Mechanical and durability properties of alkali-activated fly ash concrete with increasing slag content


Published in:
Construction and Building Materials

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
© 2021 Elsevier Ltd.
This manuscript is distributed under a Creative Commons Attribution-NonCommercial-NoDerivs License (https://creativecommons.org/licenses/by-nc-nd/4.0/), which permits distribution and reproduction for non-commercial purposes, provided the author and source are cited.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access
This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: http://go.qub.ac.uk/oa-feedback
Mechanical and durability properties of alkali-activated fly ash concrete with increasing slag content

Authors: Timothy A Aiken¹*, Jacek Kwasny¹, Wei Sha¹ and Kien T Tong²
¹ School of Natural and Built Environment, Queen’s University Belfast, Stranmillis Road, Belfast, BT9 5AG, UK
² National University of Civil Engineering, Faculty of Building Materials, 55 Giai Phong, Hanoi, Vietnam
*corresponding author email address: taiken02@qub.ac.uk

Abstract
Alkali-activated concrete is a promising alternative to conventional Portland cement-based concrete. However, further understanding in relation to the durability of alkali-activated concrete is required. This paper explores the resistance of alkali-activated concrete mixes to aggressive media that concrete is expected to encounter in service. Findings indicate that the chloride, freeze-thaw and acid resistance of alkali-activated concrete increases as the slag content and activator increased. However, performance against chloride and freeze-thaw was not as good as that of Portland cement concrete. Acid resistance seems to be a more promising characteristic of alkali-activated concrete compared with Portland cement concrete.

Keywords: Durability; Geopolymer Concrete; Fly Ash; Slag; Freeze-Thaw; Chloride Migration; Steel Corrosion

1. Introduction
The uptake of cementless alkali-activated concrete has been relatively slow, despite a significant amount of research being conducted in this area. Many factors have been cited for this including vested interests, supply chain concerns, lack of incentive, lack of knowledge/understanding within industry as well as technical concerns [1,2]. At the forefront of the technical concerns is uncertainty associated with durability in aggressive environments [3]. This study aims to assess the durability of alkali-activated concrete against some of the most common aggressive media that concrete is expected to encounter in-service. Specifically, performance when exposed to chloride, freeze-thaw and acid attack. A comparison with a traditional Portland cement concrete is also carried out.

The binder for alkali-activated concrete is produced from the activation of a solid aluminosilicate source powder under alkaline conditions with a solid or dissolved alkali metal [2,3]. This is then combined with appropriate quantities of aggregate and water to form hardened concrete. Two of the most commonly used aluminosilicate sources are fly ash and ground granulated blast furnace slag, later referred to as
slag [4,5]. A wide range of alkali metal activators have been investigated, the most widely used being alkali hydroxides and silicates (usually Na or K) [6,7]. The potential environmental benefits of alkali-activated concrete are huge due to no Portland cement being present in the system. Portland cement production is associated with many negative environmental impacts including substantial CO₂ emissions which contribute around 8% of global emissions annually [8–10]. The potential reduction in CO₂ emissions for alkali-activated concrete is a subject of much debate with values between 44 and 80% quoted [11–14]. It is worth noting that the actual environmental benefit will vary depending on source materials, transportation requirements and activator type [15,16]. Therefore, the continued drive towards a reduction in CO₂ emissions has made alkali-activated concrete an interesting proposition in order to reduce the carbon footprint of the construction industry. The alkali-activation of fly ash and slag individually as single precursors each have specific challenges. Alkali-activated fly ash usually requires curing at elevated temperatures to develop strength which is a potential barrier to widespread use in the concrete industry [17]. On the other hand, alkali-activated slag can be cured at ambient temperature but there are concerns relating to workability and rapid setting time [18–20]. The blending of fly ash and slag together has the potential to eliminate these issues. Alkali-activated fly ash/slag blends do not require elevated curing temperatures and are less prone to fast setting [21,22]. Therefore, this study investigates 100% fly ash mixes (cured at high temperature) and mixes with increasing slag content (cured at ambient temperature).

