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Review

Acid resistance of alkali-activated binders: A review of performance, mechanisms of deterioration and testing procedures

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ABSTRACT

Acid resistance is an increasingly important property for cementitious materials due to the wide range of applications where they are exposed to aggressive acidic environments. These include sewage systems, agricultural environments, food industries, oil wells, acidic precipitation and many more. Conventional Portland cement-based binders are known to be susceptible to acid attack due to the chemical nature of their main hydrated phases (i.e. C-S-H, Ca(OH)2, AFm and AFt). Alkali-activated binders are low carbon alternatives and have the potential to reduce the carbon footprint of the cement and concrete sectors. To date, wide scale uptake of alkali-activated binders has been limited. One area where they have appeared to demonstrate superior performance to traditional PC-based binders is that of acid attack. This paper critically reviews recent advances with regards to the acid resistance of alkali-activated binders. The mechanism of attack by a wide range of organic and inorganic acids is also compared. The effect and relevance of the adopted test procedures are also examined. Finally, some future research opportunities in the area are identified.

1. Introduction

Due to the significant carbon emissions associated with the production of Portland cement (PC), alternative low-carbon binders have received significant attention in recent decades. Alkali-activated binders (AABs) which also includes binders referred to as “geopolymers” are one of the most common classes of low-carbon binders [1]. Alkali-activation involves the reaction of an aluminosilicate precursor with an alkaline activator. A wide range of precursors can be used as an aluminosilicate source, including various types of fly ash [2], slag [3], calcined clay [4,5], palm oil fuel ash (POFA) [6] and biomass wood ash [7]. These precursors have much less embodied carbon than PC making them an attractive option for alkali-activation. The most commonly used activators are alkali hydroxide or silicate solutions (usually Na or K) [8]. Unfortunately, the alkaline activators generally have a much greater environmental footprint than the aluminosilicate source materials, which has resulted in a search for alternative low-carbon activators to enhance the environmental credentials of AABs further [9–13].

Recently the understanding surrounding the rheological behaviour, setting properties and structural characterisation of AABs has advanced considerably [1]. Furthermore, in 2016, a Publicly Available Specification for AABs was published by the British Standards Institute [14]. However, despite the significant progress that has been made, widespread uptake of AABs has been relatively limited [15,16]. In order to improve the adoption of AABs by industry, it may be conducive to identify niche applications where they exhibit superior performance when compared with conventional binders. Amongst various durability characteristics, acid resistance has often been cited as a strength of AABs. This is particularly interesting given that PC-based materials are known to be particularly susceptible to acid attack.

This paper reviews the performance and mechanisms of deterioration of AABs under acid attack. In particular the performance of different types of AAB are summarised and compared. The influence and relevance of testing procedures used to assess the acid resistance of AABs is also discussed.

2. Acid attack in-service - exposure environments and conditions

Acid attack is a topic of ever-growing significance driven by increasing urban, agricultural and industrial activities [17]. These activities contribute to the number of sources, types and the quantity of...
Thus, there is a broad range of acidic media within the built environment which encounters construction materials. These are described in more detail below and are summarised in Table 1.

The degradation of water and wastewater infrastructure, and, in particular concrete pipe networks is a considerable challenge worldwide, resulting in large economic losses annually [18–20]. Fig. 1 shows a photograph of a degraded concrete pipe from a sewer system [21]. This is termed as microbiologically induced corrosion, where the main attacking acid is biogenic sulfuric acid ($\text{H}_2\text{SO}_4$) that is generated from sulfur-oxidising bacteria [22,23]. Carbonic ($\text{H}_2\text{CO}_3$) and organic acids have also been reported to form in the wastewater environment [18]. $\text{H}_2\text{SO}_4$ can also be present in groundwater or produced from the oxidation of sulfur bearing compounds in backfill, such as pyrite, causing degradation to concrete substructures [24,25]. The dissolution

<table>
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<th>Acid type</th>
<th>Typical concentration</th>
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<tr>
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<td>Biogenic sulfuric acid ($\text{H}_2\text{SO}_4$) which is produced from toxic $\text{H}_2\text{S}$ gas</td>
<td>$\text{H}_2\text{S}$ concentration (up to several hundred ppm)</td>
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<td>Substructures, geothermal wells</td>
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<td>Well stimulation (oil and gas industries)</td>
<td>Cement sheath of well</td>
<td>Hydrochloric acid (HCl) and hydrofluoric acid (HF)</td>
<td>HCl (0–15%)HF (0–3%)</td>
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<tr>
<td>Acid rain</td>
<td>Concrete supporting structures and bunkers</td>
<td>Hydrochloric acid (HCl)</td>
<td>1–3 mg/m$^3$</td>
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</tr>
<tr>
<td>Manufacturing and processing (chemicals, fertilizers, ammonium nitrate and metal)</td>
<td>Storage facilities and concrete flooring</td>
<td>Sulfuric acid ($\text{H}_2\text{SO}_4$), nitric acid ($\text{HNO}_3$), hydrochloric acid (HCl) and phosphoric acid ($\text{H}_3\text{PO}_4$)</td>
<td>Various</td>
<td>[203]</td>
</tr>
<tr>
<td>Agriculture (silage effluent, liquid manure, animal feed, dairy farming and anaerobic digestion)</td>
<td>Storage facilities, animal housing, animal feed areas and flooring</td>
<td>Lactic acid (CH$_3$CH(OH)COOH), acetic acid (CH$_3$COOH), propionic acid (CH$_3$CH$_2$COOH), butyric acid (CH$_3$CH$_2$CH$_2$COOH)</td>
<td>pH approx. 3.5–7.2</td>
<td>[41–53,204]</td>
</tr>
<tr>
<td>Food and beverage industry (vinasse, whey, molasses, cane juices, milk processing, wine effluents, distillates)</td>
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<td>Citric acid (H$_2$C$_6$H$_5$O$_7$), acetic acid (CH$_3$COOH), fumaric acid (H$_2$C$_2$H$_4$COOH), lactic acid (CH$_3$CH(OH)COOH), phosphoric acid (H$_3$PO$_4$), malic acid (C$_4$H$_4$O$_4$), succinic acid ([CH$_2$]$_2$CO$_2$H$_2$) and tartaric acid (COOH(CH(OH)CHOH)COOH)</td>
<td>pH approx. 3.2–6.5</td>
<td>[45,205,206]</td>
</tr>
<tr>
<td>Bird excreta</td>
<td>Pavenements, façades and other external elements of buildings, structures, infrastructure</td>
<td>Glyoxylic acid (C$_2$H$_4$O$_2$)</td>
<td>pH 5.4–6.0</td>
<td>[54,55]</td>
</tr>
</tbody>
</table>

![Fig. 1. Photograph of concrete pipe degraded due to microbiologically induced corrosion. Figure obtained from Teplý et al. [21].](image-url)
of hydrogen sulfide has been reported to form H$_2$SO$_4$ (with a low pH of <1) on the concrete walls of geothermal wells [26].

The oil and gas industries commonly use hydrochloric acid (HCl) during well stimulation and acidizing operations [27–30]. This process allows HCl (pH 0–3) to come into contact with the cement sheath of the well causing deterioration and breakdown [31–34]. Recent studies [35,36] have also suggested that HCl is present in the coal mine environment. It also worth noting that many mining operations produce mining water with a low pH, including pyrite, copper and lignite mines [37].

In recent decades, acid rain has become more prominent, particularly in China where acid rain is reported to cover at least one third of Chinese territory [38]. In some regions, rain was reported to have an average pH of between 3.5 and 4.8 [39]. Acid rain is generated from the combustion of fossil fuels, the smelting of metal ores and various industrial pollutants. These are released into the environment as gases and react with water to form acidic precipitation (typically sulfur dioxide and nitrogen oxides forming H$_2$SO$_4$ and nitric acid (HNO$_3$) [40].

Organic acids are also found in biogas plants, vinasse, and distillates typically in the range of 5 to 6 [41]. Despite the pH of ‘weak’ strong acids [45,51], their tendency at a given pH to have a higher acid concentration than for the corresponding main acids in silage effluent are lactic acid (CH$_3$COOH) and acetic acid (CH$_3$COOH), whereas the main acids present in liquid manure are CH$_3$COOH, propionic (CH$_3$CH$_2$COOH) and butyric (CH$_3$CH$_2$CH$_2$COOH) [44–46]. Silage effluent is produced as a result of storing grass as winter feed for livestock [47]. The grass is placed in concrete silos, compacted and sealed. It then undergoes a fermentation process converting sugars to acids and producing silage effluent [48]. The resulting effluent typically has a pH value of approximately 4.0 and the concentration of CH$_3$CHOH and CH$_3$COOH in silage effluent is typically in the range of 5–44 g/L and 1–5.5 g/L, respectively [41,45,49].

Organic acids are also found in biogas plants, vinasse, and distillates [50,51]. Despite the pH of ‘weak’ organic acids often being lower than that of strong acids (such as HCl, H$_2$SO$_4$ and HNO$_3$), the attack is not necessarily less aggressive. This is due to their dissociation constant and their tendency at a given pH to have a higher acid concentration than for strong acids [45,51–53].

The deterioration of buildings due to the deposition of bird excreta has been well documented in recent years. Uric acid in bird excreta is broken down by fungi into urea and glyoxylic acid and causes deterioration to cement-based materials [54,55].

3. Performance of traditional Portland cement-based binders under acid attack

3.1. Mechanism of deterioration

The vulnerability of traditional PC binders to aggressive media is well known [56]. Their alkaline nature has been cited as a reason for their vulnerability to acidic environments [17]. When PC-based binders come in contact with acidic media ionic transfers occur between the pore solution and the acidic media which involves the dissolution of some hydration products [57]. Calcium hydroxide (Ca(OH)$_2$) also known as portlandite and ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{16}$·26H$_2$O) are among the first phases to be dissolved during acid attack [58].

Then, calcium silicate hydrate (C-S-H), the main binding gel in hardened PC binders, undergoes decalcification [57]. Dissolution combined with leaching of these phases increases the porosity and permeability of the matrix [59] which allows faster onset of further deterioration [60]. This describes the basic mechanism of acid attack on PC binders, however, the reality is much more detailed, complex and not within the scope of this review. Further details can be found in a RILEM TC 211 State-of-the-Art Report [56] which has several sections dedicated to the mechanisms of degradation of PC binders in aggressive acidic media.

3.2. Methods for obtaining improved performance

Various methods have been employed in an attempt to enhance the acid resistance of PC binders. Three of the main approaches that have been taken are; 1) prescriptive guidelines in standards, 2) mix design optimisation and 3) protective coatings.

In relation to standards, BS 8500-1:2015 + A2:2019 [61], provides guidance to specifiers regarding cement content, water/cement ratio and strength class. Acid attack is covered under the category ‘chemical attack’ and is related to the pH found in soil and groundwater to which concrete will be exposed in-service.

In terms of mix design, studies [62–65] have shown that improved acid resistance can be achieved by replacing PC with supplementary cementitious materials (SCMs) such as fly ash, silica fume, slag and natural pozzolans. According to Dyer [66], this approach is useful for contact with acidic solutions of pH above 4. However, under more acidic conditions, appropriate selection and proportioning of mix constituents is not adequate to provide significant protection.

Protective coatings are used to provide a barrier between concrete and the aggressive media. There are a variety of possible surface treatments including acrylic coatings, polyurethane coatings, epoxy coatings, silanes and siloxanes [67]. Whilst numerous studies [68–71] indicate that coatings can be an effective means of protection, there remains limitations. Cracking of the concrete and/or the coating after its application allows acid to permeate and cause deterioration [72]. Therefore, if the coating is not applied properly or cracks emerge, it may result in concentrated acid attacks in specific regions which could be more detrimental to the service life of the entire structure. Many instances of acid attack in-service (e.g. agriculture or wastewater infrastructure) also involve some form of abrasion which is likely to reduce the effectiveness of surface treatments. There are also concerns surrounding the weathering of coatings and the effect of ultraviolet radiation from the sun and the loss of adhesion between coatings and the substructure over time [73]. It is also important that surfaces are adequately prepared for surface treatment by cleaning and the use of a primer layer if necessary [66]. This adds further expense and the risk remains that the coating will not be effective. Aguiar et al. [74] reported that even for coated concretes, a lower cement content provided better performance. This indicates that coating alone may not be adequate to provide the necessary protection.

Each of the methods that have been briefly discussed for improving acid resistance, have merit. However, none of these approaches have been able to fully address all of the issues caused by acid attack. The underlying problem remains the inherent susceptibility of the main hydration products of PC to acid attack.

4. Performance of alkali-activated binders under acid attack

As discussed, one of the main factors limiting the performance of PC-based binders to acid attack is the vulnerability of the reaction products, particularly Ca rich products to dissolution and breakdown when they come into contact with acidic media. Therefore, the performance of AABs binders under acid attack is divided into three parts based on the relative Ca content within the AABs.

4.1. Low Ca AABs

This section considers AABs that have a low Ca content and are based on precursors such as fly ash, other ash types and calcined clays.

4.1.1. AABs made with fly ash

Fly ash, obtained from coal combustion is rich in Si and Al. Bakherev [75] studied the resistance of alkali-activated fly ash (AAFA) paste samples to 5% solutions of CH$_3$COOH and H$_2$SO$_4$. Samples activated with sodium hydroxide displayed superior performance compared with samples activated with sodium silicate and those activated with a
combination of sodium hydroxide and potassium hydroxide in terms of mass and strength evolution over exposure time. The deterioration of the AAFA samples was attributed to depolymerisation and dealumination of the aluminosilicate gel. A more stable and cross-linked aluminosilicate structure, along with small pore sizes, was suggested as the reason for good performance from the samples activated with sodium hydroxide. Fluctuations in strength were highlighted as a serious concern for AAFA samples and was linked to the migration of alkalis into the acidic solutions. However, it was reported that the AAFA pastes did demonstrate greater acid resistance than the PC pastes investigated.

Fernandez-Jimenez et al. [76] investigated the effect of different activating solutions on the resistance of AAFA samples to HCl (pH = 1.0) for 90 days. The first solution consisted of only sodium hydroxide whereas the second consisted of both sodium hydroxide (85%) and sodium silicate (15%). The different activators displayed very similar results in terms of visual appearance and strength loss. However, the samples activated with only sodium hydroxide displayed a mass loss of 2.5% compared with a mass loss of 4.2% for the samples activated with a blend of sodium hydroxide and sodium silicate solutions. Microanalysis of both sample types identified a drop in the Al content of the binding gel due to the acid attack. A PC sample was also investigated and displayed much lower acid resistance than the AAFA samples in terms of visual appearance, mass loss and strength loss. These findings are similar to those reported by Bakharev [75] whereby AAFA activated with sodium hydroxide performed better against acid attack than other activator types. Secondly, both studies indicate that significant leaching takes place and is likely the main mechanism of deterioration of AAFA samples. Thirdly, both studies highlighted better performance for AAFA samples than PC samples.

Rostami and Brendley [77] studied the acid resistance of AAFA concrete samples by measuring the mass change of samples submerged in acid solutions for one year. The acids studied were; 100% CH₂COOH and 20% solutions of HNO₃, HCl and H₂SO⁴. PC concrete samples with 20% addition of silica fume were also studied for comparison. After exposure to all four acids the AAFA samples exhibited a much superior performance, for example in HCl acid they lost 5% of their mass in one year whereas the silica fume PC samples lost 25% of their mass in only 7 days. PC concrete with the addition of silica fume was used in this study as it is considered more resistant to aggressive acidic environments than conventional PC concrete.

Thokchom et al. [78] also reported high acid resistance for AAFA mixes when exposed to H₂SO₄ (10%). AAFA samples activated with sodium hydroxide and sodium silicate with different concentrations of Na₂O (5–8% of fly ash) were studied. The samples with increased Na₂O percentage displayed an increased mass loss, but a decreased strength loss. However, all AAFA samples displayed a better performance in terms of mass loss observed than their heavily corroded PC counterparts.

In another study the mass loss and acid penetration depth was measured during 110 days exposure to HCl (22%) by Chaudhary and Liu [79]. They found that AAFA samples performed better than PC samples in terms of both mass loss and penetration depth. In fact, mass losses were reported as 150 times greater for PC samples.

Lloyd et al. [80] studied the corrosion depth of AAFA and PC pastes during exposure to H₂SO₄ (pH = 1.0) for 28 days. They found that the corroded depth was approximately 5 times larger for the AAFA samples compared with the PC samples.

Temuujin et al. [81] reported a gradual reduction in compressive strength of AAFA samples exposed to an 18% HCl acid solution for 5 days. The acid exposure resulted in leaching of high levels of Fe, Al and Na into the acid solution which increased linearly with time until 5 days. This leaching behaviour caused the lower compressive strength observed due to the more porous microstructure left behind.

Tahiri et al. [82] compared the resistance of AAFA and PC samples when exposed to different concentrations of HNO₃. At concentrations of 10 and 20% the AAFA samples performed better in terms of mass loss. On the other hand, when a concentration of 30% was used, the PC samples displayed smaller mass losses than the AAFA samples. The deterioration of the AAFA samples was related to the removal of Al and the formation of an imperfect highly siliceous framework. However, it is worth noting that severe concentrations of 30% are unlikely to be present in-service.

A recent study by Aliques-Granero et al. [83] compared the resistance of AAFA and PC samples to H₂SO₄ (1, 3 and 5%). They detected no changes visually or in terms of sample mass and dimensions for the AAFA samples. However, a decrease in compressive strength was observed and related to the dealumination of the main binder gel in AAFA samples. On the other hand, the PC samples exhibited mass loss and complete disintegration after 196 days exposure.

The above studies focus on the use of class F fly ash (rich in Si and Al), Lloyd et al. [80] compared the acid resistance of class F fly ash with that of class C fly ash, which was also rich in Si, but contained around 20% Ca and less Al than class F fly ash. They reported superior acid resistance for the class C fly ash in terms of corroded depth after immersion in H₂SO₄ (pH = 1.0). This was attributed to the lower permeability of the samples made with class C fly ash. It should also be noted that the compressive strengths of the class C fly ash samples was 19–59% higher than that of the class F fly ash samples studied.

4.1.2. AABs made with other ash types

Sata et al. [84] investigated the deterioration of alkali-activated bottom ash samples and PC samples exposed to 3% solutions of H₂SO₄. Bottom ash (similar chemical composition to fly ash) consists of large ash particles which are generated from the coagulation of melting fly ash particles. They found that the alkali-activated bottom ash samples exhibited superior performance with lower than 3.6% mass loss after 120 days. On the other hand, the PC samples were completely destroyed after 120 days with a 95.7% mass loss reported. The superior performance was attributed to the more stable cross-linked aluminosilicate structure compared with the PC hydration structure. Ariffin et al. [85] compared the resistance of alkali-activated blended ash concrete and PC concrete to H₂SO₄ (2%). The blended ash concrete consisted of fly ash and POFA (rich in Si) and was activated using sodium hydroxide and sodium silicate. The blended ash concrete displayed superior performance in terms of mass loss and compressive strength loss when compared with PC concrete. The mass loss after 18 months was 8% for the blended ash concrete and 20% for the PC concrete. Similarly, the compressive strength loss was 35% for the blended ash concrete and 68% for the PC concrete.

