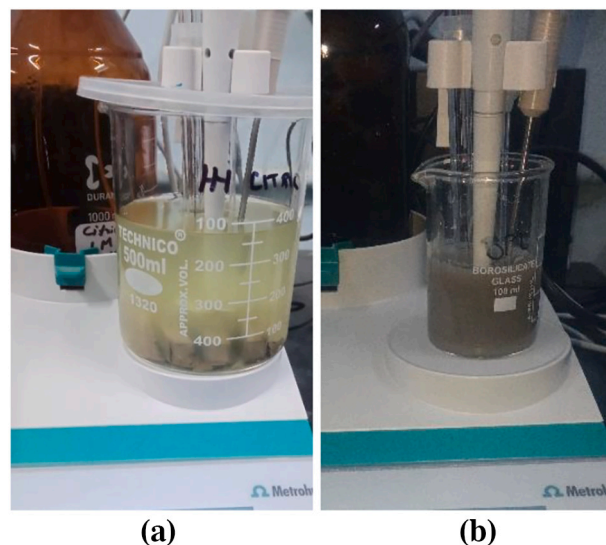


Fig. 1. Titrator running (a) STAT experiment, and (b) powder titration.

### 2.2. Acid attack tests

The acid exposure experiments were conducted using an automatic titrator (Metrohm 916 Ti Touch). The apparatus involves an intelligent pH electrode, temperature sensor, acid dosing system and a propeller type stirrer (Fig. 1). At the end of curing period, monolithic specimens were taken for constant pH experiment (STAT) as shown in Fig. 1 (a). Constant pH of 1 and 3 were maintained by titrating with diluted sulfuric acid (5 %) and citric acid (1 M), respectively ( $\pm 0.002$  ml). As autotitrator's dosing unit including the tubes were not made of glass, there was a limitation for using concentrated acid. If heavily diluted acid was used, the acid consumption would be high to make the experiment impractical in terms of volume and time management, and thus optimized concentration of 5 % and 1 M were used. Three specimens of a hydrated binder were transferred to a 500 ml beaker containing 250 ml acid solution of pH 1 or 3 (sulfuric or citric as per the test). As a result, the specimen surface area-to-solution volume ratio (A/V) becomes  $0.104 \text{ cm}^{-1}$  (solution to sample volume ratio – 13.89). An autotitrator was used for maintaining constant pH along with continuous stirring at 450–500 rpm speed, thus inducing some dynamic effect. Since the dosing of acid increased the acid volume, fresh acid solution was used after 24 h of duration for next 5 days. Cumulative consumption of acid was monitored throughout the period of 5 days. Subsequently, dimensional and mass changes in specimens were measured.

Fig. 1 (b) shows the powder titration using autotitrator. 1 g of powdered hydrated binder (size of  $<90 \mu\text{m}$ ) was mixed with 50 ml of distilled water before titration. The method involved initial 10 min of premixing. The stirrer speed was 900–1000 rpm throughout the program and this speed was optimized based on trials. The solution should be stirred continuously to ensure that the measured pH was representative of the entire volume. The stirring speed should be such that the effect of acid dosed should have immediate effect on the experiment. However, if the speed is high, the specimens would also be moved, posing a potential threat to the sensitive exposed intelligent pH

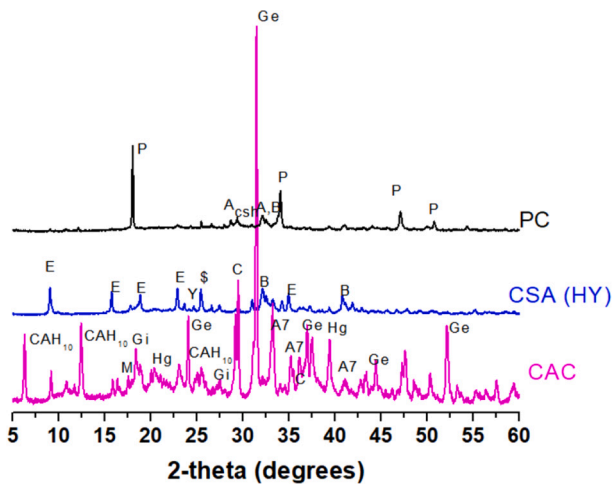


Fig. 2. XRD patterns of hydrated matrix after 28 days curing [Note: E – Ettringite, P – Portlandite, A – Alite, B – Belite, Y – Ye’elimite, \$ – Anhydrite, Ge – Gehlenite, Gi – Gibbsite, Hg – Hydrogarnet, C – Calcite, A7 – Hydrate of Mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}(\text{H}_2\text{O})$ ),  $\text{CAH}_{10}$  – Caldecyhrite ( $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ ), M – Monosulfate, csh – C-S-H].

electrode.

### 2.3. Mass and dimensional changes

In case of STAT experiment, mass change and dimensional change were measured. Normalized mass at a particular day was taken with respect to the control specimen’s mass, i.e., the 28-day cured specimen. Similarly, normalized cross-section area at the end of 5-day exposure was calculated with respect to the area of control specimen. Dimensional changes in prismatic specimens were measured using a digital caliper having a sensitivity of 0.001 mm. The width and depth at three different locations were measured and the average cross-sectional area was calculated from these measurements.

### 2.4. X-ray diffraction (XRD)

Mineralogical changes were monitored using X-ray diffraction (XRD). Samples were powdered and sieved through 75  $\mu\text{m}$ . XRD was performed using MiniFlex Rigaku powder X-ray diffraction instrument using  $\text{Cu K}\alpha$  (wavelength 1.5405  $\text{\AA}$ ). The tube voltage and current were 40 kV and 15 mA, respectively. The diffractogram was collected between the 2-theta range of  $5^\circ - 60^\circ$  with step size of  $0.02^\circ$  and scanning rate of 0.2 s per step size. The diffractograms were analysed using X’Pert HighScore plus software.

### 2.5. Scanning electron microscopy (SEM)

Scanning electron microscopy was performed using FEI-Quanta FEG 200F equipment. Specimens were subjected to gold sputter coating before performing SEM. During the SEM examination, dwell time of 30  $\mu\text{s}$ , accelerating voltage of 20 kV, beam current of 1 nA, and spot size of 2.5 nm were used.

## 3. Results

### 3.1. Mineralogy and mechanical properties of hydrated binders

The binders were characterised in terms of 28-day flexural strength of mortar as per ASTM C348. The flexural strengths of mortars (1: 2.75) having w/c ratio of 0.5 were: 5.41 MPa (SD: 0.13 MPa), 4.85 MPa (SD: 0.25 MPa), and 3.01 MPa (SD: 0.19 MPa) for PC, CSA (HY), and CAC binders, respectively. Fig. 2 shows the XRD patterns of hydrated binders

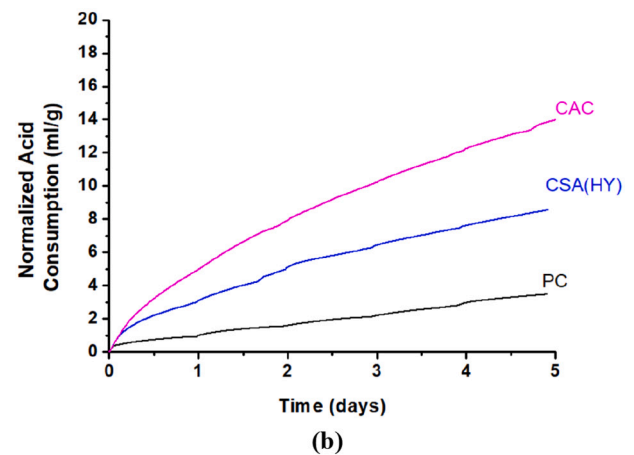
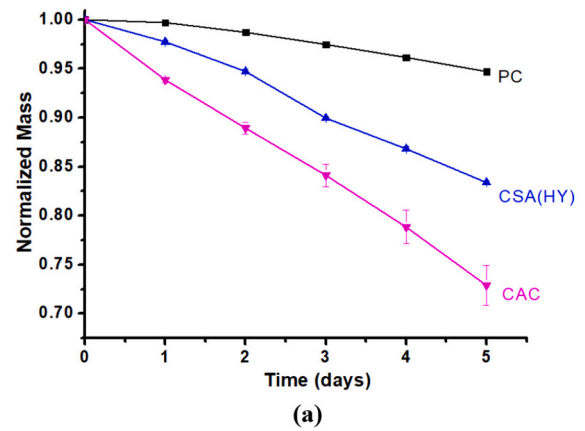


Fig. 3. (a) Normalized mass vs. time, and (b) cumulative sulfuric acid consumption (dosing precision = 0.002 ml) for STAT pH 1 sulfuric acid (5 %) test (monolithic specimens).

considered in the study. It is evident that only PC has portlandite and its relative amount is high. A diffused 2-theta peak at around  $29.4^\circ$ , corresponding to C-S-H, is visible in the XRD pattern of PC. CSA (HY) is characterised by the prominent ettringite peaks along with peaks of anhydrous phases such as calcium sulfate anhydrite along with belite and traces of ye’elimite. XRD pattern of CAC is characterised by enormous amount of different calcium aluminate hydrates and aluminium hydroxide (gibbsite). Additionally, CAC pattern has prominent gehlenite and calcite peaks with traces of monosulfate.