The corrosion of steel reinforcement is one of the main problems affecting the durability and safety of reinforced concrete structures [23]. It is most commonly caused by the penetration of chloride ions into the concrete microstructure from seawater or de-icing salts [24,25]. The chloride content at the steel surface eventually reaches a threshold value causing depassivation of the steel, which allows corrosion to begin [26]. Previous studies investigating the chloride resistance of alkali-activated concretes have at times provided conflicting results. Kupwade-Patil and Allouche [27] reported that alkali-activated fly ash concretes displayed lower chloride diffusion coefficients than corresponding Portland cement samples when using the method described in ASTM C1556 [28]. Ganesan et al. [29] used the same procedure and found that alkali-activated fly ash concrete had almost equal performance to that of Portland cement concrete. Babae and Castel [30] reported similar resistance for alkali-activated fly ash concrete and Portland cement concrete following exposure to chloride environments and assessment of their electrochemical performance. Ismail et al. [31] and Mackechnie and Scott [32] investigated the chloride migration coefficient of alkali-activated fly ash/slag blends and Portland cement mixes according to NT Build 492 [33]. They reported that the chloride migration coefficient was larger for Portland cement materials. Olivia et al. [34] investigated the chloride ion penetration in alkali-activated fly ash concrete using the method described in NT Build 443 [35]. They found that the alkali-activated fly ash mixes had a higher chloride ion penetration than Portland cement concrete. The majority of studies are focused on chloride penetration or migration and results are variable. Therefore, analysis of
durability performance of alkali-activated concrete mixes particularly related to protection of embedded steel requires further research [36].

In many countries, harsh winters with cold temperatures provide challenges for concrete durability [37]. Concrete is susceptible to freeze-thaw attack when temperatures rise above and fall below the freezing point of water. The two most common modes of failure due to freeze-thaw are surface scaling and internal structural damage. Both failure modes are detrimental to the long-term durability of concrete. Internal structural damage reduces the concrete mechanical properties due to cracking which can also lead to further durability issues [38,39]. Surface scaling leaves a rough concrete surface which diminishes the depth of cover to steel reinforcement and is particularly common in the presence of de-icing salts which are often used to remove snow and ice from roadways and footpaths [40–42]. Many theories exist to explain in more detail the precise mechanisms involved. These include the hydraulic pressure theory [43], the microscopic ice lens theory [44,45], the glue-spall mechanism [46], the osmotic pressure theory [47] and the critical degree of saturation [48]. Skvara et al. [49,50] suggested that alkali-activated fly ash materials possess excellent freeze-thaw resistance. They carried out an investigation where the mass of the samples did not change during freezing and thawing cycles in the presence of NaCl solution (164 g/dm³) according to Czech standard CSN 72 2452 with no visible defects or deformation noticed after 150 cycles. However, after 150 cycles the compressive strength dropped to 70% of the samples which were not exposed to freeze-thaw cycles. Sun and Wu [51] reported on the compressive strength loss of alkali-activated fly ash and Portland cement concrete after exposure to distilled water and testing according to ASTM C666. They found that the fly ash samples retained greater than 90% of their strength after 300 cycles whereas the Portland cement samples retained approximately 80% during the same period. On the other hand, Montes et al. [52] investigated the freeze-thaw resistance of alkali-activated fly ash concrete and reported poor resistance as the samples were unable to complete the test (ASTM C666 [53]) without suffering complete degradation. No comparison with Portland cement concrete was carried out. Ionescu and Ispas [54] prepared concrete containing fly ash, slag and sodium silicate as activator. They reported good freeze-thaw resistance after exposure to 50 freeze-thaw cycles [55]. Puertas et al. [56] compared the resistance of Portland cement, alkali-activated fly ash, alkali-activated slag and a combination of 50% fly ash and slag mortars. They prepared beams (40 x 40 x 160 mm) for each mix, which were subjected to freeze-thaw cycles with water, not de-icing salt. They studied the strength change after 50 freeze-thaw cycles and reported good resistance (i.e. no strength loss) for the Portland cement, alkali-activated slag and slag/fly ash combination. On the other hand, the alkali-activated fly ash samples suffered a 24% strength loss. There is not a large volume of work reported on the freeze-thaw resistance of alkali-activated materials. In particular, the literature available on surface scaling with the use of de-icing salts is scarce. Furthermore, comparisons with Portland cement materials are not often available in literature [55].
Acid attack is a topic of increasing significance driven by increasing urban and industrial activities [57]. There is a broad range of acid media which come into contact with concrete structures including organic acids from agri-food industries and mineral acids from wastewater treatment and acid precipitation [58–61]. