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Performance of cementless binders produced from industrial waste products in strong acid

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ABSTRACT

There is a growing demand for alternative low carbon binders. For these relatively new binder systems to be well received in industry it is important that detailed understanding of their durability performance is available. This paper investigates the hydrochloric acid resistance of geopolymer binders containing 100% fly ash and various blends of fly ash and blast furnace slag. Both physical and microstructural properties changes were examined to assess acid resistance and the leaching behaviour was also monitored. As the slag content of geopolymer binders increased, the resistance to hydrochloric acid also increased, evidenced by the reduced mass and strength loss observed. Findings also illustrate that geopolymer binders have hydrochloric acid resistance which exceeds that of traditional Portland cement binders in terms of the mass losses observed. The process of hydrochloric acid attack for each binder is also studied.

1. Introduction

It is well documented that the cement and concrete industry is under increasing pressure to reduce its contribution to global CO2 emissions. This has led to considerable interest in alternative low-carbon binders such as alkali-activated or geopolymer (GP) systems (Shi et al., 2019). The alkali-activation of fly ash and slag to form GP binders has received significant attention. Fly ash and slag are by-products from coal combustion and steel production, respectively. Therefore, they are considered as ideal components to produce a low-carbon binder whilst also reducing landfilled or stockpiled waste from other industries. In many countries, significant volumes of fly ash are disposed of in landfill sites each year, with as little as 7% being utilised effectively in some cases (Kovtun et al., 2016). To date, industrial applications and use of GP binders has been relatively limited (Berndt et al., 2013). Therefore, to give confidence in their performance and help their uptake become more widespread it is vital their performance is as well understood as traditional Portland cement (PC) based systems.

The vulnerability of traditional PC based binders to aggressive media is well known (Alexander et al., 2013). The alkaline nature of PC materials has been cited as a reason for their vulnerability to acidic environments (Zivica and Bajza, 2001). When PC materials come into contact with acidic media ionic transfers occur between the pore solution and the acidic media which involves the dissolution of hydration products (Kamali et al., 2008). Calcium hydroxide and ettringite are among the first phases to be dissolved during acid attack (Duchesne and Bertron, 2013). The main binding gel present in PC materials, calcium silicate hydrate (C–S–H) gel then undergoes decalcification (Duchesne and Bertron, 2013). Dissolution of these phases increases porosity and permeability (Bertron et al., 2007) which allows faster onset of further deterioration (Zivica and Bajza, 2002). This is the basic mechanism of acid attack of PC materials, though the reality is much more complex. For example, a recent state-of-the-art RILEM report (Alexander et al., 2013) has dedicated several sections to the mechanisms of degradation of PC materials in aggressive acidic media. Therefore, it is important that similar detailed knowledge and understanding is attained regarding the performance of alternative low-carbon binders such as geopolymers.

Hydrochloric acid has many uses including desalination, neutralisation of waste, cleaning, refinement and the production of chemicals (Australian Government, 2019). Despite cases where cementitious materials are exposed to hydrochloric acid in-service appearing limited, such instances do occur. Hydrochloric acid is present in acid rain (Evans et al., 2011) and has been used along with other acids to simulate accelerated attack by acid rain on cementitious materials (Miyamoto et al., 2014). A recent study (Zhou et al., 2019) has also suggested that hydrochloric acid is present in the coal mine environment. The oil and gas industries commonly use hydrochloric acid during well stimulation and acidizing operations (Stringfellow et al., 2017). This process allows

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hydrochloric acid to come into contact with the cement sheath of the well causing deterioration and breakdown (Ridha et al., 2018). Hydrochloric acid has been described as a strong acid with a mechanism of degradation of PC binders similar to that of nitric acid and pure water (Duchesne and Bertron, 2013). Therefore, the performance of a relatively new class of GP binders when exposed to hydrochloric acid is important to gain a full understanding of their performance, towards their increased adoption. In addition, it may be possible to use GP binders in niche applications such as oil wells, if they perform better than the Portland cement binders currently employed.

Previous research (Fernandez-Jimenez et al., 2007) investigated the effect of two different activating solutions on the resistance of fly ash GPs to hydrochloric acid for 90 days. The first solution consisted of only sodium hydroxide whereas the second consisted of both sodium hydroxide and sodium silicate. The different activators displayed very similar results in terms of visual appearance and strength loss. Microanalysis of both sample types identified a drop in the aluminium content of the binding gel due to the acid attack. A PC sample was also investigated and displayed lower acid resistance than the fly ash GP samples. The effect of different fly ash sources and activator type on hydrochloric acid resistance has also been investigated (Zhao et al., 2019). Fly ash mixes activated with sodium hydroxide were found to have increased mass loss compared with mixes activated with sodium silicate after hydrochloric acid exposure. Another study (Chaudhary and Liu, 2009), measured the mass loss and acid penetration depth during 110 days exposure to hydrochloric acid. They found that fly ash GP samples performed better than PC samples in terms of the assessed parameters. Another study (Temuujin et al., 2011) reported a gradual reduction in compressive strength of fly ash GP samples exposed to an 18% hydrochloric acid solution for 5 days. The acid exposure resulted in leaching of high levels of iron, aluminium and sodium into the acid solution. They observed that this leaching behaviour caused a reduction in compressive strength due to the porous microstructure left behind. Recently, the hydrochloric acid resistance of a fly ash GP binder combined with added calcium aluminate cement (24%) was investigated and compared with Portland cement and high alumina cement mortars (Vafaei et al., 2019). Findings show that after two years exposure, the fly ash GP binder with added calcium aluminate cement had increased resistance to hydrochloric acid, both in terms of mass and compressive strength.