### 3.2. Static pH tests on monolithic specimens (STAT)

As per [70], the preferred pH range for the growth of *Thiobacillus thiooxidans* is 0.5–3. In biogenic acid attack, the pH of exposed concrete surface becomes constant at around 1 by the activity of *Thiobacillus thiooxidans* [71]. Hence, the results with acid pH of 1 and 3 are reported in the further sections. The deterioration with sulfuric acid having pH of 3 would be insignificant for comparison.

#### 3.2.1. Sulfuric acid

Fig. 3 shows the mass loss and acid consumption for three binders during titration period. In sulfuric acid STAT test at constant pH of 1, mass loss of the binders was observed in the order: CAC > CSA(HY) > PC (Fig. 3). There was no evidence of mass increment in CAC and CSA(HY) binders in the initial period of exposure in contrast to PC validating the observation in [72]. The absence of mass loss in PC is attributed to precipitation of gypsum in initial days [56,73]. In PC, gypsum deposition in pores causes pore blocking, creating a barrier for further attack



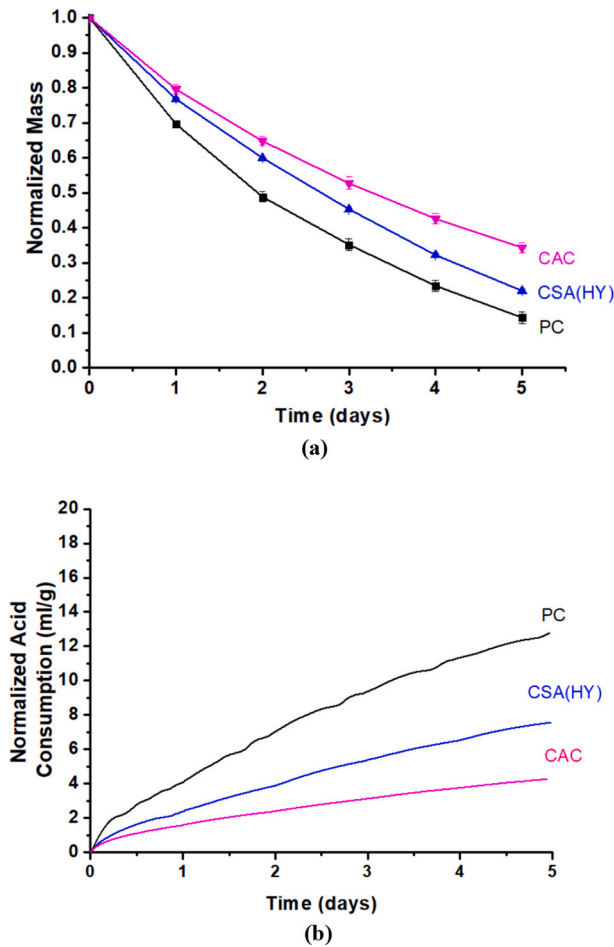


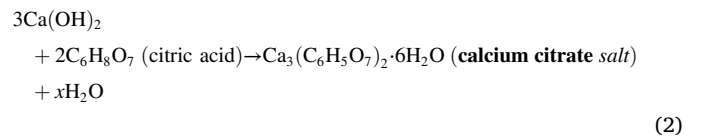
Fig. 4. (a) Normalized mass vs. time, and (b) cumulative citric acid consumption in STAT pH 3 citric acid (1 M) test (monolithic specimens).

[46,74,75]. However, the phases themselves get converted into gypsum and aluminium hydroxide in case of CSA cement [76] and CAC [72].

The pH of acid solution increased due to the leaching of alkalis from specimens. The constant pH of solution was maintained by dosing the required amount of acid for neutralisation. Acid consumption is the amount of acid added into the system to maintain the pH at 1 (± 0.001). For the results in Fig. 3(b), one-way ANOVA test was performed to analyse the difference between binders and F-statistic of 85 was obtained, indicating the binders were statistically different in acid consumption response. Sulfuric acid consumption to maintain the pH of 1 showed the order: CAC > CSA(HY) > PC. The barrier formation in PC stopped perpetual neutralisation of interior region; hence, acid consumption was least in PC. The relative higher amount of acid consumption in CAC can be attributed to higher acid neutralisation capacity offered by aluminium hydroxide whose amount was more in CAC than in CSA(HY). Aluminium hydroxide reacts with sulfuric acid to form aluminium sulfate [44]. It can be observed that the deterioration in form of mass loss could be correlated to the acid consumption.

### 3.2.2. Citric acid

In citric acid STAT test of constant pH of 3, mass loss followed the order: PC > CSA(HY) > CAC (Fig. 4). The higher deterioration in PC could be attributed to the presence of the significant amount of calcium hydroxide. Calcium hydroxide gets easily converted into expansive calcium citrate salt on reaction with citric acid.



Because of the chelating effect of citric acid, excessive Ca leaching and complex formation occur [77], indicating poorer performance of calcium rich binder.

Citric acid consumption to maintain the pH of 3 in three binders followed the order: PC > CSA(HY) > CAC (Fig. 4). Aluminium hydroxide is a stable compound up to pH 3–4. The attack on CAC involves gradual

Sulfuric Acid Exposure			
	Area Loss = 4 %	Area Loss = 12.4 %	Area Loss = 18.3 %
	Citric Acid Exposure		
Area Loss = 84.4 %		Area Loss = 72.1 %	Area Loss = 59.1 %
PC		CSA(HY)	CAC

Fig. 5. Visual comparison of control specimen (left) and acid-attacked specimen (right).

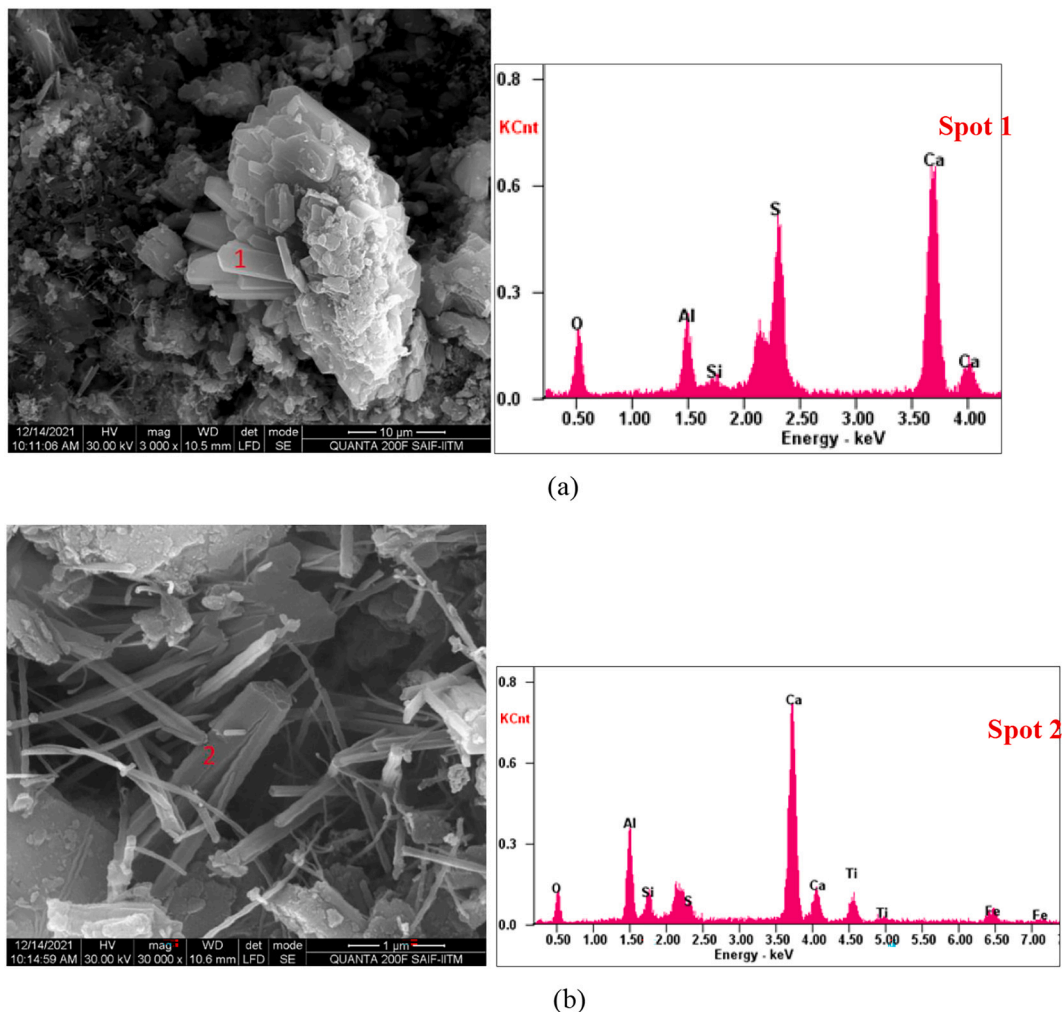


Fig. 6. SEM-EDS of unattacked core region of CAC.

neutralisation and dissolution of the phases present such as  $\text{CAH}_{10}$ ,  $\text{C}_2\text{AH}_8$ ,  $\text{C}_3\text{AH}_6$ , and  $\text{AH}_3$  [44]. The acid attacked specimens in case of citric and sulfuric acid tests are shown in Fig. 5. The appearance is validated by the results presented here.

Citric acid attack led to extensive cross sectional area loss, maximum (~84 %) in case of PC and minimum (~59 %) in CAC. Comparatively, the cross-sectional area loss in case of sulfuric acid attack (pH of 1) was least (~4 %) for PC and maximum (~18 %) for CAC. The least area loss in case of PC in sulfuric acid of pH 1 could be attributed to the barrier formation at this pH. Mass loss includes effect of leaching and cross-sectional area loss. Hence, in most cases, the mass loss was slightly greater than the area loss. It can be observed that the deterioration in form of mass loss could be correlated to the acid consumption. Higher acid consumption was found as an indicator of higher phase dissolution in case of ANC test with soluble salt forming acid, HCl [40]. In addition to that, in this study with insoluble salt forming sulfuric acid and citric acid, the acid consumption was directly proportional to deterioration.

### 3.2.3. Microstructural characterization

As the STAT test is performed with constant stirring at 450–500 rpm, it allows dynamic immersion in contrast to conventional experiments. It is interesting to explore the nature of the available exposed surface to study whether adhesive products are there or the products are loose enough to move into solution on stirring, making the exposure solution turbid with extensive sedimentation as well. Again, acid resistance of a binder is not only dependent on ability to neutralise acid, but also on the

acid attack products and microstructure of the specimens, which determines the exposed area to acid [16]. Hence, SEM analysis of the acid attacked cross section was performed.

Fig. 6 shows the microstructure of unattacked core region of CAC, showing the calcium aluminate hydrate along with monosulfate formation.

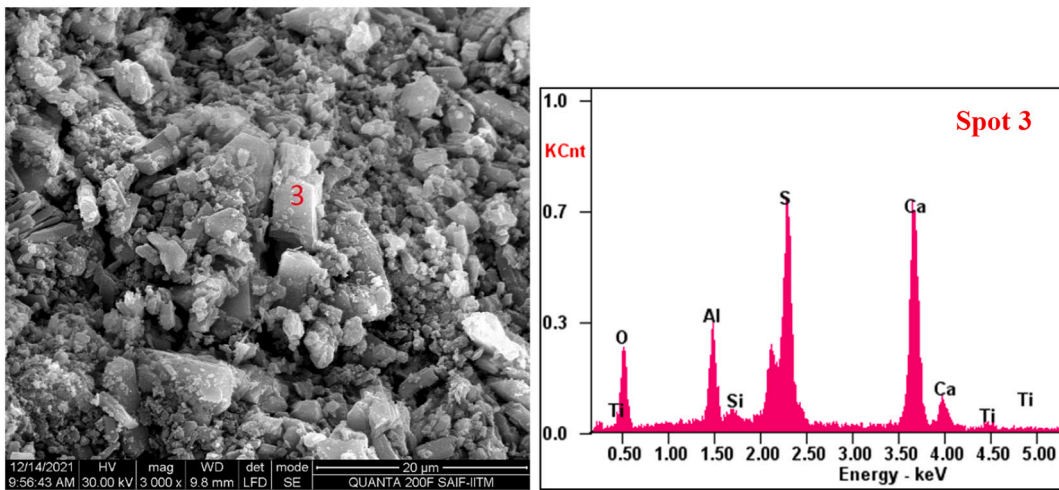
The major sulfuric acid attack product in case of CAC was gypsum (Fig. 7(a)). The EDS spectrum in Fig. 7(b) also had Al peak. This suggests the presence of aluminium hydroxide as well, supporting the findings of [78]. Similarly, sulfuric acid attacked region in CAC contained small amount of aluminium hydroxide precipitated over large amount of gypsum crystals [72].

The acid attacked region in PC had wide deposits of gypsum as observed in Fig. 8(a). EDS analysis across the region showed significant Si signal which can be attributed to silica gel [31]. There were certain features with predominant Si signal. One such feature is shown in Fig. 8 (b) that shows Ca and S signals due to gypsum, which can get incorporated into silica gel [47,52,57,59,69,79,80]. It should be investigated whether the expansive nature of gypsum has any effect on the cracks observed in the image. However, the gypsum incorporated silica gel can act as a characteristic protective barrier in high pH acid attack [16,69,81].

The unattacked core region of CSA(HY) was examined by SEM as shown in Fig. 9. Large deposits of hexagonal monosulfate crystals along with needle like ettringite were observed. However, these phases could not be found in attacked region.



(a)



(b)

Fig. 7. Sulfuric acid attacked region of CAC (a) SEM showing gypsum crystals (b) SEM-EDS showing presence of gypsum and aluminium hydroxide/ $\text{Al}_3\text{OH}$  gel.

Acid attacked region had a wide deposits of small gypsum crystals precipitated as acid attack products. However, Fig. 10 shows that the SEM-EDS performed on these crystals had limited Si signal as compared to PC. Hence, the precipitated product was mainly gypsum, and silica gel incorporated gypsum barrier was not observed in CSA (HY).

From the SEM images, the morphology of the sulfuric acid attack products was explored. Another important inference obtained was that sulfuric acid (pH of 1) did not create large amount of loose products, allowing the solution to be less turbid. This will not be the case with lower pH ( $< 1$ ) exposure of sulfuric acid or citric acid.

The STAT test performed with pH 3 citric acid was characterised by the fragmentation and transformation of transparent solution into a turbid solution. This change was more pronounced in PC and least in CAC. The expansive citrate salt was easily fragmented from the surface of PC specimen. This was validated by the SEM as shown in Fig. 11. The continuous stirring was able to remove the citrate products into solution and the removal efficiency followed the order: PC > CSA (HY) > CAC.

### 3.3. Powder titration

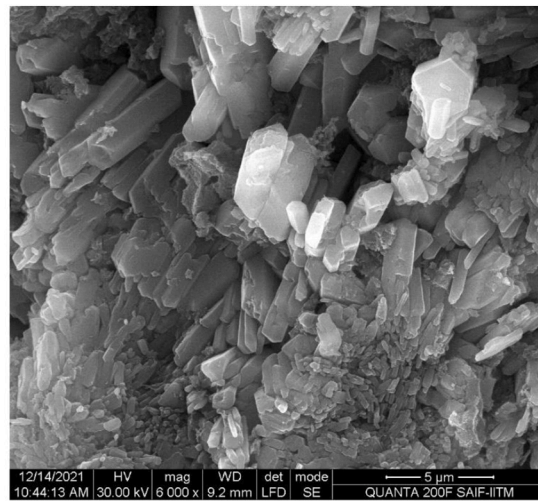
The titration curve obtained in case of sulfuric acid titration is shown in Fig. 12 (a). Certain plateau regions were observed corresponding to various phase neutralisation. This could be better visualized by transforming the axes and plotting the derivative [23,34,82]. The area under

the derivative curve Fig. 12 (b) can be related to ANC. The phases causing the buffering are visible as peaks in the differential curve. Ettringite or monosulfate peak was visible for CSA (HY) between pH 9–10. The doublet peak between 3 and 4 for CAC and CSA(HY) could be attributed to aluminium hydroxide. The reason for doublet could not be confirmed in the study. Portlandite peak was only evident in PC at around pH of 12. The portlandite gets readily dissolved and that may be the reason why it did not evolve in form of a prominent peak. Hence, a peak in a differential neutralisation curve indicates the region of acid attack resistance.

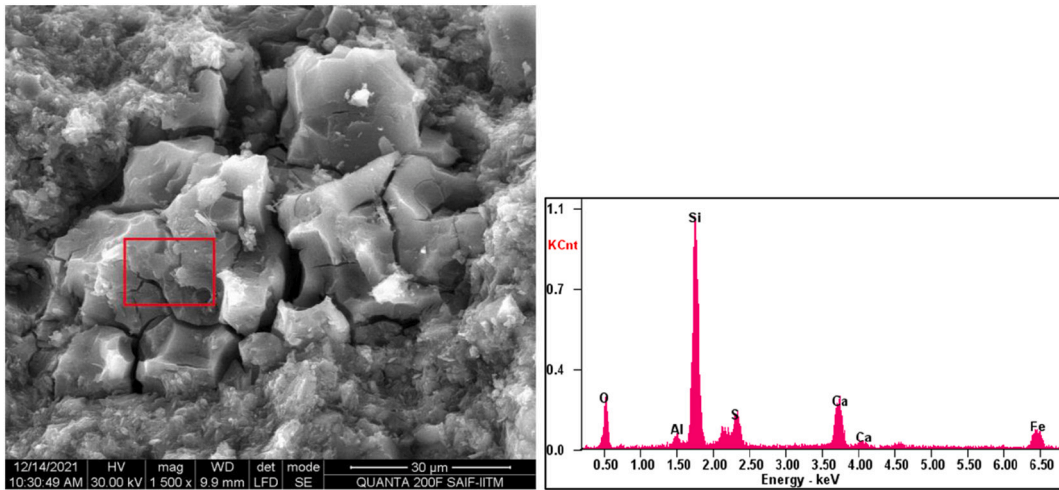
It is shown in Fig. 12 (c) that there is a change in slope of acid consumption curve in the case of powder titration after a particular threshold pH near 3. For any pH down till 3, the corresponding amount of acid consumed to reduce till that pH was highest for PC. For pH values lower than 3, PC possessed the least value. It is to be noted that PC was near pH 3, when CAC and CSA(HY) attained pH 1. The acid consumption was dependent on the time of titration at which it is calculated, as seen in Fig. 12 (c). According to [59], higher acid consumption should indicate more deterioration both in powder titration and STAT test. Hence, a consensus needs to be developed whether powder titration can measure susceptibility to leaching and can be correlated with STAT tests.

Titration was then performed on the hydrated binders with citric acid (Fig. 13 (a)). In Fig. 13(b), prominent peaks were not visible as observed with sulfuric acid titration, indicating vigorous reaction of





(a)



(b)

Fig. 8. Sulfuric acid attacked region of PC (a) SEM showing gypsum crystals (b) SEM-EDS showing presence of silica gel with Ca peak.

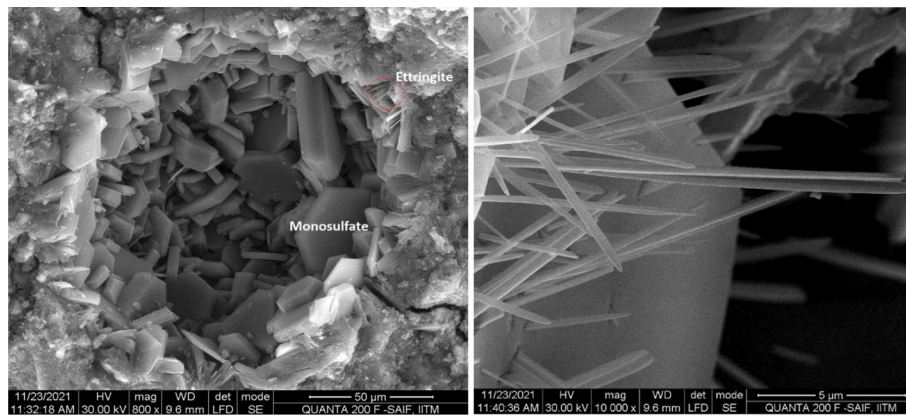


Fig. 9. Monosulfate and ettringite in unattacked core region of CSA(HY).

citric acid with the binders. However, ettringite or monosulfate peak near pH of 9 in CSA(HY) and portlandite peak near pH of 12 in PC were faintly observed. The plateau in Fig. 13(a) and valley in Fig. 13(b), between pH 3–4, could be attributed to aluminium hydroxide degradation.

From Fig. 13, the binders could be easily distinguished. Here, the threshold pH was found to be in the range of 5.3 (for CAC and CSA(HY)) to 5.5 (for PC). The change in slope was observed after the threshold pH. However, the change in performance at higher and lower pH was not



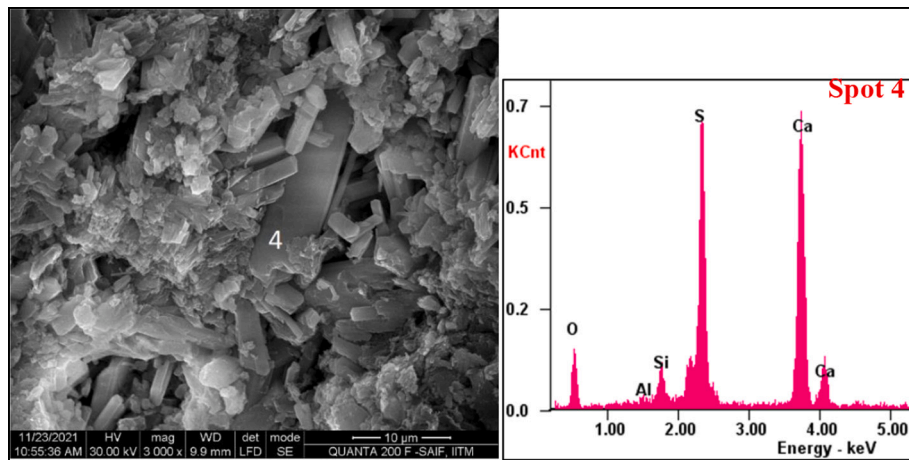


Fig. 10. SEM-EDS showing presence of gypsum in acid attacked CSA(HY).

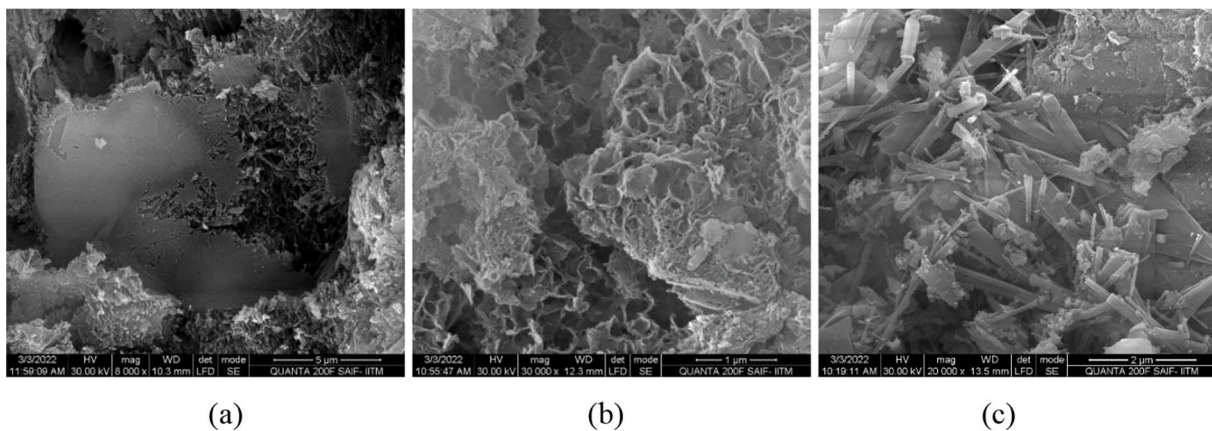


Fig. 11. SEM of citric acid attacked surface of (a) PC (b) CSA, and (c) CAC.

evident. PC took more time to reach the threshold pH. Some time lag was observed in case of CSA(HY) as compared to CAC due to its plateau corresponding to pH of 9 (Fig. 13). This could be attributed to the higher amount of monosulfate/ettringite in CSA(HY). The time lag at threshold pH was least in case of CAC. The sample with low Ca gets neutralised quickly and remains stable, and that with high Ca gets neutralised continuously [59]. The same observation could be made in case of Ca rich Portland cement with respect to low Ca binders: CAC and CSA(HY).

Explaining in terms of ANC, the titration curves in case of citric acid and sulfuric acid were similar to pH vs. ANC curve in [51] at pH above 4. Although PC has a higher acid neutralisation capacity initially at higher pH, it falls continuously to comparatively negligible value. In case of CAC, initial pH drop is sharp, and the pH stabilizes between 3 and 4. In short, PC has higher ANC than CAC at pH above 3–4 and converse is true at pH below 3–4 [51]. A quick look at titration curves may indicate higher ANC of PC among all binders particularly at higher pH. In other words, PC attains lower change in pH for same volume of acid added, as reported in [82]. But, ANC is pH dependent and a method to evaluate it is introduced in discussion section.

#### 4. Discussion

##### 4.1. Monolithic test result - prediction from initial test period till 'stabilizing point'

It has been discussed that acid consumption is directly proportional to the deterioration. The total acid consumption is mainly contributed

during the initial period. Hence, the proportionate acid consumption can be calculated from the initial period of the test when there is significant leaching from a fresh specimen. Fig. 14 is a zoomed-in version of STAT test from the initial period. Once the specimens were introduced into acid solution the pH increased from 1 or 3, due to leaching and acid attack. Once the titrator program started, it dosed acid to reduce the pH to the set value. Initially, leaching/acid attack dominated, and the pH increased till the point of maximum pH. Thereafter, the acid dosing by titrator reduced the pH of the solution. For sulfuric acid (pH of 1) test, the maximum value of pH was reached quickly while it took time in case of citric acid, indicating heavy deterioration in latter case. As dosing continued, the pH decreased at a constant rate and reached the set value of pH 1 and 3. Thereafter, the pH vs. time curve was flat; hereafter only, the test could be called at constant pH. The onset of original pH after initial fluctuation in pH vs. time curve was termed 'stabilizing point (SP)'.

The point of maximum pH is also the point after which the slope of acid consumption curve changes. The corresponding point in the acid consumption curve was called 'divergence point (DP)' as till this point acid consumption curves were overlapping for all three binders. The point of maximum pH (divergence point) was defined as the point in pH vs. time curve where the slope is zero and the pH is maximum.

In Fig. 15, the moles of acid consumed for the three binders are shown. The moles of  $H^+$  ions in the case of sulfuric acid would be twice the amount of acid consumed. However, that may not be the case with citric acid due to the poor dissociation of organic acid molecule. Thus, acid consumption (moles of acid molecule) would be an appropriate

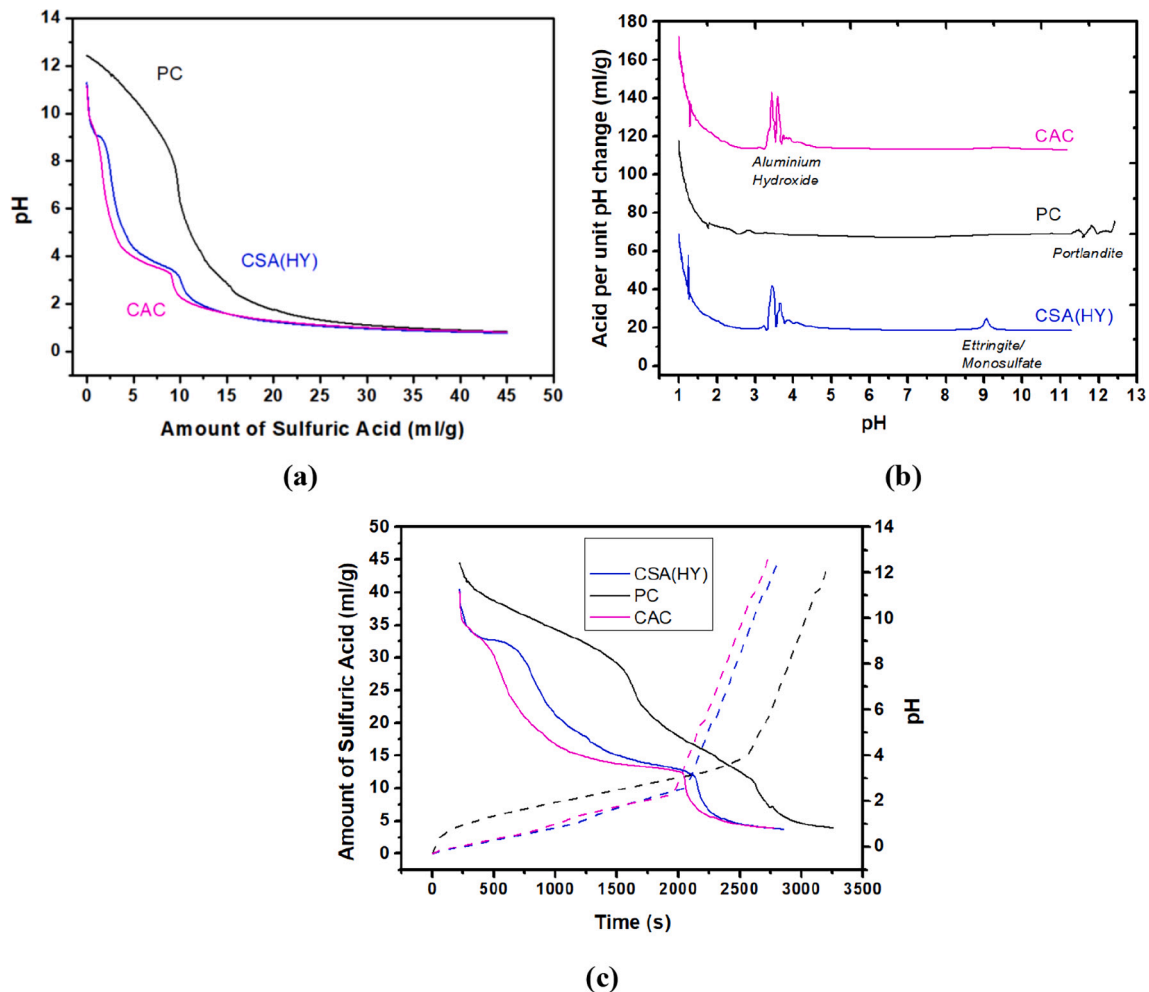


Fig. 12. (a) Powder titration curve (dosing precision = 0.002 ml) with titrant sulfuric acid (5 %), (b) differential neutralisation curve, and (c) acid consumption (dotted line) and pH evolution with time.

parameter to compare both acid results. The trend in acid consumption during the initial test period was found to be similar to that during the entire test period. As the F-statistic or ANOVA coefficient was quite large or the  $p$ -value was approaching zero in one-way ANOVA test, the binders could be differentiated at initial test period. This high F-statistic is because of the dosing precision of 0.002 ml of the dosing unit and automated working of the machine. Hence, the initial test period results could serve as a marker to predict the overall performance.

#### 4.2. Correlation between powder and monolithic tests

Till now the results from STAT pH (monolithic) and dynamic pH (powder) tests were discussed. In this section the correlation between the two test results is discussed. For that acid consumption per gram of sample in STAT pH and in that of powder test for the corresponding pH was determined and correlated through a procedure developed as described in Fig. 16.

In step 1, the titrator's stabilizing point (SP) is considered to determine acid consumption (ANC) in static pH (STAT) test. For CSA (HY), acid consumption till stabilizing point (SP) was 1.004 ml/g. The procedure for determining acid consumption in powder test starts with step 2. First, the pH corresponding to divergence point (DP) in pH vs. time curve (in STAT pH test) is identified and it is 1.063 for CSA(HY). This pH vs. time curve shows the trajectory of pH evolution in the initial period of STAT pH test. The remaining step is performed in powder test results curve, at a region around pH 1–1.063. The corresponding acid

consumption in case of pH 1.063 and pH 1 are determined in the step 3. The difference between this acid consumption was taken as acid consumption in case of powder and it was 2.7 ml/g in case of CSA (HY). The acid consumption was expressed as mmoles/g to represent it as ANC. The ANC in case of powder and monolithic specimens were compared in Fig. 17.

From Fig. 17, the trend seemed to be similar in case of powder and monolithic specimens. The Pearson's correlation coefficients ( $r$ ) are 0.91 and 0.99 in case of sulfuric and citric acid, respectively. The correlation coefficient above 0.9 in both tests indicate 'very high positive correlation'. The acid consumption in case of powder was greater than monolithic specimens, particularly in case of sulfuric acid. This could be attributed to the higher surface area for reaction offered by <90  $\mu\text{m}$  powder to that of monolithic specimen. The powder test was only influenced by the chemical nature of binders, assuming that the powder was sufficiently fine. However, monolithic test was influenced by chemical nature as well as physical characteristics of specimen such as permeability, cohesiveness, surface cracks/ flaws, etc. It was also affected by the nature of secondary products formed after acid attack: whether the insoluble products form barrier or lead to expansion [16]. As a result, ANC in monolithic specimens could be used to differentiate the binders, while ANC of powder was similar for CAC and CSA binders.