4.1.3. AABs made with calcined clays

Calcined kaolinite clays, often termed as metakaolin contain predominantly Al and Si [86]. They can also be used to produce low Ca AABs when activated. Ukrainczyk and Vogt [87] investigated the elemental leaching of alkali-activated metakaolin in CH₂COOH (0.1 M, pH = 2.8). They found that CH₂COOH exposure resulted in dissolution of Al and depletion of K. Kwasny et al. [88] studied the resistance of alkali-activated kaolinite-rich clay to HCl (1, 3 and 5%) and H₂SO₄ (1, 3 and 5%). Within the same strength grade, the AABs samples displayed lower surface deterioration and mass loss than PC samples. In a study by Davidovits [89], it was reported that the resistance of metakaolin based AABs to acid corrosion (5% H₂SO₄ and HCl) was better than the resistance of specimens containing PC and calcium aluminate cement. It was estimated the mass loss ranged between 30 and 60% for the calcium aluminate cement and even greater for the PC, compared to 5–8% for the metakaolin based specimens. Recently, Gevauadan et al. [90] reported on the H₂SO₄ resistance of alkali-activated metakaolin cements supplemented with Mg(OH)₂. Findings indicated that the addition of Mg(OH)₂ improved acid resistance through reduced dealumination and Si and Na leaching. This was attributed to MgO retention within the microstructure which increased Mg-Al coupling and ultimately stabilised the sodium aluminosilicate hydrate (N-A-S-H) binder gel.
4.2. Ca rich binders

One of the main mechanisms of deterioration of PC concretes, mortars and pastes due to acid attack is decalcification [91,92]. Decalcification is the dissolution and migration of Ca ions from cement paste into surrounding aggressive media [93,94]. Decalcification is also prevalent in alkali-activated slag (AAS) binders due to their Ca rich nature [95]. Decalcification in AAS was studied by Komljenovic et al. [96] and Varga et al. [97]. Ammonium nitrate solution was used to cause leaching of Ca ions. Both studies report superior decalcification resistance in AAS samples when compared with PC samples. This was attributed to the absence of calcium hydroxide as a reaction product in AAS, a lower Ca/Si ratio and a high level of polymerisation of silicate chains [96,97]. Furthermore, various slag sources were investigated and it was concluded that AAS with a higher Al content had longer polymer chains, is more intensely cross linked, consequently more stable and capable of resisting acid attack more effectively [97]. Shi [98] studied the performance of AAS and PC paste when exposed to HNO$_3$ and CH$_3$COOH. After 580 days immersion in HNO$_3$ the AAS and PC pastes were corroded to a depth of approximately 1 and 2.5 mm, respectively. In the case of CH$_3$COOH, after 60 days of immersion, 5 mm of AAS and 15 mm of PC pastes were corroded. The pH of both acids was maintained at 3 throughout. CH$_3$COOH caused faster corrosion than HNO$_3$ for both AAS and PC samples. These results are similar to earlier results obtained by Shi and Stegemann [99] and suggest that AAS is more resistant to acid attack than PC based on corroded depth measurements. Bakharev et al. [100] investigated the resistance of AAS and PC concrete to CH$_3$COOH (pH = 4.0) attack during 12 months of exposure. Fig. 2 displays the compressive strength evolution of AAS and PC concrete exposed to acid and control samples stored in water. The AAS samples had a compressive strength loss of 33% compared with 47% for PC samples after 12 months exposure to CH$_3$COOH. The depth into the concrete which had a pH below 9 was also measured and found to be 22 and 16 mm for PC and AAS concrete respectively. This suggests that the CH$_3$COOH travelled 16 mm into AAS concrete and 22 mm into PC concrete after 12 months. Bernal et al. [101] examined the resistance of AAS and PC mortars to CH$_3$COOH with a pH maintained at 4.5 for 150 days. As shown in Fig. 3 the PC mortars suffered severe cracking and spalling compared with AAS mortars after 150 days exposure. They also lost almost all of their strength compared with AAS mortars which endured smaller variations in strength during exposure and retained 75% of their strength after 150 days (Fig. 4). The authors concluded that while decalcification of the main binder gel takes place in AAS samples the residual aluminosilicate type gel is less soluble and more mechanically sound than the silicate gel formed in PC mortars during acid attack.

Aliques-Granero et al. [83] investigated the performance of AAS and

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Fig. 2. Compressive strength evolution of AAS and PC concrete during 12 months exposure to CH$_3$COOH. Figure obtained from Bakharev et al. [100].

Fig. 3. Photographs of (A) PC mortars and (B) AAS mortars, after 150 days of exposure to CH$_3$COOH. Specimens are 50 mm cubes. Figure obtained from Bernal et al. [101].
PC samples when exposed to H$_2$SO$_4$ (1, 3 and 5%). The AAS samples displayed splitting and cracks as well as mass gains and dimensional increases. These findings can be associated with the formation of gypsum. Gypsum was also the main corrosion product in the PC samples, however, mass losses and dimensional decreases were observed instead. This may be due to different amounts of gypsum formed in AAS and PC samples due to different initial Ca content. Arbi et al. [102] suggested that the role of Ca on the durability of AABs needs further investigations to draw suitable correlations between Ca content and durability properties. Buchwald et al. [103] investigated the resistance of AAS to silicate effluent by preparing a synthetic effluent consisting of 75% CH$_3$COOH and 25% CH$_3$COO$. Two AAS mixes were studied, one activated with sodium sulfate and the other with sodium silicate. They compared the mass loss with a PC mix after 42 days immersion in the synthetic effluent. The AAS mix activated with sodium silicate had a smaller mass loss (2%) than the mix activated with sodium sulfate (5%). Both mixes had smaller mass losses than the PC mix (8%).

4.3. Blended systems

The blending of different precursors together is becoming more common and in many cases provides AABs with a range of enhanced properties. Some studies have reported on the acid resistance of blended systems containing a mixture of low Ca and Ca rich precursors and are described below. Allahverdi and Skvara [104,105] studied the mechanism of HNO$_3$ (pH = 1.0, 2.0 and 3.0) attack on pastes consisting of equal proportions of fly ash and slag. They described a mechanism which consisted of the leaching of Ca and Na ions which were replaced by H$^+$ and H$_2$O$^-$ ions from the acid solution. An electrophilic attack by acid protons on Si-O-Al bonds was also reported. This resulted in the ejection of Al from the aluminosilicate network. The Al was mostly substituted by Si atoms resulting in an imperfect highly siliceous framework. The same authors also studied the resistance of these mixes to relatively high, medium and low concentrations of H$_2$SO$_4$ [106,107]. They found that at high concentrations (pH = 1.0) the mechanism is similar to that observed during HNO$_3$ attack. However, the diffusing Ca ions reacted with counter-diffusing sulfate ions to form gypsum crystals inside the corroded layer. The deposition of gypsum crystals inside the corroded layer was reported to provide a protective effect inhibiting further deterioration. At lower concentrations (pH = 3.0) the deterioration mechanism was exactly the same as that reported for HNO$_3$ and no gypsum formation was observed [104,105]. Lloyd et al. [80] investigated the effect of slag content on AAS pastes exposed to H$_2$SO$_4$. Corroded depth was used as an indicator of acid resistance. After 28 days immersion, the corroded depth of the AAF pastes was approximately 6 mm, which reduced below 3 mm with 50% substitution of fly ash for slag. The reduced depth of corrosion was explained by a reduction in permeability and pore size due to the addition of slag. Lee and Lee [108] studied the resistance of different blends of fly ash and slag to H$_2$SO$_4$ (10%) attack. They reported that after 56 days of immersion, AAF with 0, 10 and 30% slag displayed negligible mass changes. However, when the binder contained 50% slag a mass gain was observed, similar to the mass increase observed by Aliques-Granero et al. [83] when AAS samples were exposed to H$_2$SO$_4$. The corresponding PC samples suffered mass losses of greater than 30% of their initial mass. All samples exhibited significant compressive strength losses after both 28 and 56 days exposure. Lee and Lee [108] concluded that there are two causes of deterioration on fly ash and slag blends due to H$_2$SO$_4$ attack. The first one is the corrosion by means of sulfate penetration which they associated with permeable voids and water absorption rate. The second is the corrosion of the reaction products (calcium aluminosilicate hydrate gel (C-A-S-H) and N-A-S-H) which differ depending on the fly ash/slag ratio used.

Özcan and Karakoç [109] produced alkali-activated concrete samples from blast furnace slag and ferrochrome slag. The ferrochrome slag had a much lower Ca content and increased Mg and Al content compared with the blast furnace slag. This study exposed samples to various acids (5%) and concluded that as the ferrochrome slag content of the concrete samples was increased, the resistance to acid attack also increased. This was particular evident in terms of the length changes observed as the samples with increased ferrochrome slag suffered less shrinkage following HCl and phosphoric acid (H$_3$PO$_4$) exposure. They also suffered less expansion following exposure to H$_2$SO$_4$. This was likely due to the less availability of Ca in ferrochrome slag to form gypsum. Another
study [110] combined blast furnace slag with silico-manganese fume to produce alkali-activated mortars. Slag free specimens were also studied. After exposure to H$_2$SO$_4$ (5%), they found that the slag free specimens exhibited high resistance attributed to the lack of Ca in silico-manganese fume. The blended specimens were reported to have undergone dealumination along with gypsum formation which resulted in severe spalling.

Wu et al. [111] found that adding up to 10% calcium aluminate cement had a positive impact on the H$_2$SO$_4$ (pH = 2.0) resistance of alkali-activated metakaolin. This was attributed to the reduced volume of permeable voids and the enhanced neutralisation capacity.