As described above, the hydrochloric acid resistance of GP binders has previously been studied. However, within GP systems there are numerous variables which may be considered, making comparison difficult between one study and another. The present study investigated the hydrochloric acid resistance of fly ash binders with increasing slag content. Crucially, the addition of slag to fly ash binders eliminates the need for high temperature curing (Rafeet et al., 2019) which is a significant benefit that can reduce energy consumption. A previous study by these authors (Aiken et al., 2018) has investigated the resistance of fly ash GP binders with increasing proportions of slag to sulfuric acid. One of the key findings regarding sulfuric acid attack is the formation of gypsum in binders containing increased slag content. This meant that mixes with increased slag content (i.e. also increased calcium content) had increased gypsum formation. Gypsum is an expansive mineral which results in internal stresses and breakdown of samples (Gu et al., 2018). On the other hand, gypsum can have a space filling effect which can aid acid resistance. Gypsum formation also makes the interpretation of mass loss/gain difficult. Therefore, acid attack by sulfuric acid is complicated by the formation of gypsum. On the other hand, hydrochloric acid attack allows understanding of pure acid attack by dissolution mechanisms. This study aims to understand how the performance and failure mechanism differs under hydrochloric acid attack for fly ash GP binders with increasing slag content. The resistance of traditional Portland cement samples to hydrochloric acid is also investigated for comparison. Recently it has been suggested that a multiscale approach is necessary to fully understand the degradation mechanism for cementitious materials when exposed to acids (Gu et al., 2020). Therefore, this research also uses multiple indictors to assess hydrochloric acid resistance.

2. Experimental programme

2.1. Materials

The fly ash conformed to BS EN 450–1:2012 (British Standards Institution, 2012) and was supplied by Power Minerals Ltd., North Yorkshire, UK. The slag conformed to BS EN 15167–1:2006 (British Standards Institution, 2006) and was supplied by Civil and Marine Ltd-Hanson Company, Essex, UK. The Portland cement CEM I 42.5N was obtained from Quinn Cement, Ireland and conformed to BS EN 197–1:2011 (British Standards Institution, 2011). The oxide compositions for each powder binder component were attained from X-ray fluorescence (XRF) and are shown in Table 1. The X-ray diffraction (XRD) patterns of each powder binder component are presented in a previous publication (Aiken et al., 2018). The particle size distribution of fly ash, slag, Portland cement and sand is shown in Fig. 1.

Solutions of sodium silicate and hydroxide were used as activators. The sodium silicate solution was obtained from Fisher Scientific and contained 12.8% sodium oxide, 25.5% silicon dioxide and 61.7% water by mass. Sodium hydroxide solution with a concentration of 30% by weight was prepared by dissolving solid commercial grade (99% purity) NaOH in water.

Siliceous lough sand containing quartz was used as aggregate. The water absorption and density were obtained in accordance with BS 812–2:1995 (British Standards Institution, 1995). The sand had a water absorption of 0.92% after 1 h and 1% after 24 h. Its oven-dry particle density was 2695 kg/m³. It was dried in an oven at a temperature greater than 100 °C for a minimum of 48 h to ensure moisture was removed before subsequently being allowed to cool and be used for mixing.

Laboratory grade hydrochloric acid (≥37% HCl) and distilled water were used to produce the acid solutions at concentrations of 0.10, 0.31 and 0.52 mol/L (i.e. 0.37, 1.12 and 1.86%). These are the same molar concentrations used in the previous study for sulfuric acid but herein described as 1, 3 and 5% solutions by mass (Aiken et al., 2018). It should be noted that sulfuric acid has twice as many protons as hydrochloric acid.

2.2. Mix proportions

The mix proportions employed are shown in Table 2. The mixes were developed through previous work carried out by The Geopolymer Team at Queen’s University Belfast. The alkali dosage and Na₂O/SiO₂ ratio were chosen based on previous mix optimisation investigations (Rafeet, 2016). The alkali dosage is the percentage mass ratio of sodium oxide in the activating solutions to powder binder component (fly ash and slag). The alkali dosage and Na₂O/SiO₂ ratio were fixed at 7.5 and 1.25, respectively for each mix with increasing slag proportions. (GP1-GP4). GP5 was a 100% fly ash mix and had an increased alkali dosage and Na₂O/SiO₂ ratio which increased its compressive strength significantly compared with GP1. The water/solids ratio is the ratio of water and solids including the solid and water parts of the activators. The water/solids ratios chosen were based on findings from previous research (Rafeet et al., 2017) which found that mixes with an increased slag content had an increased water demand. The chosen water/solid ratios provided mixes with similar workability and the optimum compressive strength for each GP binder composition. The total added water is the total amount of water needed plus the absorption water (water needed to bring the sand to saturated surface dry condition) less the water contained within activating solutions. Each of the mortar mixes contained 50% paste and 50% sand by volume to facilitate equal comparison between different binder types.
2.3. Procedure for mix preparation, samples manufacturing and curing

Mortar and paste samples were prepared using a Hobart rotating paddle mixer. The mix procedure was similar to the procedure used in a previous study (Kwasny et al., 2018b) and is described below:

1. The sand was placed into the mixing bowl and then approximately half of the total water was added. Aggregates were mixed together with the water for 1 min and then were allowed to absorb moisture for 15 min. This step was not necessary for the paste samples as they contained no aggregate.