The PC binder had the highest acid consumption in case of citric acid and least in case of sulfuric acid. When fragmentation occurred in citric acid attack in static pH test, the test shifted toward powder test: statistically speaking, the Pearson's correlation coefficient ( $r$ ) thus became

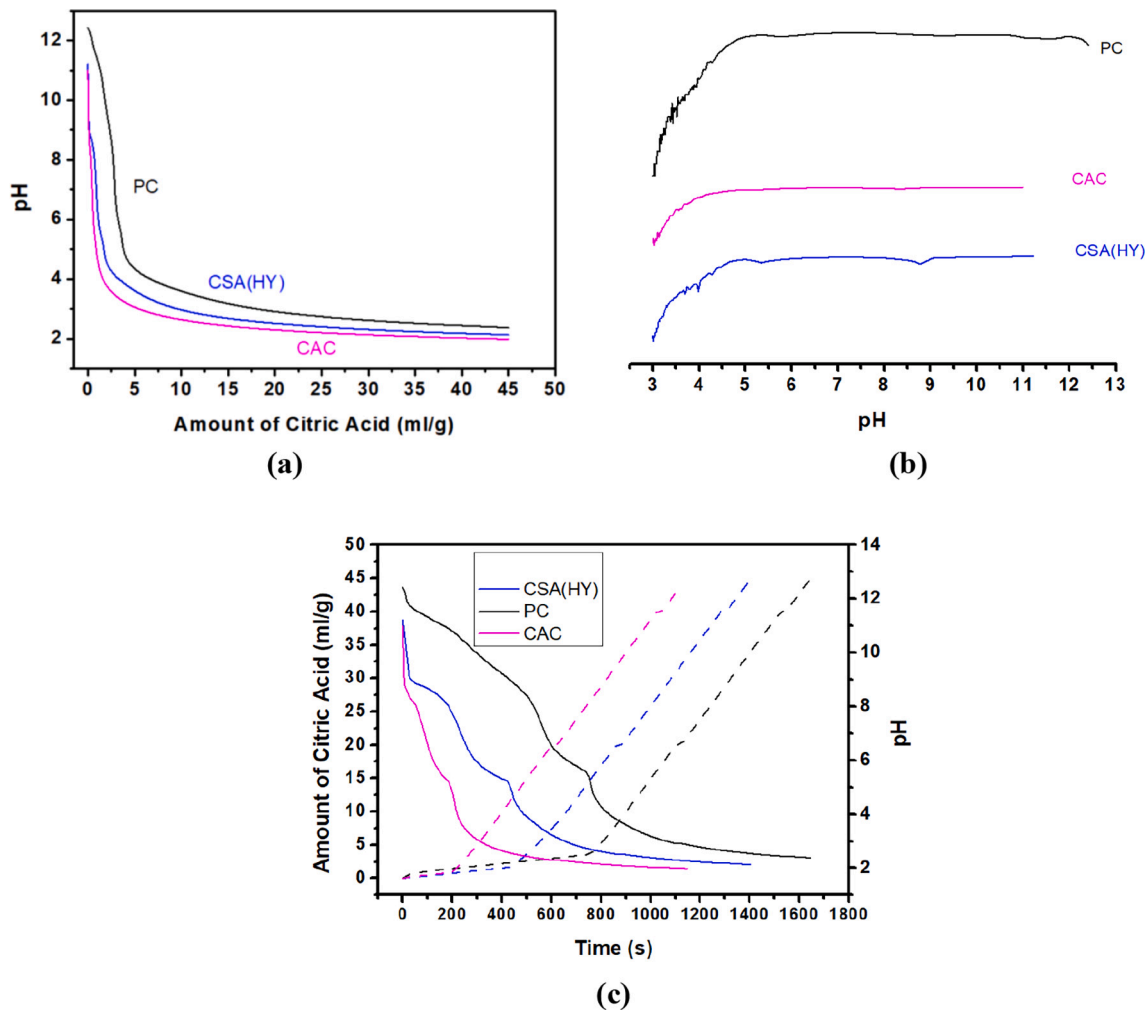


Fig. 13. (a) Powder titration curve (dosing precision = 0.002 ml) with titrant citric acid (1 M), (b) differential neutralisation curve, and (c) acid consumption (dotted line) and pH evolution across time.

0.99. That means the solution became turbid with deposits at bottom, leaving severely degraded specimen, ultimately providing more surface area for further reaction. In this scenario, it's good to ponder the fact that ANC is equivalent to alkalinity of the material when the aqueous system is devoid of any particulate matter [83]. An important observation is that the citric acid consumption was lower than that of sulfuric acid. In citric acid attack, the citrate anion effect is more dominant than the neutralisation effect of  $H^+$  ions. The citrate ion can form complexes with various cations leached from the hydrated matrix such as of calcium, aluminium, and iron. This complexolysis is also possible with silicic acid [31]. The solution turned into green colour which is characteristic in case of Portland cement immersed citric acid tests and it could be attributed to the iron complex formation. The colour intensity increased across test period, possibly due to the increment in concentration of complexes. Hence, the binder providing enough calcium ions for citrate anion to form expansive calcium citrate salt would be the least performing one: PC in this study.

#### 4.3. Correlation between ANC and acid resistance

The acid resistance can be evaluated based on the criteria such as retained cross-sectional area or mass loss as discussed before. Fig. 18 shows the correlation between acid resistance and acid consumption. One of the criteria for measuring acid resistance is the ratio of cross-sectional area after and before acid exposure. Irrespective of the type of acid, the acid consumption was inversely proportional to acid

resistance of the binder. The standard deviation in case of acid consumption is negligible and the binders are quite different when acid consumption is used as a criterion: *t*-test score for different binders was higher in case of acid consumption than conventional parameters of deterioration such as area ratio.

The difference in acid resistance trend in STAT 1 and STAT 3 may also be explained in terms of low and high pH. CAC outperformed PC at higher pH (above 3) because of insoluble aluminium hydroxide. As pH decreases,  $Al(OH)_3$  dissolves and the degradation proceeds [84]. A plateau in titration curve means the amount of acid consumed without a change in pH due to buffering capacity. Although the acid was added, pH was not reduced because of phase degradation at that pH. Hence, the plateau indicates the neutralisation capacity offered by particular phase. Higher the amount of phase better the neutralisation capacity.

On reducing the pH between 4 and 6.5, the system became deficient in  $Ca^{2+}$  but contained aluminium and iron containing residual phases [80]. It should be explored whether the acid resistance trend is similar at high and low concentration of acid. If so, the effect of higher leaching of  $Al^{3+}$  and  $Fe^{3+}$  ions at lower pH needs to be investigated. For CSA(HY) and CAC binders, even if the leaching is high, aluminium is not completely leached out due to its high concentration in the binders. For PC, lower pH marks the complete leaching of all elements. A phenomenon of unrealising full neutralisation capacity of  $Al(OH)_3$  at low concentration (high pH) has been described elsewhere [52]. A similar trend is observed in silicate minerals which have higher ANC, that is realised in longer duration as silicate dissolution is slow [85]. As per [40], solid



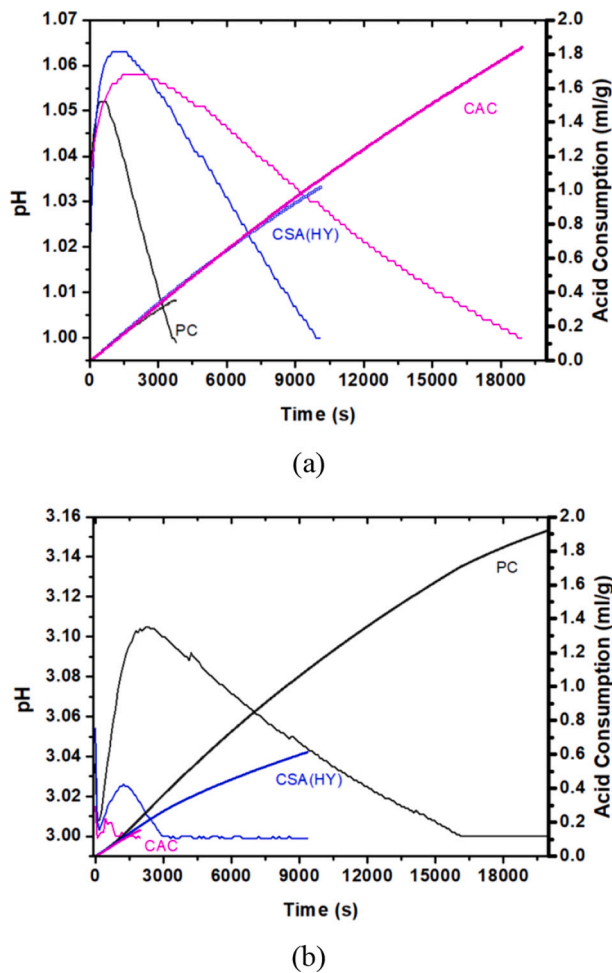


Fig. 14. pH evolution and acid consumption (thick line) during the initial period of STAT test for (a) pH 1 sulfuric acid, and (b) pH 3 citric acid.