Ahmad et al. [112] studied the effect of different admixtures on the H$_2$SO$_4$ (5%) resistance of blended fly ash and slag AABs. Silica fume, MgO, cement clinker and metakaolin were added to the AABs in the following proportions: 1.5, 3 and 4.5%. Acid resistance was assessed after 270 days immersion in a H$_2$SO$_4$ (5%). From visual examination, it was observed that the AAB specimens’ presented different degrees of deterioration with the removal of binder paste from the surface and sample edges. The amount of removed binder or exposed sand particles was highest for the mortars containing 1.5% admixture and gradually decreased as the admixture content increased to 4.5%. As shown from Fig. 5, the specimens which contained silica fume, MgO and metakaolin, displayed lower mass losses than the control samples and the samples which contained cement clinker. Compared to the control sample, the AABs containing the admixtures content resulted in lower pH readings of the acid solution, indicating lower dissolution of binder paste in the acid solution. The lowest pH value at the end of first and second cycle was shown by the mixture containing 4.5% metakaolin. These results show very close relation with the visual appearance and mass loss findings. The high H$_2$SO$_4$ resistance of the AAB containing metakaolin was attributed to a higher degree of geopolymerisation due to the content of alumina-silicates in metakaolin. However, it is worth noting that similar performance was observed when silica fume was used as an admixture. Also, the particle size of the chosen admixtures was not considered in this study. Future work could consider the influence of the particle size of admixtures on the acid resistance of AABs.

Huseien et al. [113] evaluated the effect of slag content on the H$_2$SO$_4$ (10%) resistance of AAS incorporating waste ceramic powder (WCP) and fly ash (FA), it was reported that the reduction in the slag content from 50% to 10% led to reduced strength loss from 21.7% to 1% after 6 months and from 32.2% to 11.8% after 12 months of immersion. Likewise, deterioration and surface cracks decreased when slag was replaced as shown in Fig. 6. It was also noted that gypsum formed due to interaction between Ca and SO$_4^{2-}$ ions and caused expansion and cracking, this phenomenon decreased as the slag content and Ca content decreased, in agreement with other studies [83,114]. In another study [115], the effect of replacing fly ash with POFA in fly ash/slag blended mortars was studied. The results indicated that the increased POFA content led to a decreased Al content and increased the Ca/Al ratio which negatively effected the H$_2$SO$_4$ (10%) resistance of the tested specimens. The residual strength of specimens evaluated after 12 months decreased from 57% to 32% with increasing POFA content from 0% to 50%, respectively.

It was reported [116,117] that self-compacting concrete made with AAS as the binder presented higher durability performance in an H$_2$SO$_4$ (10%) environment compared to PC concrete. However, in terms of AAS specimens, those prepared with a high content of Ca displayed lower performance compared to those prepared with less Ca. For example, reducing the slag content from 100% to 30% enhanced the resistance of the specimens to acid solution by reducing the strength loss from 74% to 16%, respectively. This performance was also linked to the formation of less expansive gypsum minerals at lower slag content.

Khan et al. [118] investigated the replacement of fly ash with waste glass (up to 40%) in alkali-activated fly ash slag. They exposed mortars to H$_2$SO$_4$ (3%) and HCl (3%) for one year and found that waste glass improved the acid resistance in terms of the mass and strength losses observed. It was also reported that 10–20% was the optimum level of replacement.

Recently, some studies [119,120] have investigated the acid resistance of AABs blended with PC to assess the performance of a blended...
Dealumination was also confirmed as the dominating microstructural change of synthetic N-A-S-H gels under H$_2$SO$_4$ attack [123]. Further work could investigate other low Ca materials that could be added to the system to reduce porosity and/or pore connectivity. In turn the corrosion depth and subsequent strength loss of low Ca binders may be improved. Additionally, it would be valuable for scientists to understand how low Ca binders can be made more resistant to dealumination which is the detrimental mechanism limiting their performance. As described previously, recent work by Gevaudan et al. [90] reported that the addition of Mg(OH)$_2$ to alkali-activated meta-kaolin cements reduced their susceptibility to dealumination.

In the case of Ca rich binder systems, the behaviour is similar to that observed in PC-based binders, where, decalcification is the main mechanism of deterioration [124]. Unlike, low Ca AABs such as AAFA, the outer surface of Ca rich AABs such as AAS does undergo visible deterioration [125]. Acids were also found to penetrate into the samples and cause a significant degradation of the microstructure close to the sample surface resulting in strength losses. Crucially, this corroded layer was often significantly smaller than that observed for low Ca binders and slightly smaller than for PC-based binders. Therefore, although Ca rich AABs are more prone to surface deterioration than low Ca AABs, they do not suffer from such a sizeable corroded layer meaning that their overall performance is often superior. The surface deterioration is predominately caused by the combined decalcification and dealumination of calcium sodium aluminosilicate hydrate (C-N-A-S-H) gels [114,123]. One benefit for C-N-A-S-H is that highly polymerised Si often remains behind which helps to resist further acid penetration and attack [52,114,123]. Significantly, the overall performance of alkali-activated Ca rich binders is also superior to that of PC binders. A schematic diagram which summarises the acid degradation mechanism in various AABs as described above is shown in Fig. 7.

Recent developments in this area are using blended systems which often offer superior performance through combining precursors and benefiting from specific traits from each individual precursor such as low Ca content and particle size distribution.

The literature available on the acid attack of AABs shows that there have been numerous studies conducted on these materials. The majority of these studies report good performance when comparison is made with PC counterparts. However, there are a wide range of variables considered and many authors only consider a single deterioration mechanism. Few studies consider multiple indicators which is necessary when studying different binder types. Furthermore, there remain limitations in the understanding of acid attack on these materials, particularly at a microstructural level [101]. The effect of the activator dosage was studied on AABA. However, no studies reported the effect of alkali-activator dosage on fly ash/slag blends. In addition, the majority of studies used commercially available activators. No studies reported on the acid resistance of AABs prepared with novel low-carbon activators, such as those developed using rice husk ash, bamboo leaf or waste glass [11-13]. The effect of the curing regime on acid resistance was also rarely considered. Methods to reduce the corrosion depth and dealumination susceptibility of low Ca binders are worthy of further investigation. It is also worth noting that normally studies compare the performance of AABs with neat PC mixes. Nowadays, a significant proportion of commercially used PC concrete and mortar contains SCMs, which would likely have superior performance under acid attack than neat PC mixes. Therefore, future studies comparing PC mixes using SCMs against AABs would be valuable and more relevant to current industry practice.

5. Testing procedures

In this section, research findings related to the testing procedures employed in the study of the acid resistance of AABs are examined. Consideration is given to the influence of the testing procedures adopted on the findings obtained. The relevance of adopted testing procedures to in-service conditions is also presented. Table 2 presents a summary of the testing procedures used by numerous authors to study the acid resistance of AABs.

5.1. Influence of testing procedures on findings

Many of the studies discussed above suggest that AABs have superior acid resistance when compared with PC binders. However, there has not been a widely adopted set of testing procedures for studying acid resistance. This is likely in part due to the complexity of the topic but also due to a lack of specific standards for assessing the acid resistance of...
Table 2
Summary of test procedures used to study the acid resistance of alkali-activated binders.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Mass change</th>
<th>Strength loss</th>
<th>Corrosion depth</th>
<th>Dimensional change</th>
<th>Leaching behaviour</th>
<th>Microstructural and other techniques</th>
<th>Sample type (P, M, Mortar (M) and Concrete (C))</th>
<th>Sample size</th>
<th>Acid solution</th>
<th>Acid replenished/ pH maintained</th>
<th>Exposure duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ahmad et al. [112]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>pH</td>
<td>SEM</td>
<td>M</td>
<td>Prisms (40 × 40 × 70 mm)</td>
<td>H$_2$SO$_4$ (5%)</td>
<td>–</td>
<td>270 days</td>
</tr>
<tr>
<td>Aiken et al. [152]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>XRD, TGA, FTIR and SEM-EDX</td>
<td>P and M</td>
<td>50 mm cubes</td>
<td>Raw silage effluent</td>
<td>Irregular replacement</td>
<td>8 weeks</td>
</tr>
<tr>
<td>Aiken et al. [114,121,125]</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>pH and chemical analysis</td>
<td>XRD, TGA, FTIR and SEM-EDX</td>
<td>P and M</td>
<td>50 mm cubes</td>
<td>H$_2$SO$_4$, HCl and HNO$_3$ (0.10, 0.31 and 0.52 mol/l for each acid)</td>
<td>Replaced weekly</td>
<td>8 weeks</td>
</tr>
<tr>
<td>Aiken et al. [52,122]</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>pH and chemical analysis</td>
<td>XRD, FTIR and SEM-EDX</td>
<td>P and M</td>
<td>50 mm cubes</td>
<td>CH$_3$COOH and CH$_3$COOH (0.10, 0.31 and 0.52 mol/l for both)</td>
<td>Replaced weekly</td>
<td>8 weeks</td>
</tr>
<tr>
<td>Aliques-Granero et al. [83]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>Y</td>
<td>XRD and SEM-EDX</td>
<td>M</td>
<td>50 mm cubes</td>
<td>H$_2$SO$_4$ (1, 3 and 5%)</td>
<td>Irregular replacement</td>
<td>196 days</td>
</tr>
<tr>
<td>Allahverdi and Skvara [104,105]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
<td>C</td>
<td>100 mm cubes</td>
<td>H$_2$SO$_4$ (2%, pH = 1.0)</td>
<td>pH maintained</td>
<td>Up to 90 days</td>
</tr>
<tr>
<td>Allahverdi and Skvara [106,107]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>XRD, SEM-EDX</td>
<td>P</td>
<td>20 mm cubes</td>
<td>H$_2$SO$_4$ (pH = 1, 2 and 3)</td>
<td>pH maintained</td>
<td>Up to 90 days</td>
</tr>
<tr>
<td>Bakharev [75]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>XRD, TGA, FTIR and SEM-EDX</td>
<td>P</td>
<td>Cylinders (Ø25 × 50 mm)</td>
<td>CH$_3$COOH (5%)</td>
<td>CH$_3$COOH (pH = 4)</td>
<td>Irregular replacement</td>
</tr>
<tr>
<td>Bakharev et al. [100]</td>
<td>–</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
<td>C</td>
<td>Cylinders (Ø100 × 200 mm)</td>
<td>H$_2$SO$_4$ (pH = 3), HCl (pH = 3), HNO$_3$ (pH = 3) and CH$_3$COOH (pH = 4.5)</td>
<td>Maintained fortnightly</td>
<td>150 days</td>
</tr>
<tr>
<td>Bernal et al. [101]</td>
<td>–</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>VPV, XRD and FTIR</td>
<td>M and P</td>
<td>M – 50 mm cubes and P – cylinders (Ø30 × 60 mm)</td>
<td>H$_2$SO$_4$ (pH = 1 and 3)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bondar and Nanukuttan [207]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>pH and chemical analysis</td>
<td>–</td>
<td>C</td>
<td>70 mm cubes</td>
<td>H$_2$SO$_4$ (pH = 1 and 3)</td>
<td>Maintained until 88 days when replaced</td>
<td>Up to 820 days</td>
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<tr>
<td>Burciaga-Diaz and Escalante-Garcia [132]</td>
<td>–</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>Chemical analysis</td>
<td>XRD, FTIR and SEM-EDX</td>
<td>P</td>
<td>25 mm cubes</td>
<td>HCl (0.5 N) at 60 °C</td>
<td>–</td>
<td>10 days</td>
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<tr>
<td>Charkhtab et al. [167]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>UPV, XRD and SEM</td>
<td>C</td>
<td>100 mm cubes</td>
<td>H$_2$SO$_4$ (5%)</td>
<td>–</td>
<td>90 days</td>
</tr>
<tr>
<td>Chatveera and Lertwattanarak [40]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>M</td>
<td>50 mm cubes and bars (25 × 25 × 285 mm)</td>
<td>HNO$_3$ and CH$_3$COOH (both 5%)</td>
<td>Maintained</td>
<td>90 days</td>
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<tr>
<td>Chaudhary and Liu [79]</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cylinders (Ø100 × 200 mm)</td>
<td>HCl (12 and 22%), exposure temperature varied</td>
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<td>110 days</td>
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<td>Davidovits [89]</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
<td>–</td>
<td>–</td>
<td>H$_2$SO$_4$ (5%) and HCl (5%)</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Fernandez-Jimenez et al. [176]</td>
<td>Y</td>
<td>Y</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
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<td>30 mm cubes</td>
<td>HCl (0.1 N)</td>
<td>–</td>
<td>90 days</td>
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<tr>
<td>Gao et al. [170]</td>
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<td>Y</td>
<td>–</td>
<td>–</td>
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<td>XRD, FTIR and SEM</td>
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<td>Cylinders (Ø15 × 30 mm)</td>
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<td>1.HCl solution unchanged</td>
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<th>Physical measurements</th>
<th>Leaching behaviour</th>
<th>Microstructural and other techniques</th>
<th>Sample type (Paste (P), Mortar (M) and Concrete (C))</th>
<th>Sample size</th>
<th>Acid solution</th>
<th>Acid replenished/ pH maintained</th>
<th>Exposure duration</th>
</tr>
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<tr>
<td>Gevaudan et al. [180]</td>
<td>– – Y – –</td>
<td>pH and chemical analysis</td>
<td>Bulk permeable porosity, XRD and SEM-EDX</td>
<td>P Cylinders (Ø24 × 15 mm and Ø14 × 40 mm)</td>
<td>Ø25-27 mm</td>
<td>H₂SO₄ (1%)</td>
<td>Replaced every day</td>
<td>7 days</td>
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<tr>
<td>Gevaudan et al. [90]</td>
<td>– – – – –</td>
<td>pH and chemical analysis</td>
<td>XRD, nitrogen absorption, µ-CT, SEM-EDX</td>
<td>P Cylinders (Ø3100 × 200 mm) and prisms (75 × 75 × 285 mm)</td>
<td>–</td>
<td>H₂SO₄ (pH = 2)</td>
<td>Replaced twice until pH equilibrium obtained</td>
<td>–</td>
</tr>
<tr>
<td>Gu et al [159]</td>
<td>Y Y Y Y –</td>
<td>Acid consumption</td>
<td>XRD and SEM-EDX</td>
<td>C Cylinders (Ø100 × 200 mm) and prisms (75 × 75 × 285 mm)</td>
<td>–</td>
<td>H₂SO₄ (1 and 3%), 12 hr wet/dry cycles also studied</td>
<td>Maintained twice per week</td>
<td>Up to 144 days</td>
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<tr>
<td>Gu et al. [160]</td>
<td>Y Y Y Y –</td>
<td>Acid consumption</td>
<td>XRD and SEM-EDX</td>
<td>C Cylinders (Ø3100 × 200 mm) and prisms (75 × 75 × 285 mm)</td>
<td>–</td>
<td>H₂SO₄ (1%)</td>
<td>Maintained twice per week</td>
<td>495 days</td>
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<tr>
<td>Gu et al. [157]</td>
<td>Y Y Y Y –</td>
<td>Acid consumption</td>
<td>XRD, FTIR, SEM-EDX</td>
<td>M and P Cylinders (Ø375 × 150)</td>
<td>–</td>
<td>H₂SO₄ (5%)</td>
<td>Maintained twice per week</td>
<td>12 weeks</td>
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<tr>
<td>Huseien et al. [113,115]</td>
<td>Y Y – – –</td>
<td>Acid consumption and chemical analysis</td>
<td>XRD and SEM</td>
<td>M 50 mm cubes</td>
<td>–</td>
<td>H₂SO₄ (10%)</td>
<td>Replaced every 2 months</td>
<td>1 year</td>
</tr>
<tr>
<td>Huseien et al. [117]</td>
<td>Y Y – – –</td>
<td>–</td>
<td>UPV and XRD</td>
<td>C 100 mm cubes</td>
<td>–</td>
<td>H₂SO₄ (10%)</td>
<td>Replaced every 3 months</td>
<td>1 year</td>
</tr>
<tr>
<td>Khan et al. [194,195]</td>
<td>Y Y Y Y –</td>
<td>H₂S gas concentration and temperature within sewer monitored, pH and chemical analysis</td>
<td>Surface pH, pH profile, VPV, XRD, FTIR, SEM-EDX and Raman spectroscopy</td>
<td>M 50 mm cubes</td>
<td>–</td>
<td>Samples suspended within a real sewer environment at a wastewater treatment plant, samples separately exposed to H₂SO₄ (1.5%)</td>
<td>–</td>
<td>Up to 2 years</td>
</tr>
<tr>
<td>Khan et al. [118]</td>
<td>Y Y Y Y –</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
<td>M 50 mm cubes</td>
<td>–</td>
<td>H₂SO₄ and HCl (both 3%)</td>
<td>Replaced monthly</td>
<td>pH regulated by automatic titration and replaced every 4 weeks</td>
</tr>
<tr>
<td>Koenig et al. [141]</td>
<td>Y Y Y Y –</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
<td>M 50 mm cubes</td>
<td>–</td>
<td>Synthetic mix (pH = 3) of CH₃COOH (1.5%), CH₃COOOH (3%) and CH₃CO₂CH₃ (0.5%)</td>
<td>–</td>
<td>1 year</td>
</tr>
<tr>
<td>Kwasny et al. [88]</td>
<td>Y Y – – –</td>
<td>pH and chemical analysis</td>
<td>pH</td>
<td>M 50 mm cubes</td>
<td>–</td>
<td>H₂SO₄ and HCl (0.10, 0.31 and 0.52 mol/L) for both</td>
<td>Replaced weekly</td>
<td>8 weeks</td>
</tr>
<tr>
<td>Lee and Lee [108]</td>
<td>– – – – –</td>
<td>–</td>
<td>XRD, FTIR and NMR</td>
<td>P 50 mm cubes</td>
<td>–</td>
<td>H₂SO₄ (10%)</td>
<td>pH maintained daily</td>
<td>–</td>
</tr>
<tr>
<td>Lloyd et al. [80]</td>
<td>Y – Y – –</td>
<td>–</td>
<td>–</td>
<td>P Cylinders (Ø25 × 50 mm)</td>
<td>–</td>
<td>H₂SO₄ (pH = 1.0, 2.0 and 3.0)</td>
<td>pH maintained daily</td>
<td>–</td>
</tr>
<tr>
<td>Mallikarjuna road and Kireety [166]</td>
<td>Y Y – – –</td>
<td>–</td>
<td>–</td>
<td>C Cubes</td>
<td>–</td>
<td>H₂SO₄ and HNO₃</td>
<td>–</td>
<td>28 days</td>
</tr>
<tr>
<td>Mehta and Siddique [165]</td>
<td>Y Y – – –</td>
<td>–</td>
<td>XRD and SEM-EDX</td>
<td>C 100 mm cubes</td>
<td>–</td>
<td>H₂SO₄ (2%)</td>
<td>pH maintained</td>
<td>1 year</td>
</tr>
<tr>
<td>Nastir et al. [110]</td>
<td>Y Y – – –</td>
<td>pH</td>
<td>XRD, FTIR and SEM-EDX</td>
<td>M and P</td>
<td>–</td>
<td>H₂SO₄ (5%, pH = 0.24)</td>
<td>pH maintained every 5 weeks</td>
<td>–</td>
</tr>
</tbody>
</table>