2. The appropriate powder binder component of each mix was then added to the mixer and mixed together with the aggregate for 1 min.

3. The remaining water and activating solutions were then added and mixing continued for 5 min before casting. No activating solutions were used in the Portland cement mixes.

The mixes were cast in the appropriate moulds in two layers and compacted using a vibrating plate. They were then wrapped in cling film for 24 h to avoid rapid moisture removal and placed in the appropriate curing conditions. The samples were demoulded after 24 h and immediately returned to the appropriate curing environment (described below). The GP samples containing 100% fly ash (GP1 and GP5) were cured at 70 °C for 7 days and then placed at 20 ± 1 °C and 50± 5% humidity. The fly ash and slag samples (GP2, GP3 and GP4) and the PC samples (PC1 and PC2) were cured at 20 ± 1 °C and relative humidity of greater than 90%. These conditions were achieved by placing the samples inside sealed plastic boxes on plastic supports with a height of 15 mm. The boxes were filled with water to a depth of 5 mm in order to avoid contact between the samples and water which may result in leaching (Kwasny et al., 2018a). The curing conditions for the GP samples were chosen based on findings from a previous study (Rafeet, 2016).

2.4. Testing procedures

Following curing for 21 days, samples were immersed in water for 7 days and their mass recorded. At 28 days four 50 mm mortar cube samples from each mix were immersed in 0.10, 0.31 and 0.52 mol/L solutions of hydrochloric acid for 56 days. Each mix had its own individual container and the acid solution to sample volume ratio in each container was maintained at 0.9. Every 7 days the samples were inspected visually, their mass recorded, and the acid solution replaced with fresh solution. After 56 days the compressive strength was obtained for comparison with control samples which were tested at the same age. The average compressive strength was determined by testing three samples (using a continuous load rate of 50 kN/min). The loading zones were protected with softboard to reduce the effect of uneven surfaces. This method was used instead of capping or grinding to allow immediate testing following acid attack, avoiding testing delays which would have caused issues regarding intermediate sample storage conditions and drying during processing. The compressive strength was calculated using the samples original cross-sectional area before any erosion took place (Bassuoni and Nehdi, 2007). The remaining fourth specimen was used to assess the pH of the samples cross-section following acid exposure. The samples were split and phenolphthalein solution applied. This highlighted the area where the pH is greater than around 9 (Chinchón-Payá et al., 2016). This provided some suggestion of how far the acid had travelled into each sample or at least to what extent ion exchange had occurred.

Table 1

| Material     | CaO  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | Na$_2$O | K$_2$O | SO$_3$ | MgO  | TiO$_2$ | MnO | LOI  |
|--------------|------|---------|-------------|-------------|---------|-------|-------|------|--------|-----|------|
| Fly ash      | 02.24| 46.78   | 22.52       | 9.15        | 0.89    | 4.09  | 0.90  | 1.33 | 1.76   | 6.94| 0.67 |
| Slag         | 43.72| 29.38   | 11.23       | 0.36        | 1.05    | 0.93  | 1.76  | 6.94 | 0.67   | 0.51| 2.40 |
| PC           | 63.01| 20.21   | 04.79       | 2.78        | 0.19    | 0.59  | 2.60  | 1.93 | 0.27   | 0.08| 3.16 |

Table 2

| Mix composition | GP1 | GP2 | GP3 | GP4 | GP5 | PC1 | PC2 |
|-----------------|-----|-----|-----|-----|-----|-----|-----|
| Binder composition | Fly ash (%) | 100 | 80  | 60  | 30  | 100 | –   |
| Slag (%)         | 0   | 20  | 40  | 70  | 0   | –   | –   |
| PC (%)           | –   | –   | –   | –   | –   | 100 | 100 |
| Paste content (%) | 50  | 50  | 50  | 50  | 50  | 50  | 50  |
| Water/solid ratio | 0.37| 0.38| 0.40| 0.42| 0.37| –   | –   |
| Water/cement ratio | –   | –   | –   | –   | –   | 0.60| 0.42|
| Alkali dosage (M+) | 7.5 | 7.5 | 7.5 | 7.5 | 11.5| –   | –   |
| Na$_2$O/SiO$_2$  | 1.25| 1.25| 1.25| 1.25| 0.95| –   | –   |
| Fly ash (kg/m$^3$) | 577 | 463 | 344 | 172 | 538 | –   | –   |
| Slag (kg/m$^3$)   | –   | 116 | 229 | 401 | –   | –   | –   |
| Portland cement (kg/m$^3$) | –   | –   | –   | –   | 544 | 676 |
| Sodium silicate (kg/m$^3$) | 136 | 136 | 135 | 135 | 256 | –   | –   |
| Sodium hydroxide (kg/m$^3$) | 111 | 112 | 111 | 111 | 126 | –   | –   |
| Sand (kg/m$^3$)   | 1348| 1348| 1348| 1348| 1348| 1348| 1348|
| Absorption water (kg/m$^3$) | 12  | 12  | 12  | 12  | 12  | 12  | 12  |
| Total added water (kg/m$^3$) | 93  | 100 | 112 | 125 | 13  | 339 | 296 |
occurred between the sample and acid solution. The depth of pH change for each sample was calculated by measuring the width of the unaffected area in two directions with a Vernier caliper and taking the average. This average was taken away from the original sample width (50 mm) and the result divided by two to give the depth of pH change for each mix.