phase dissolution and neutralisation of pore water species contributes to ANC. But some fraction of phase dissolution happens across time and ANC gets realised late [40]. The effects of neutralising cations such as Na, K, Ca, and Mg and non-neutralising (due to hydrolysis) cations such as Fe and Al are not explored in this study [85]. It should be discussed whether there is a clear agreement with the definition of neutralisation capacity in the literature. Can it be expressed only in terms of CaO

content as seen in [80]? However, calcium aluminate cement (though low Ca content!) and CSA cement have higher acid neutralisation capacity than Portland cement [52]. It is considered that neutralisation happens when a phase dissolves or through the mechanism of dissolution. When the dissolution rate is slow, low ANC was observed in case of PC-Slag concrete in spite of its superior acid resistance [82]. From above discussion, it is clear that  $AH_3$  does not dissolve at lower concentration. Hence, it may be required to mention the concentration (pH) at which ANC is calculated. Furthermore, not only calcium hydroxide amount as suggested by [80], but other hydroxides such as  $AH_3$  need to be accounted. This ambiguity urges to view the ANC for PC different from that of  $AH_3$  containing special binders such as CAC and CSA. Importantly, stability of phase such as N-A-S-H and C-A-S-H gel matters [59]. The matrices with large proportion of stable phases perform better.

Limitation of the acid consumption – mass loss correlation is that it may not accurately predict the performance of matrices developing cracks [59]. When crack widths are high, the acid consumption would be higher than expected [59]. The effect of cracking could not be verified in this study. However, the correlation was reasonably good in this study; that too in insoluble salt-forming acids such as citric and sulfuric acid. Although the neutralisation capacity of CAC is higher, the citric acid consumption was the least for CAC. This is because of the anion ‘citrate’ in citric acid. It is to be noted that stoichiometric buffering capacity is determined in terms of  $H^+$  ion neutralisation. But acid molecule has cation ( $H^+$ ) and anion ( $X^-$ ) parts. The anion determines the type of acid attack product and acts as ligand to the leached cations to form complexes. But  $H^+$  ion determines the extent of neutralisation. Hence, the stoichiometric neutralisation capacity should be called  $H^+$  ion neutralisation capacity. ANC and acid consumption can be used interchangeably, as it involves both cation and anion. It is seen in this study that the acid consumption was able to address the fragmentation effect in citric acid and the barrier effect in sulfuric acid.

Hydrated CSA(HY) paste doesn't have portlandite and the acid attack product mineralogy is dominated by gypsum, obviously in sulfuric acid and surprisingly in citric acid. This points to the decomposition of ettringite and monosulfate at low pH to gypsum and aluminium hydroxide [69]. In case of CSA(HY), the effect of citrate anion is thus mainly limited to complexolysis and playing less role in expansive calcium citrate salt formation.  $H^+$  ion-dominated acid attack mechanism observed in CSA cement [69] is clear from the similar acid consumption in CSA (HY) in case of citric and sulfuric acid attack (Fig. 18). Portlandite phase makes a binder vulnerable to acid anion attack and Portland cement contains this phase. Depending on the acid anions, corresponding calcium salts are formed and their effects on PC can be described as below:

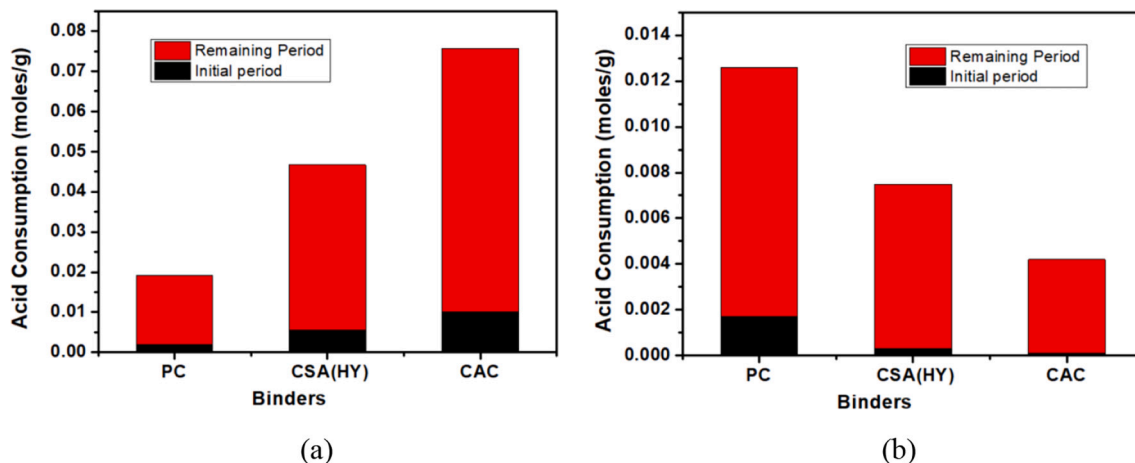
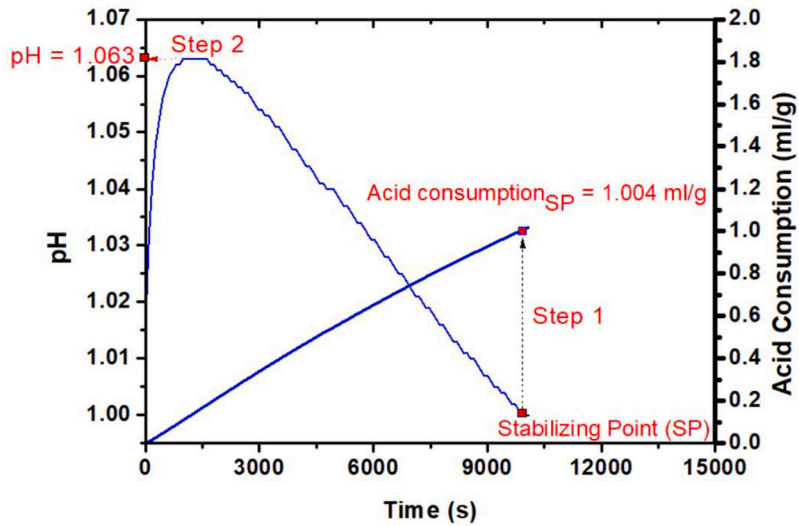
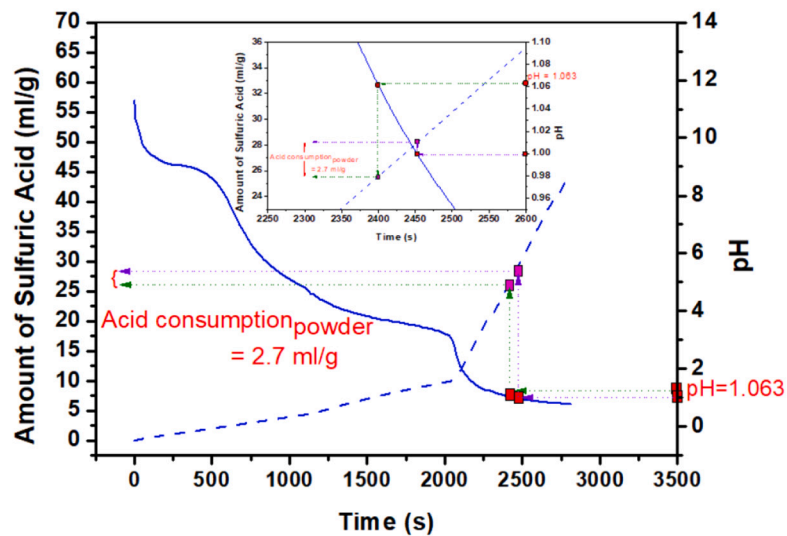


Fig. 15. The cumulative acid consumption during the entire period of test and during the initial period (up to SP) for (a) sulfuric acid (pH 1), and (b) citric acid (pH of 3).



Monolithic (STAT) Test - Step 1 & 2



Powder (Dynamic pH) Test - Step 3 (dashed line – amount of acid)

Fig. 16. The procedure developed to calculate the acid consumption corresponding to monolithic test from powder test in case of CSA(HY).