(continued on next page)
Table 2 (continued)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Physical measurements</th>
<th>Leaching behaviour</th>
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<th>Sample type (Paste (P), Mortar (M) andConcrete (C))</th>
<th>Sample size</th>
<th>Acid solution</th>
<th>Acid replenished/ pH maintained</th>
<th>Exposure duration</th>
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</thead>
<tbody>
<tr>
<td>Ozcan and Karakoc [109]</td>
<td>Y Y – – –</td>
<td>pH</td>
<td>UPV and SEM</td>
<td>C</td>
<td>M = 50 mm cubes and P = 25 mm cubes</td>
<td>H₂SO₄, HCl, H₃PO₄ and HF (all 5%)</td>
<td>Replaced every 4 weeks</td>
<td>12 weeks</td>
</tr>
<tr>
<td>Pacheco-Torgal et al. [129]</td>
<td>Y – – – –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>C and M</td>
<td>H₂SO₄, HCl and HNO₃ (all 5%)</td>
<td>Replaced every 14 days</td>
<td>Up to 56 days</td>
</tr>
<tr>
<td>Qu et al. [161]</td>
<td>Y Y Y –</td>
<td>Chemical analysis</td>
<td>XRD, TGA, FTIR and SEM-EDX</td>
<td>M</td>
<td>Cylinders (Ø50 × 100 mm)</td>
<td>H₂SO₄ (1, 3 and 5%)</td>
<td>Irregular replacement</td>
<td>18 months</td>
</tr>
<tr>
<td>Ren et al. [172]</td>
<td>– – Y –</td>
<td>–</td>
<td>P</td>
<td>Cylinders (Ø27.5 × 55 mm)</td>
<td>H₃PO₄ (pH = 2 and 3 and 4)</td>
<td>Irregular replacement</td>
<td>150 days</td>
<td></td>
</tr>
<tr>
<td>Ren et al. [173]</td>
<td>Y – Y –</td>
<td>pH and chemical analysis</td>
<td>XRD, TGA, SEM-EDX and µ-CT</td>
<td>P</td>
<td>50 mm cubes and cylinders (Ø27.5 × 55 mm)</td>
<td>H₃PO₄ (pH = 2)</td>
<td>Irregular replacement</td>
<td>44 days</td>
</tr>
<tr>
<td>Rostami and Brendley [77]</td>
<td>Y – – – –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cylinders (Ø150 × 300 mm)</td>
<td>CH₃COOH (100%), HNO₃ (20%), HCl (20%) and H₂SO₄ (20%)</td>
<td>–</td>
<td>1 year</td>
</tr>
<tr>
<td>Sata et al. [84]</td>
<td>Y – – – –</td>
<td>–</td>
<td>SEM-EDX</td>
<td>M</td>
<td>50 mm cubes</td>
<td>H₂SO₄ (3%)</td>
<td>Irregular replacement</td>
<td>120 days</td>
</tr>
<tr>
<td>Siddique and Jang [206]</td>
<td>Y Y – –</td>
<td>–</td>
<td>MIP, XRD, FTIR and NMR</td>
<td>P</td>
<td>50 mm cubes</td>
<td>H₂SO₄ (3%)</td>
<td>–</td>
<td>90 days</td>
</tr>
<tr>
<td>Shi [98]</td>
<td>– – Y –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cylinders (Ø345 × 74 mm)</td>
<td>HNO₃ (pH = 3) and CH₃COOH (pH = 3)</td>
<td>pH maintained manually</td>
<td>80 days</td>
</tr>
<tr>
<td>Shi and Siegmann [99]</td>
<td>– – Y –</td>
<td>Acid consumption and chemical analysis</td>
<td>–</td>
<td>–</td>
<td>Cylinders (Ø345 × 75 mm)</td>
<td>HNO₃ (pH = 5) and CH₃COOH (pH = 3 and pH = 5)</td>
<td>pH maintained manually</td>
<td>Up to 580 days</td>
</tr>
<tr>
<td>Sturm et al. [209]</td>
<td>– Y Y –</td>
<td>Acid consumption</td>
<td>XRD, SEM and NMR</td>
<td>M and P</td>
<td>M = Prisms (40 × 40 × 80 mm) and P = 20 mm cubes</td>
<td>H₂SO₄ (pH = 1)</td>
<td>pH regulated by automatic titration and replaced every week</td>
<td>70 days</td>
</tr>
<tr>
<td>Sun and Wu [156]</td>
<td>Y – – – –</td>
<td>pH</td>
<td>Dynamic modulus</td>
<td>M</td>
<td>Prisms (23.5 × 23.5 × 50.8 mm)</td>
<td>H₂SO₄ (0.05 and 3%)</td>
<td>Replaced weekly</td>
<td>24 weeks</td>
</tr>
<tr>
<td>Tahri et al. [82]</td>
<td>Y – – – –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>100 mm cubes</td>
<td>H₂SO₄, HCl and HNO₃ (all 10, 20 and 30%)</td>
<td>–</td>
<td>56 days</td>
</tr>
<tr>
<td>Temuujin et al. [81]</td>
<td>Y Y – –</td>
<td>Chemical analysis</td>
<td>XRD and SEM</td>
<td>P</td>
<td>Cylinders (Ø255 × 52 mm)</td>
<td>HCl (18%)</td>
<td>–</td>
<td>5 days</td>
</tr>
<tr>
<td>Thokchom et al. [79]</td>
<td>Y Y Y –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>50 mm cubes</td>
<td>H₂SO₄ (10%)</td>
<td>Replaced after 12 weeks</td>
<td>18 weeks</td>
</tr>
<tr>
<td>Ukrainczyk and Vogt [87]</td>
<td>– – Y –</td>
<td>Chemical analysis</td>
<td>XRD and SEM-EDX</td>
<td>P</td>
<td>Cylinders (Ø88.5 × 30 mm)</td>
<td>CH₃COOH (0.1 M, pH = 2.8)</td>
<td>Irregular replacement</td>
<td>56 days</td>
</tr>
<tr>
<td>Vafaei et al. [118,210,211]</td>
<td>Y Y – –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>50 mm cubes</td>
<td>H₂SO₄ and HCl (pH = 3)</td>
<td>Maintained periodically</td>
<td>2 years</td>
</tr>
<tr>
<td>Vogt et al. [185]</td>
<td>– – Y –</td>
<td>Acid consumption and pH</td>
<td>XRD and SEM-EDX</td>
<td>P</td>
<td>Cylinders (20 × 20 × 80 mm)</td>
<td>CH₃COOH (pH = 1)</td>
<td>Maintained once per day</td>
<td>70 days</td>
</tr>
<tr>
<td>Wang et al. [123]</td>
<td>Y – – – –</td>
<td>pH and chemical analysis</td>
<td>XRD, TGA, FTIR, NMR and SEM-EDX</td>
<td>P</td>
<td>Cylinders (Ø310 × 20 mm)</td>
<td>H₂SO₄ (5%)</td>
<td>–</td>
<td>56 days</td>
</tr>
<tr>
<td>Wu et al. [111]</td>
<td>Y Y Y –</td>
<td>pH</td>
<td>UPV, XRD, FTIR</td>
<td>M</td>
<td>Cylinders (Ø505 × 100 mm)</td>
<td>H₂SO₄ (pH = 2)</td>
<td>pH maintained every 5 days</td>
<td>75 days</td>
</tr>
</tbody>
</table>

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5.1. Effect of sample type and size

Acid resistance studies have been carried out on pastes, mortars and concretes. This makes comparison between tests difficult because of differences in microstructure due to the interfacial transition zone between paste and aggregate in mortar and concrete samples [136]. Studies on mortars and concretes are more representative of real service scenarios. However, studies on paste are extremely valuable, as they allow for in-depth microstructural analysis and understanding of the mechanism of the acid degradation of the binder without the influence of the aggregate phase. Furthermore, aggregate used in concrete is generally inert unless it contains reactive silica species [137]. Only the cement paste is vulnerable to acid attack in concrete made with acid resistant aggregate such as quartz [138]. Chemical degradation by acidic media usually occurs due to the vulnerability of the cement paste which should be the focus of studies investigating the acid resistance of AAB’s via microstructural investigations. It is good practice to use inert or acid resistant aggregates when comparing the acid resistance of different binders. It should be noted that some aggregate types such as calcareous limestone, dolomite or reactive silicate aggregates are vulnerable to acid attack [137–139].

A study on PC mortars and pastes by Pavlik and Uncik [140] has shown how the corrosion rate differs for mortars and pastes, especially in the case of HNO₃. The reduced corrosion rate for mortars was due to the presence of sand which prevented the formation of cracks and increased the diffusion pathway for the attacking acid [140]. In addition, mortars have much less paste which may support their enhanced resistance compared with paste samples. Concrete samples typically have even less paste than mortars which allow concrete samples to provide enhanced performance when compared with mortars. This was confirmed by Beddoe [138], who also noted that the degree of tortuosity due to aggregate particles and the degree of packing were key parameters in acid resistant concrete. Few studies [141] were found to have directly compared the performance of alkali-activated mortars and concretes. In general, less studies have been carried out on the acid resistance of alkali-activated concrete compared with mortar and paste (Table 2).

Sample size will also have an impact on the results obtained. For example, in the case of compressive strength larger samples will indicate a smaller percentage strength loss than smaller samples because less of the sample volume will have been affected by the acid attack. Therefore, comparison of the strength loss from samples of different dimensions is not recommended. Similar is true when considering mass loss measurements. This means it is difficult to compare values for performance indicators such as mass/strength loss between different studies where different sample sizes are employed.

5.1.1. Type and severity of acids studied

Several acid types have been used to investigate the acid resistance of cementitious materials. This means that most studies which have been carried out are following different ad hoc testing procedures, making it difficult to draw comparisons between investigations. However, it is worth noting that in recent years, more standard documentation in this area has been published such as ASTM C1894-19 [126], ASTM C1904-20 [127] and ASTM 1898-20 [128]. The main differences between studies in literature include sample type, sample size, acid type, acid concentration, exposure duration and whether or not acid is replenished during the exposure period. These variables have been compared in Table 2. Some studies also include some form of mechanical abrasion, manual brushing [129] or exposure to high temperatures [130–132] to accelerate the deterioration process. In some cases, studies on traditional cementitious materials have investigated the effects of cyclic exposure to acidic media by placing samples in continuously flowing acidic media in an attempt to mimic real-life conditions [133–135].