The porosity (%) of each mix was obtained by mercury intrusion porosimetry (MIP) in accordance with BS ISO 15901–1:2005 (British Standards Institution, 2005). At 28 days mortar pieces approximately 2 x 8 x 20 mm were taken from the centre of 50 mm cubes. The samples were dried for 24 h at 60 ± 1 °C, then immersed in acetic acid for 4 h and dried in a desiccator for 24 h. The equipment used was a Pascal 140/240 mercury intrusion porosimeter which was supplied by Thermo Scientific. The volume of voids was obtained from the average of three mortar samples according to the standard procedure given in ASTM C642 (American Society for Testing and Materials, 2006). This involves recording the mass of samples in various conditions which are given below. This test was carried out on 100 mm long and 75 mm diameter cores which were extracted from 100 mm cubes. Three samples were tested for each mix and the VPV was calculated according to equation (1).

\[ VPV(\%) = \frac{C - A}{C - D} \times 100 \]  

\[ A = \text{Mass in air after oven drying}, \]  
\[ C = \text{Mass in air after immersion and boiling}, \]  
\[ D = \text{Apparent mass in water after immersion and boiling}. \]

The standard recommends an oven drying temperature of between 100 and 110 °C. However, in this study, an oven drying temperature of 40 °C was used to avoid excessive drying which can cause changes to binding phases such as calcium aluminium silicate hydrate gel within GP mortar containing slag (Ismail et al., 2013).

Following curing for 28 days, paste samples were immersed in a 0.52 mol/L hydrochloric acid solution for 21 days. Similar to the mortar samples, each mix had its own individual container and the acid solution to sample volume ratio in each container was maintained at 0.9. The acid solution was replaced with fresh acid every 7 days and the pH of the acid solution was monitored during each cycle. Inductively coupled plasma mass spectrometry (ICP) was used to assess the composition of the leachate solution. Certified reference standards were used to calibrate the equipment. The limit of detection was 0.1 ppm for aluminium, sodium, silicon and potassium. It was 0.01 ppm for calcium, magnesium and iron. Paste samples following 21 days of acid exposure were used for analysis by XRD, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis. Powdered samples were used for XRD and FTIR by crushing and grinding both control samples and samples exposed to acid in a pestle and mortar. The powders were dried at 35 °C for 24 h in a desiccator before analysis. XRD was carried out with a PANalytical X’Pert PRO diffractometer applying CuKα radiation of wavelength 1.54 Å. Diffraction patterns were collected between 5 and 65° 2θ with a step size of 0.02°. PANalytical X’Pert Highscore software with the powder diffraction file database was used to analyse the diffraction patterns. FTIR data was obtained using Jasco 4100 series FTIR Spectrometer with attenuated total reflectance attachment. The spectra were gathered between 650 and 4000 cm⁻¹ wavenumber at 8 cm⁻¹ resolution. The equipment used for SEM was QUANTA FEG250 with OXFORD X-Act as chemical composition analyser. EDX was run by Aztec version 2.0 software for chemical composition analysis. Paste samples were sectioned and polished in preparation for SEM and EDX analysis.

3. Results

3.1. Physical properties of unexposed mortars

Fig. 2 shows the porosity and volume of permeable voids for each mortar mix. The trends are similar for both test methods. Larger values are obtained from the volume of voids method, which is likely due to the larger sample volume tested and the inclusion of air voids which are not present in the small samples used for MIP. The most porous samples were the unblended fly ash mortars (GP1 and GP5) and the mix containing 80% fly ash (GP2). With increasing slag proportions, the mortars became less porous. The PC samples had relatively similar porosity and volume of permeable voids values as GP3 which consisted of 60% fly ash and 40% slag.

The compressive strength development of each mortar mix between 1 and 28 days is displayed in Fig. 3. The 28 day strength of GP1 was 21.5 MPa which became 87.5 MPa for GP4 as the slag proportion in the mix was increased to 70%. A significant strength increase was also observed for GP5 (55.5 MPa) which contained an increased activator dosage compared with GP1 (21.5 MPa). Therefore, as the slag and activator content of neat fly ash GPs increased their compressive strength also increased. Conversely, the early strength of GP2 was lower than that of GP1 despite GP2 having a slag content of 20%. This was due to the high temperature curing of GP1 which accelerated polymerisation in the early stages.

Similar to the PC samples, the fly ash/slag blends continued to gain strength until 28 days. However, the 100% fly ash samples gained no further strength beyond 7 days, in fact a small reduction in strength was observed for GP1 and GP5 after 28 days. It is likely no further strength gain was observed after 7 days because the samples were removed from high temperature curing at this time and further reactions were limited at ambient temperature. The small strength loss observed at 28 days may be due to shrinkage and micro cracks forming as a result of the high temperature curing employed for GP1 and GP5 (Thomas et al., 2017).