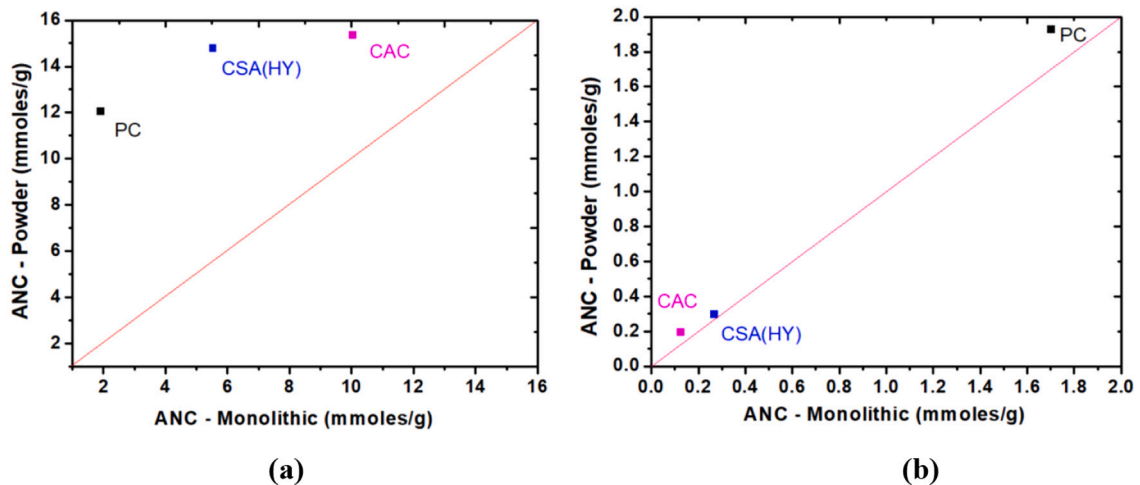


Fig. 17. Correlation of ANC between powder (dynamic pH) and monolithic (STAT pH) test at (a) sulfuric acid (pH of 1), and (b) citric acid (pH of 3).

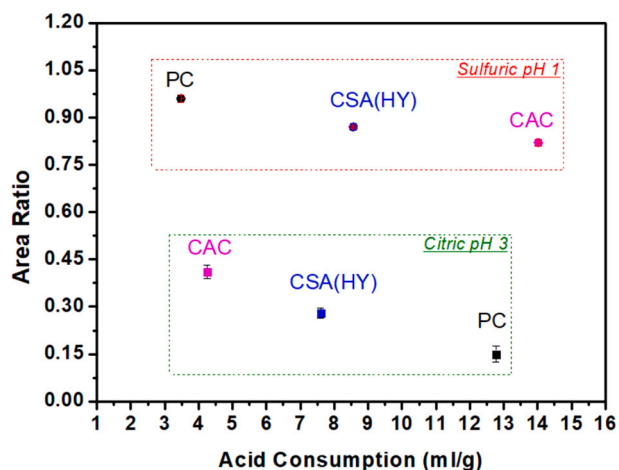


Fig. 18. Acid consumption vs. area ratio (or acid resistance) after 5-day STAT test.

Table 5  
Mechanism of acid attack in CSA(HY).

pH	Phases	H <sup>+</sup> ion neutralisation	Anion effect	Remarks
12.4–12.6				No portlandite
10.6–11.6	Monosulfate, Ettringite	Monosulfate, Ettringite dissolution at low pH to form gypsum, AH <sub>3</sub> [69,86,87]	Less effect: Leached Ca <sup>2+</sup> from monosulfate, ettringite	
8.8–9	C-S-H	Incongruent dissolution (pH 12.5–9.8) when Ca/Si ratio > 0.8 and thereafter congruent (pH < 9.8) [39,88]	Less effect: Leached Ca <sup>2+</sup> from C-S-H	
3–4	Aluminium hydroxide	Aluminium hydroxide neutralisation  H <sup>+</sup> ion neutralisation capacity of the binder	Leached Al <sup>3+</sup> (need to be explored): Complexolysis	ANC of the binder inclusive of anion attack and H <sup>+</sup> ion neutralisation

- Soluble salt-forming acid attack (such as hydrochloric acid, acetic acid, and nitric acid) as reported elsewhere is characterised by leaching. The corresponding calcium salt is soluble depending on the solubility product. Hence, the portlandite is easily leached out increasing porosity or resulting in material loss.
- Sulfuric acid attack results in the formation of gypsum and ettringite, leading to pore filling. The complete filling of porosity or partial filling is possible depending on the concentration of acid solution. Hence, there could be an effect of acid concentration on the performance of binder.
- Citric acid attack leads to formation of highly expansive product leading to fragmentation.

Table 5 shows the mechanism of portlandite-less binders such as CSA (HY). In Table 5, the effect of H<sup>+</sup> ion neutralisation and anion effect on different phases are shown. As the deterioration of CSA cement is less dependent on acid anion and has more dependence on neutralisation of H<sup>+</sup> ions, ANC methods are suitable for acid resistance of CSA and similar

binders such as CAC.

#### 4.4. Implications on biogenic acid resistance and future research

The results of this research are relevant to the chemical acid resistance of cementitious binders. Though acid attack is observed in underground structures, chemical warehouses, radioactive waste disposal structures, and agri-food industries [89–92], biogenic acid attack in sewers is a major concern. The STAT test can imitate the stage 3 of biogenic acid attack better than the conventional acid immersion test because a constant pH is maintained, similar as in biofilm attached sewer surface. The biogenic acid attack can be slow enough for the calcium aluminate binder surface to reach in equilibrium with the acidic environment, and hence, a protective alumina gel is formed. This gel maintains the surface pH between 3 and 4 [51]. CSA(HY) specimens were observed to be smooth after acid attack. It is difficult for bacteria to colonise as biofilm over smooth surface in biogenic acid attack [93]. The biogenic acid resistance is better evaluated through in-situ sewer tests than the microbiological simulation tests [94]. Depending on the methodology, the latter may sometimes be just an advanced version of conventional acid immersion test without focussing on stage 1 and 2 [95], and these simulation tests are complicated and pose some safety issues [96]. However, there are many uncertainties in field conditions such as fluctuations in temperature, gaseous concentration, relative humidity, and waste water level along with the differences in bacterial species, sewage characteristics, and turbulence [71,97]. Again, the sewer test requires a long period for comparative study of binders [98], as the deterioration rate can be as low as 0.6 mm/yr [99]. Considering the long test duration requirement and dilemma over a standardised sewer condition with less uncertainties, for reproducible results [48], a novel method to evaluate biogenic acid resistance needs to be designed.

Future research should focus on STAT test using sulfuric acid at pH of 0.5 and 2, as suggested by [94]. The tests with pH of 0.5 are quite vigorous, and that with pH of 2 are very slow and negligibly damaging. For pH of 0.5, small A/V ratio is preferred. Otherwise, acid consumption would be high leading to quick automatic stoppage of the test. In that case, some solution has to be removed in a short period, which may induce additional ‘interaction’ effects, if any, in the tests. A suitable modification of the test procedure needs to be adopted in these cases. The study should be extended to soluble salt forming acids such as acetic acid and hydrochloric acid. Moreover, the future research should involve a field evaluation of biogenic acid resistance of cementitious binders in sewer environment.

#### 5. Conclusions

Acid consumption was proportional to the extent of deterioration of cementitious binders. The method was modified and extended to CAC and CSA binders as well. When the acid consumption criterion was used, it resulted in higher *t*-test score than conventional deterioration criteria, showing its effectiveness in differentiating the binders. Main conclusions of the study are summarized below:

- Special binders such as CSA and CAC performed better than PC in citric acid environment (pH 3). This is because of the absence of portlandite in these binders.
- PC outperformed CAC and CSA binders in sulfuric acid environment of pH 1.
- The acid resistance could be evaluated based on the ‘stabilizing point’ of pH vs time curve or much before the total test period of 5 days. This contributed to the feasibility of a mini short-term test.
- The trend in acid consumption/ANC was similar for powder and monolithic tests while comparing PC, CSA (HY), and CAC. This further indicates that the difference in acid resistance among these three binders is mainly due to their difference in chemical composition.



- ANC obtained with monolithic specimens was exactly similar to that of powder for citric acid attack. This can be attributed to the extensive fragmentation induced sedimentation and turbidity of the solution, shifting the monolithic test toward powder test.
- CSA and CAC binders are characterised by the absence of portlandite. As a result, the acid attack product mineralogy of these binders has less anion dependency and is largely dependent on H<sup>+</sup> ion neutralisation. Neutralisation capacity tests are quite relevant for these binders. However, 'acid' neutralisation capacity ('acid' means both anion and H<sup>+</sup> ion) could be correlated with deterioration in case of citric acid and sulfuric acid attack (insoluble salt forming) of CAC, CSA(HY), and PC binders.

### CRedit authorship contribution statement

**Tom Damion:** Investigation, Methodology, Formal analysis, Writing – original draft. **Piyush Chaunsali:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

### Declaration of competing interest

The authors have no conflicts of interest to disclose.

### Data availability

Data will be made available on request.

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