The following sections discuss the influence of different testing procedures in more detail.
AABs, generally they can be divided into mineral acids (such as H₂SO₄, HNO₃ and HCl) and organic acids (such as CH₃COOH and (CH₂)₆COOH). In most cases laboratory grade chemicals are used. Many studies have been carried out using H₂SO₄ solutions, likely to mimic corrosion in sewer networks [142]. However, in order to effectively simulate corrosion in sewage systems microbiological tests may also need to be considered alongside chemical deterioration by H₂SO₄ [143,144].

Similarly sludge effluent is detrimental to concrete structures in the agricultural industry which has significant economic and environmental implications [145–151]. Numerous studies have been conducted on the resistance of traditional PC concrete to sludge effluent attack [41,42,44,47,150,151]. On the other hand, the resistance of AABs to raw sludge effluent has received limited attention [103,152]. Therefore, in general, there is a gap in literature assessing the resistance of AABs to real world acidic media. Most studies use laboratory grade acid solutions (Table 2) which are incredibly valuable, but there is also a need to understand further the performance of AABs when exposed to acidic media prevalent in real in-service conditions.

The concentration of the acid employed is a key parameter in determining the rate of deterioration [153]. In many studies highly concentrated acids are used to accelerate deterioration. However, care should be taken with this approach because highly concentrated acids are often not representative of real life scenarios. Accelerating the process can change the mechanism of attack, for example, in the case of H₂SO₄, gypsum is formed more rapidly at higher concentrations [154] and in some cases was not observed to form at lower concentrations [106,107]. Gypsum can act as a protective barrier to further acid attack which may affect how representative results are of real life scenarios. Bakharev et al. [75] used 5% solutions of H₂SO₄ and CH₃COOH and reported that their strengths were not equal. The H₂SO₄ had a pH value of 0.8 and the CH₃COOH had a pH of 2.4. These acid types and concentrations were used based on typical values observed in sewage pipes, mining and food processing industries which is an expedient approach.

As shown in Table 2, in many studies, authors maintained the pH at a particular value by adding additional acid to keep the pH constant by counteracting leaching alkali ions from the cementitious material [80,104]. This can be problematic if done manually because if samples are stored in separate containers, they may leach ions at different rates meaning the pH change may vary resulting in different samples undergoing different exposure conditions. Guthrie et al. [155] carried out this approach mechanically where the pH was adjusted by titration every 9 min. When using this approach, it is also important to consider the influence of increasing the volume of acid solution. A common approach is to use acid at a fixed concentration which is then replenished by fresh acid after a specified time period [100,156]. It is important to maintain a constant acid volume per sample, particularly when using the replenishment approach. Small acid volumes will be easier to neutralise via leaching than larger acid volumes, which will require more leaching to occur before the acid solution and samples are in equilibrium.

### 5.1.3. Physical measurements of degradation

There are many different methods used for measuring the physical degradation of samples when exposed to acid attack. These include measurements of mass change, corrosion depth, strength loss and dimensional change. There is some debate regarding which measurements provide the most meaningful indication of acid resistance. A summary of the main advantages and disadvantages with the most commonly used performance indicators and test methods is provided in Table 3.

<table>
<thead>
<tr>
<th>Test method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass loss</td>
<td>Simple and effective measurement. Limited testing equipment required.</td>
<td>Can be influenced by the formation of additional products due to acid attack, such as gypsum.</td>
</tr>
<tr>
<td>Corrosion depth</td>
<td>Provides a visual representation of the front of the acid ingress.</td>
<td>Can be difficult to define depth of ‘penetration’ and depth of ‘degradation’. Different authors use different methods of assessment and terminology.</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>A direct assessment of the structural performance of attacked samples.</td>
<td>Difficult to accurately deal with the issue of rough testing surfaces following acid attack. Each of the commonly used methods such as capping and using soft broad have their own niche problems.</td>
</tr>
<tr>
<td>Dimensional change</td>
<td>Useful method for detecting both loss of material and expansion. For example, mass loss measurements can only assess mass losses.</td>
<td>Acidic environments can cause corrosion of metal end gauges affecting readings. AABs with low residual strength after acid attack cannot be properly evaluated.</td>
</tr>
<tr>
<td>Leaching behaviour</td>
<td>Useful for understanding the mechanism of failure related to phases dissolved in the AAB matrix during acid attack.</td>
<td>Chemical analysis can be more expensive than some of the physical methods of assessment. Not feasible in most Civil Engineering laboratories. Requires sophisticated equipment. Preparation of SEM samples is time consuming. Typically, multiple methods have to be employed to properly characterise the cause of the deterioration. Does not normally allow for quantification of performance and comparing different binders.</td>
</tr>
<tr>
<td>Analysis of degraded paste</td>
<td>Useful for understanding the mechanism of failure. via microstructural techniques such as XRD, TGA, FTIR and SEM.</td>
<td>Requires sophisticated equipment. Preparation of SEM samples is time consuming. Typically, multiple methods have to be employed to properly characterise the cause of the deterioration. Does not normally allow for quantification of performance and comparing different binders.</td>
</tr>
</tbody>
</table>

As shown in Table 2, in many studies, authors maintained the pH at a particular value by adding additional acid to keep the pH constant by counteracting leaching alkali ions from the cementitious material [80,104]. This can be problematic if done manually because if samples are stored in separate containers, they may leach ions at different rates meaning the pH change may vary resulting in different samples undergoing different exposure conditions. Guthrie et al. [155] carried out this approach mechanically where the pH was adjusted by titration every 9 min. When using this approach, it is also important to consider the influence of increasing the volume of acid solution. A common approach is to use acid at a fixed concentration which is then replenished by fresh acid after a specified time period [100,156]. It is important to maintain a constant acid volume per sample, particularly when using the replenishment approach. Small acid volumes will be easier to neutralise via leaching than larger acid volumes, which will require more leaching to occur before the acid solution and samples are in equilibrium.
and spalling of matrix and aggregates, other measurements (i.e. corrosion depth and compressive strength reduction) must be conducted to comprehensively and objectively to identify the entire nature of acid attack on AABs. Additionally, as the acid attack on AABs gradually causes degradation from the outer surface towards the inside of specimens, the effect of specimen size must be considered when comparing different studies. Mass loss is a relevant and useful indicator of deterioration, but it should not be used as the sole measurement of deterioration.

Corrosion depth is arguably the most important measurement to quantify acid attack on AABs as it intuitively shows the degraded layer and non-degraded layer of AABs after acid attack. Lloyd et al. [80] stated that corroded depth is a direct measurement which is least likely to develop systematic errors. Corrosion depth is commonly measured via direct observation, pH indicator, and residual size after the degraded parts are removed. The direct observation of corrosion depth requires examination of the cross-section of specimens to identify the degraded layer and non-degraded layer, and this measurement relies on macroscopic change of the materials (i.e. colour, density, cracking, porosity etc.) [79,98,99,157,158]. The matrix of AABs which have not been subject to acid attack generally has high alkalinity (i.e. over 10.5 [169]). On the other hand, the degraded parts of AABs after acid attack have a much lower alkalinity. This means that pH indicators like phenolphthalein solution [78,100,114,157,159–161,170] and thymol blue [170] can be used to identify the corrosion depth after acid attack. Measuring the residual size of AABs specimens generally requires mechanical methods (i.e. washing and brushing) to remove the degraded layer [49,62,69,80,157,162,171]. This measurement relies on the differences in strength between the degraded layer and non-degraded layer, whereas the measurement cannot accurately reflect the corrosion depth when the degraded layer has a high residual strength or the entire specimen has a low strength [80,157]. Recently, Ren et al. [172,173] neatly defined a method for characterising the total corrosion depth or total degradation depth (TDD). As illustrated in Fig. 8, the TDD

was defined as the sum of the degraded depth (DD), which has been physically removed due to acid attack and the apparent degraded depth (ADD) which has had its pH lowered due to acid attack.

Compressive strength reduction or residual compressive strength of specimens is widely used to identify the effect of acid attack on AABs [34,75,76,78,81,85,100,101,108–110,114,132,157–161,163–168]. Compressive strength reduction reveals the global decrease in strength capacity after acid attack. However, the compressive strength reduction of partial degraded specimens is significantly affected by the area of non-degraded layer rather than the residual strength capacity of degraded parts [157]. Therefore, the size effect of specimens must be considered when comparing different studies and when the test results are obtained from partially degraded specimens. Abora et al. [136] suggested that compressive strength is the most meaningful measure of degradation, but noted it can be problematic due to possible increasing strength of the samples internal core over time due to continued hydration and reactions taking place.

The degradation of cementitious materials caused by acid attack can cause dimensional changes in specimens [40,134,159,160,166]. Therefore, the measurement of length change using prism specimens is a useful technique when the degraded matrix potentially involves phases causing expansion [40,159,160]. It is possible to measure deterioration of cementitious materials through non-destructive techniques such as ultrasound and impact echo [174]. These techniques normally provide information about the internal structure, whereas acid attack normally propagates itself on the outer surfaces. Therefore, few studies have used non-destructive techniques when assessing the acid resistance of AABs.

There is no common indicator for measuring acid resistance in all systems [83]. Therefore, a combination of physical degradation measurements is probably the most reliable approach, particularly when considering and comparing the performance of multiple binders which may undergo different mechanisms of deterioration [175,176]. It is also worth noting that visual observations, whilst not physical measurements, are a valuable tool for assessing and gaining an understanding of the nature and severity of acid attack.