The type of the dominant binding gel present in each mix explains the observed increase in strength and decrease in porosity as the slag content increased. Fig. 4 shows a ternary plot illustrating the calcium, aluminium and silicon content of each GP paste mix. The unreacted fly ash and slag are also shown. Data for each mix was obtained via EDX point analysis. The circles suggest the nature of gel present using a similar approach as previous studies (Ismail et al., 2014; Lee and Lee, 2015). This confirms the presence and likely coexistence of calcium sodium aluminium silicate hydrate (C–N–A–S–H) and calcium aluminium silicate hydrate (C–A–S–H) gels in blended fly ash and slag mixes. The 100% fly ash samples contain sodium aluminium silicate hydrate (N–A–S–H) gel. The N–A–S–H gel found in the unblended fly ash pastes (GP1 and GP5) is relatively porous. With increased slag proportions, C–N–A–S–H or C–A–S–H gels are formed which are more dense and described as space filling in comparison to N–A–S–H (Provis et al., 2012).
3.2. Physical changes following hydrochloric acid attack

Fig. 5 shows photographs of each mortar mix following 56 days of hydrochloric acid attack. The unblended fly ash mortars (GP1 and GP5) displayed very little visible damage except they appeared lighter in colour following attack by a more concentrated acid solution. The GP mixes with slag (GP2, GP3 and GP4) suffered the removal of cement paste causing sand particles to become exposed, leaving behind a rough surface. This was more pronounced with increased acid concentrations. The PC mixes also suffered the loss of cement paste causing sand particles to become exposed and leaving behind a rough surface. However, the deterioration appeared more pronounced for the PC mixes, particularly for the samples exposed to the most concentrated hydrochloric acid solution.

Fig. 6 shows the mass loss of each mortar mix following 56 days of hydrochloric acid attack, where the vertical axis scale is made the same in the three subfigures for easy comparison of the different acid concentrations. The mass losses increased following exposure to more concentrated acid solutions. Exposure to 0.10 and 0.31 mol/L solutions of hydrochloric acid resulted in mass losses of smaller than 2 and 6%, respectively for each mix. The trends are more easily interpreted following exposure to the highest concentration of 0.52 mol/L. The unblended fly ash mortars (GP1 and GP5) had the smallest mass losses throughout and lost less than 3% after 56 days acid exposure. During the first 21 days exposure, the blended fly ash/slag samples suffered larger losses than the PC samples. After 21 days the mass loss for the GP samples continued at a constant rate whereas the mass losses for the PC samples continued to accelerate. After 56 days exposure the mass losses were 12.3 and 9.6% for PC1 and PC2, respectively. The mass loss for GP2 was 7.2% which decreased as the slag content increased to 6.5 and 5.6% for GP3 and GP4, respectively. The superior performance of the mixes with increased slag content could be related to the lower porosity (Fig. 2), allowing less ingress of acid. These results suggest that GP mixes provide an outer surface which is more resistant to the loss of paste than PC samples. Therefore, for applications where a durable surface is desired for aesthetic reasons, GP binders provide a better alternative than traditional Portland cement binders.

Fig. 7 shows the compressive strength of each mix after exposure to 0.10, 0.31 and 0.52 mol/L of hydrochloric acid for 56 days. The compressive strength of the samples kept in water (unexposed), tested at the same age as the acid attacked samples is also shown. The percentage compressive strength reduction is also shown at the base of each bar. In general, the largest percentage compressive strength losses were observed for the neat fly ash samples. The percentage compressive strength loss seemed to decrease as the slag proportion increased. For the GP mixes, the smallest percentage compressive strength losses were observed for GP4 which were comparable with those obtained for PC1 and PC2. The losses for PC1 and PC2 were similar regardless of the acid concentration compared with the GP mixes whose percentage loss was significantly different depending on the acid concentration.

Fig. 8 shows the cross-section of each mortar mix following the application of phenolphthalein solution. Samples were exposed to a 0.52 mol/L solution of hydrochloric acid for 56 days. Control samples which were not exposed to acid (stored in water) are also shown for comparison. The entire cross-section of the samples not exposed to acid appeared pink/purple which suggests their pH was greater than 9.0 across their entire cross-section and this is the case for each mix. Following attack by a 0.52 mol/L solution of hydrochloric acid the entire cross-sections no longer appeared pink/purple following the application of phenolphthalein solution. This suggests that the pH has decreased in the region which has not turned pink/purple and may provide an indication of the acid penetration depth. Fig. 9 shows the depth of pH change for each mix which was calculated as described in section 2.4. The entire cross-section of GP1 no longer turned pink/purple which suggests significant acid ingress. With increased slag proportions, less of the samples cross-sections was affected by significant pH change. A significant portion of the cross-section of GP5 also changed following acid exposure. Similar to GP4, almost the entire cross-sections of PC1 and PC2 appeared pink/purple suggesting their pH remained greater than 9.0. These findings are broadly in agreement with the porosity values reported for each mix (Fig. 2). Additionally, less of the cross-sections of GP4, PC1 and PC2 suffered pH change and these samples also suffered less percentage compressive strength losses (Fig. 7). This suggests the more porous samples (GP1, GP2, and GP5) suffered more damage to their internal core and as a result suffered larger percentage compressive strength losses.

3.3. Leaching behaviour during hydrochloric acid attack

Fig. 10 shows the pH of each hydrochloric acid solution following each 7 day exposure cycle for each mortar mix. Larger pH values were observed for the solutions where the PC samples were stored meaning the PC samples had greater ability to neutralise the acid solution than the GP samples. As the number of exposure cycles increased the pH of the acid solutions generally decreased suggesting less leaching occurred and the ability to neutralise the acid solution decreased. This may explain the lower mass losses observed initially for the PC samples but as the
neutralisation capacity decreased the mass losses increased. For the GP samples, the mixes with an increased slag proportion resulted in a slightly increased pH of the acid solution suggesting more leaching may have occurred.

Fig. 11 shows the pH evolution of 0.52 mol/L hydrochloric acid solutions during immersion of each paste mix for 21 days. The pH of the solutions into which the PC samples were immersed, increased significantly (pH > 8) during each 7 day cycle until the acid solutions were replenished. This is likely due to leaching of ions into solution and less leaching seems to occur during each consecutive 7 day cycle. For the GP samples, the mixes with increased content of slag (hence calcium) resulted in a slightly higher pH for the acid solution.

Fig. 12 shows the cumulative concentration of various metals found in acid solutions during exposure of each paste mix to 0.52 mol/L solutions of hydrochloric acid for 21 days. The main leachates observed for the unblended fly ash mixes are aluminium and sodium. As the proportion of
slag in the mix increased the amount of both aluminium and sodium that leached into the acid solution decreased. Overall, the main component leached into solution was calcium, particularly for the PC samples. The GP samples resulted in less calcium being leached into acid solution which decreased further as the slag proportion decreased. This is most likely due to the content of calcium in slag (Table 1). Relatively small amounts of the other metals were found in solution.

3.4. Microstructural changes due to hydrochloric acid attack

Fig. 13a shows the XRD patterns of control samples of each paste mix. In the GP pastes the main peaks are related to quartz, mullite and hematite (Lloyd et al., 2009). With increased slag proportions in the mix the intensity of these peaks reduced. The GP mixes have a broad hump between 20 and 35° 2θ which can be attributed to existence of amorphous silicate and aluminosilicate gel phases (Bernal et al., 2013). Samples containing a blend of fly ash and slag have a broad peak at around 29° 2θ which can be described as C-S-H type gel (Ben Haha et al., 2011). The dominant gel product is most likely C-N-A-S-H, C-A-S-H or a combination of both (Fig. 4). The control PC pastes (Fig. 13a) contain calcium hydroxide and ettringite.

After hydrochloric acid attack the 100% fly ash samples exhibited no change via XRD (Fig. 13b). Mullite, quartz and hematite were still present and no additional peaks were observed. The GP pastes containing fly ash/slag blends also still contained mullite, quartz and hematite. However, the broad peak at around 29° 2θ was not observed suggesting susceptibility of C-A-S-H type gels to hydrochloric acid.

Considerable changes were observed in the PC pastes following hydrochloric acid attack. Calcium hydroxide and ettringite were not observed suggesting their vulnerability to hydrochloric acid. Instead calcite was observed which was also observed in another study (Bernal et al., 2012) following attack of PC samples by various acids. Calcite is likely formed due to the carbonation of calcium available following the dissolution of phases with high calcium content such as calcium hydroxide and ettringite. Note that Fig. 13b shows that calcite is the only dominant phase detected by XRD in PC samples, so the major calcite peak height is irrelevant as there is no peak from another phase to compare with it.

Fig. 14a shows the FTIR spectra of control pastes which were not attacked by hydrochloric acid. The bands at around 1640 and 3400 cm⁻¹ are due to water molecules. The main band at approximately 1000 cm⁻¹ indicates the nature of the gel present (García-Lodeiro et al., 2008). In the PC pastes the small bands observed at around 1105 and 3635 cm⁻¹ are related to ettringite and calcium hydroxide (Puertas et al., 2011), respectively.

Fig. 14b shows the FTIR spectra of each paste mix following 21 days of hydrochloric acid exposure. The most notable change is the shift of the main band to higher wavenumber. This shift can be an indication of decalcification (Puertas et al., 2012) and/or dealumination (Bascarevic et al., 2013) of the main binding gel, leaving a highly siliceous gel behind. In the PC pastes the bands corresponding to ettringite and calcium hydroxide were no longer observed, and calcite was identified instead by bands at around 875 and 1425 cm⁻¹ (Yu et al., 2004), in agreement with findings from XRD.

Fig. 15 shows SEM images of GP1, GP4 and PC2 pastes following attack by hydrochloric acid. EDX map analysis is also shown. Fig. 15a shows the outside region of GP1. The surface and outer region appear relatively intact, although some cracks perpendicular to the exposed face can be observed. The EDX analysis suggests that the acid has penetrated which can be attributed to existence of amorphous silicate and aluminosilicate gel phases (Bernal et al., 2013). Samples containing a blend of fly ash and slag have a broad peak at around 29° 2θ which can be described as C-S-H type gel (Ben Haha et al., 2011). The dominant gel product is most likely C-N-A-S-H, C-A-S-H or a combination of both (Fig. 4). The control PC pastes (Fig. 13a) contain calcium hydroxide and ettringite.
beyond this outer layer because there is no visible variation in elemental intensity within this region. Fig. 15b shows a slightly further in section of GP1 which appears to contain the front of acid attack along the middle of the image. In this region there appears to be an increase in concentration of aluminium, calcium and sodium.