5.1.4. Leaching behaviour and microstructural measurements of degradation

Degradation may also be evaluated by assessing the acid solution. This may be done by pH measurements, electrical conductivity measurements [177] and chemical analysis of the solution to determine the nature and quantity of ions leaching from the samples into the acid solution [176,178]. Techniques such as inductively coupled plasma–atomic emission spectroscopy (ICP-AES) and ion chromatography (IC) are typically used. This data can provide useful information indicating the failure mechanism which has taken place. Some studies have also used the observed leaching behaviour to determine the acid neutralisation capacity of AABs [179,180].

Following exposure, it is also possible to assess the degraded layers using techniques such as X-ray diffraction, thermogravimetric analysis and Fourier transform infrared spectroscopy [132,181,182]. These methods allow assessment of degraded regions which can be compared with unaltered samples to determine the effect of the attack on existing phases and determine if any new compounds were formed. Scanning electron microscopy with elemental analysis is another useful tool for determining deterioration visually and by means of elemental composition [183–185]. Vafaei et al. [186] has effectively demonstrated the use scanning electron microscopy for assessing the microstructure and breakdown of the geopolymer network following acid attack. As shown in Fig. 9, using scanning electron microscopy it was also possible to identify gypsum crystals formed during H₂SO₄ exposure. Micro-CT scanning is another technique that has been successfully used to assess the acid resistance of AABs. Gu et al. [157] were able to use this technique to measure the porosity in degraded and undegraded layers following acid attack. Gevaudan et al. [90] used nitrogen absorption to
successfully characterise the nano-scale gel porosity of acid exposed AABs. Grengg et al. [187,188] and Muller et al. [189] recently presented optical pH imaging measurements as shown in Fig. 10 which were able to effectively show the pH distribution in the cross section of freshly cut specimens. This technique is valuable for understanding the nature and severity of degradation in different specimens. Whilst assessing the long-term performance of samples exposed to microbiologically induced acid corrosion, Grengg et al. [187] used DNA extraction to analyse the dominant bacterial species type observed. This is novel approach not previously undertaken for assessing the performance of AABs exposed to acidic media.

5.2. Relevance of testing procedures to in-service conditions

Cementitious materials in aggressive environments are regularly attacked by various types of acid as summarised in Section 2 and Table 1. Normally, infrastructures in direct contact with industrial wastewater are potentially attacked by inorganic acids like HCl, HNO_3, and H_2SO_4 [81,104,105]; infrastructures like sewage pipes are attacked by microbiologically induced corrosion [154]; infrastructures directly in contact with silage effluent and buildings in animal husbandry are attacked by organic acid (i.e. CH_3CHOOCH and CH_3COOH) [43,47]. The corrosion processes of different types of acid are obviously distinct, therefore the testing procedures to evaluate the resistance of cementitious materials to various types of acid require different methodologies.
from Grengg

Fig. 10. pH images recorded using a digital imaging technique. Figure obtained from Grengg et al. [187].

5.2.1. Inorganic acid attack
To evaluate the resistance of AABs to inorganic acid (i.e. HCl, HNO₃, and H₂SO₄), specimens were simply fully immersed in inorganic acid solution [22,34,75,76,78,79,81,84,85,88,101,108–110,114,132,157–161,164–168,170]. To achieve a one-dimensional corrosion, epoxy or wax sealing of part of the surfaces of specimens were applied in a few studies [78,157,159]. To avoid rapid consumption of acid, the acid solution to specimen volume ratio was usually maintained over 3 [78,157,159–161,168], or the acid solution volume to specimen surface area ratio was usually maintained over 10 [76,137]. Regular addition of concentrated acid was applied to maintain the pH level of the acid solution in a few studies [19,80,85,101,106,107,157,159,160,165]. Regular replacement of acid solution was applied [75,76,88,109,110,114,137,161,170,182] especially when the solubility of leaching phases got saturated [88,114].

The acid concentration of inorganic acid directly affects the corrosion speed of AABs [83,106,107,159,161]. The use of inorganic acid solution with low concentration (i.e. pH higher than 1) generally requires a long testing period (i.e. over 4 months) before obvious corrosion can be observed [85,101,109,156,159,160,164,165]. To accelerate the corrosion process, use of inorganic acid solution with high concentration (i.e. pH less than 1) was adopted in a few studies [26,75,78,79,81,84,108,109,114,132,157–159,161,163]. Thokchom et al. [78] tested the acid resistance of AAFA in 10% H₂SO₄, the results showed that AAFA specimens (50 mm cubes) fully lost their alkalinity within 12 weeks.

Apart from simple immersion of specimens in different concentration of inorganic acid solution, other accelerating test regimes were used to simulate the environment impact. Wet and dry cycling was used to mimic the water level change in the wastewater infrastructures [159,170,190,191]. Gu et al. [159] suggested that expansive degraded products crystallise in the pores of cementitious materials during the drying process, potentially causing more rapid corrosion due to the formation of micro-cracks (caused by tensile stresses) in the wastewater infrastructures. Brushing was used to mimic the high-speed water containing rigid solids flowing through the wastewater infrastructures [159,171]. Monteny et al. [154] suggested that the degraded layer of cementitious materials can be removed via brushing process, leading to direct reaction of acid with non-degraded cementitious materials, potentially accelerating the corrosion process. De Belie et al. [171] designed an apparatus combining both of the wet and dry cycling regime and brushing regime to accelerate the acid corrosion process, shown in Fig. 11. Cylindrical specimens were rotated in acid solution at speed of 1 revolution per hour, 1/3 of the specimens were immersed in the acid solution during the rotation. After each cycle of 12 days, the specimens were air dried, followed by a brushing procedure to remove the weakly adhering concrete particles before measurements [62,69,162,171,192]. The corrosion directly caused by inorganic acids in real in-service conditions (i.e. infrastructures directly in contact with industrial wastewater) can be simulated using the above methods if appropriate acid types and concentrations are employed. Whereas microbiologically induced corrosion cannot simply use the inorganic acid test methodologies to predict the service life of a given material due to the different corrosion mechanism which also involves bacterial processes [20,154].

5.2.2. Microbiologically induced corrosion
Microbiologically induced corrosion of cementitious materials in sewage system can be directly investigated by in-situ tests [142,193–195] or simulated by tests in biogenic simulation chambers [20,69,144,162,196–199]. In in-situ tests, the specimens are exposed in the sewage system [193–195] or directly taken from the degraded infrastructure [142]. The in-situ test is the most reliable test methodology to reveal the behaviour of materials under in-service conditions. However, the in-situ test takes a number of years [142,193–195] before meaningful data can be obtained, making it an unrealistic methodology for rapid testing requirements. The tests in biogenic simulation chambers generally require complex control systems to monitor and adjust the humidity, temperature, water level, and the concentration of H₂S gas to create a similar environment to that experienced in-service [196], for example, shown in Fig. 12. In biogenic simulation chamber tests, microbiologically induced corrosion can be accelerated by increasing the H₂S gas concentration, allowing the testing duration to be reduced [144,197]. The tests in biogenic simulation chambers directly represent the in-service condition [154], however, the complexity of the biogenic simulation chamber makes it infeasible in most civil engineering labs [159]. Therefore, considering the long test periods of in-situ tests and the complexity of the tests in biogenic simulation chambers, the inorganic acid test methodologies can still be employed to act as indicators of materials susceptibility to microbiologically induced corrosion [159].

6. Conclusions and opportunities
In general, the acid resistance of alkali-activated fly ash and alkali-activated slag binders are relatively well understood. Less work has been carried out on the performance of alkali-activated calcined clays under acid attack. Therefore, further work in this area is recommended. For all AAB systems, it is important that studies use multiple indicators of deterioration and do not only rely on mass loss as an indicator of
deterioration in isolation. Findings have shown that while mass loss data is valuable it can be misleading as samples can present a minor mass loss with an outer surface that appears intact but at the same time have significant depth of corrosion/alkalinity loss under the surface, combined with a substantial strength loss. Few studies have investigated genuine acidic media encountered in real world applications. Understandably most studies have investigated acid resistance using laboratory grade chemicals. In some cases, authors have attempted to prepare synthetic acidic solutions with a composition similar to real world acidic media. However, even these studies do not account fully for the real exposure experienced in-service and ignore factors such as microbiologically induced corrosion. In general, it would be beneficial if more studies reported on performance against raw acidic media that cementitious materials actually encounter in-service. It should be noted that such studies are difficult to undertake as meaningful results may take several years to obtain.

In general, AABs have the potential to be used in niche applications requiring a high level of acid resistance. They generally provide much superior performance than that observed for traditional PC binders. It is worth noting that the majority of studies compare the performance of AABs against neat PC binders that do not contain any SCMs. Nowadays, most commercially used PC concrete and mortar contains a significant proportion of SCMs. Therefore, more studies comparing the performance of AABs against PC mixes containing SCMs would be recommended. Comparison with calcium aluminate cement binders would also be novel and valuable.

Recent findings suggest that the addition of new admixtures and SCMs (such as silica fume, MgO, metakaolin, waste ceramic powder, waste glass and Mg(OH)_2) can improve the resistance of AABs even further, despite them already exceeding the resistance of PC binders significantly. Further advancement in this area is expected in the coming years.

There is huge potential for AABs to act as a surface repair material to increase the service life of existing PC-based concrete infrastructure. AABs have also shown promise in terms of their binding strength when applied to existing concrete surfaces. Therefore, AABs should be an ideal

Fig. 11. Apparatus for accelerated degradation developed at Ghent University. Figure obtained from De Belie et al. [171].

Fig. 12. Schematic diagram of a biogenic simulation chamber. Figure obtained from Jiang et al. [196].
material with which to repair existing structures which have been deteriorated by acidic media. Further research to validate this specific application would be valuable.

**CRediT authorship contribution statement**

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**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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