Fig. 15c shows the outside region of GP4. There are two distinct layers visible, an outer layer which is darker in colour, appears porous due to the presence of dark voids and also has some cracks. Along the exposed face it seems that some of the sample has been detached from the edge but it is unclear how much. The inner layer is lighter in colour, has fewer cracks and voids and appears unaffected by acid attack. The elemental analysis shows that the outer layer has suffered a significant depletion of calcium and also depletion of aluminium and magnesium. On the other hand, for sodium, silicon and potassium the outer layer is divided into two parts. The first layer which is depleted is followed by a highly concentrated layer. This highly concentrated layer may act as a barrier for further acid penetration and could explain the decelerating mass losses observed for GP4 in Fig. 6. This highly concentrated layer of sodium and silicon is potentially a layer of sodium and silicon rich gel which has formed following the calcium depletion of calcium from C-A-S-H type gels. The depletion of elements observed by EDX analysis is in agreement with the leaching behaviour observed (Fig. 12).

Fig. 15d shows the outer region of PC2. A large crack is visible parallel to the exposed surface and the outer section appears fragile. It is unclear how much of the sample has been removed due to hydrochloric acid attack. EDX analysis indicates that elements are relatively evenly distributed in this region. This suggests that the PC samples decline in a layer by layer manner with little acid ingress as shown in Figs. 8 and 9. Instead the outer layer suffers significant depletion of calcium and then falls off before the subsequent layer is then attacked.
be suitable for applications where an intact surface is desired for cross-section was less affected. Therefore, the 100% (Provis et al., 2012) reported that binders dominated by N-A-S-H gels do not provide connectivity within neat samples. This is most likely caused by the development of C-A-S-H and C-N-A-S-H gels in systems with more slag whereas N-A-S-H gel was found in unblended fly ash binders.

Fig. 16 shows a schematic diagram of the mechanism of hydrochloric acid attack for each binder type investigated. Once slag was added to the system (GP2) significantly more damage was visible (Fig. 5) and larger mass losses (Fig. 6) were observed compared with the unblended fly ash samples. This is most likely caused by the increased content of calcium in slag and the breakdown of C-A-S-H and C-N-A-S-H gels via calcium dissolution (comparing GP1 and GP2). However, when the slag proportion was further increased (GP3 and GP4), the visible damage and loss of mass and compressive strength decreased. This is likely due to the decreased porosity (Fig. 2) and increased compressive strength (Fig. 3) with increased slag proportions allowing less ingress of hydrochloric acid (Figs. 8 and 9). Besides porosity, the silicon rich layer seen in GP4 (Fig. 15) may act as a barrier and further help explain this observation (Gevaudan et al., 2019).

GP1 (100% fly ash) displayed superior hydrochloric acid resistance to the fly ash/slag blends based on visual appearance and mass loss. This is because of the nature of the N-A-S-H binding gel formed which had a lower calcium content and was not as susceptible to decalcification as the fly ash/slag blends. Here, when comparing the different binder types, the absence of calcium and nature of the gel is the reason why 100% fly ash mixes have much smaller mass losses than those measured for mixes made with fly ash/slag blends. Dealumination and removal of cations in GP1 all cause mass losses, but these are substantially smaller than mass losses caused by decalcification in the blends. When comparing different blends, other factors play a part such as strength and porosity as mentioned in the previous paragraph. However, the percentage compressive strength loss was larger for GP1. This is due to dealumination of N-A-S-H gel (Figs. 13 and 14). Additionally, the entire cross-section of GP1 suffered a reduction in pH due to hydrochloric acid attack indicating a larger corroded depth (Fig. 16). This was likely caused by the relatively large porosity observed in GP1 and may also be related to pore connectivity within neat fly ash mixes. A previous study (Provis et al., 2012) reported that binders dominated by N-A-S-H gels do not provide the same extent of pore network obstruction as gels formed in binders with increased slag content. With increased slag content the pH of the cross-section was less affected. Therefore, the 100% fly ash samples could be suitable for applications where an intact surface is desired for aesthetic reasons. They are not suited to structural applications due to their increased strength loss and porosity allowing significant acid ingress which would be problematic for steel reinforcement.

4.2. Comparison with Portland cement

The PC samples appeared more damaged visually than the GP samples and this is reflected in the mass losses observed (Fig. 6). Crucially the mass losses observed for PC1 and PC2 were accelerating following each acid attack cycle. However, the mass losses for the GP samples were relatively constant following each exposure cycle. This suggests much superior long term resistance for the GP mixes. The loss of mass observed for the PC samples was due to the breakdown of calcium hydroxide and ettringite by dissolution alongside the decalcification of C–S–H gel.

The percentage compressive strength losses observed for PC1 and PC2 are similar to those observed for GP3 and GP4, but smaller than those observed for GP1, GP2 and GP5. This is likely related to porosity and the failure mode for each binder type. The mixes with increased porosity have an increased depth of sample exposed to acid. For PC1 and PC2 the porosity is low and the mechanism of attack is layer by layer with one small layer attacked and removed before the following layer is attacked. This means a large portion of the internal core of the PC samples was relatively unaffected by hydrochloric acid attack, despite the significantly deteriorated outer layers with paste removed.

4.3. Comparison of hydrochloric acid attack with that of sulfuric acid attack

A previous publication (Aiken et al., 2018) investigated the resistance of the same mixes to sulfuric acid attack. This section provides a comparison between hydrochloric and sulfuric acid attack. The visual appearance of fly ash/slag blends and PC mortars was different following attack by each acid type. The samples exposed to hydrochloric acid appear more square edged than the samples exposed to sulfuric acid which appeared more rounded and large cracks were present around the edges of GP4 (Aiken et al., 2018). These were caused by expansion following gypsum formation in the samples exposed to sulfuric acid, but did not happen due to hydrochloric acid attack.

When compared with sulfuric acid exposure (Aiken et al., 2018), the main difference in leaching behaviour for hydrochloric acid solutions is the amount of calcium leached into solution. In the case of sulfuric acid exposure, very little calcium is released into solution as it is used up in the formation of gypsum. This resulted in more aluminium, sodium, potassium, magnesium and iron ions being drawn into solution due to exchange with aggressive H2O2 and SO42− ions. Hydrochloric acid attack caused significant quantities of calcium to be drawn into the acid solutions. Subsequently, more of the other ions mentioned above remained behind in the samples compared with sulfuric acid attack. The SO42− ions in sulfuric acid allowed the formation of gypsum, whereas no products were observed due to the Cl− ions present in hydrochloric acid. This suggests that hydrochloric acid attack is mainly based on the exchange of ions between attacking acid solution (H2O2 and Cl−) and sample (mainly calcium) (Allahverdi and Skvára, 2001). It is worth noting that a previous study (Okoye et al., 2017) reported mass losses and strength losses for fly ash GPs when exposed to a 5% solution of NaCl which suggests the effect of Cl− ions may not be negligible. Similarly Duchesne and Bertron (2013) reported that Cl− ions were responsible for decalcification of hydrated cement paste. For both hydrochloric and sulfuric acid, silicon ions appear to remain behind in the attacked samples resulting in highly siliceous networks being formed.

The main difference in the exposure of GP and PC mixes to hydrochloric acid compared with exposure to sulfuric acid is that no gypsum is formed. Gypsum is an expansive mineral which caused significantly more damage and mass losses for PC1 and PC2. Gypsum was also formed in the slag containing GP mixes.

Considering the samples which consisted of blends of fly ash and slag,
mixes with increased slag content have superior overall performance when exposed to hydrochloric acid (GP4 > GP3 > GP2). On the other hand, mixes with increased fly ash content have superior performance when exposed to sulfuric acid (GP2 > GP3 > GP4) due to reduced gypsum formation. The unblended fly ash samples (GP1 and GP5) performed similarly to both hydrochloric and sulfuric acid attack due to their low calcium formation and limited gypsum formation. The PC samples performed better when exposed to hydrochloric acid compared with sulfuric acid. However, their performance was inferior to the blended GP samples for both acids.

5. Conclusions

This paper has investigated the hydrochloric acid resistance of geopolymer and Portland cement binder systems. The following conclusions have been made:

- In terms of the exposed surface, binders consisting of 100% fly ash displayed improved hydrochloric acid resistance, when compared to the blends of fly ash/slag and traditional Portland cement. The exposed surface remained intact. However, the high porosity of 100% fly ash mixes and the more rapid surface deterioration observed for Portland cement mixes.

- As the slag content of fly ash/slag blends increased their resistance to hydrochloric acid also increased in terms of the appearance of the

Fig. 12. Cumulative concentration of metals leached into acid solution during exposure of paste samples to 0.52 mol/L hydrochloric acid solutions for 21 days.
exposed surface, mass losses and compressive strength losses. This is due to their decreased porosity allowing less ingress of acid.

Compared with traditional Portland cement samples, the fly ash/slag blends displayed a similar mechanism of hydrochloric acid attack, whereby the attack was layer by layer. However, the fly ash/slag blends showed improved performance, particularly in terms of the exposed surface highlighted by visual appearance and mass losses. It would be useful to investigate and compare the performance of geopolymer mixes with that of Portland cement mixes containing partial replacement by fly ash or slag.

- Hydrochloric acid is less aggressive than sulfuric acid due to no additional compounds being formed such as gypsum. This is the case for both geopolymer and Portland cement binders. Blends of fly ash/slag with increased slag content are more resistant to hydrochloric acid attack whereas blends with increased fly ash content are more suited to sulfuric acid attack.

This study highlights that geopolymer binders have better acid resistance than traditional Portland cement binders. Therefore, exposure to acidic solutions should not be a barrier to their widespread implementation towards the reduction of CO₂ emissions associated with cementitious materials. Furthermore, it may be possible to use geopolymer binders for niche applications where long term resistance to dissolution by acid is required.

Fig. 13. XRD patterns of each paste mix, a) not exposed to acid and b) following hydrochloric acid attack.

Fig. 14. FTIR spectra of each paste mix, a) not exposed to acid and b) following hydrochloric acid attack.
Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Author contributions

Timothy A Aiken: Conceptualisation, Methodology, Investigation, Writing - Original Draft, Visualisation. Jacek Kwasny: Conceptualisation, Methodology, Investigation, Writing - Review and Editing, Visualisation. Wei Sha: Conceptualisation, Methodology, Writing - Review and Editing.

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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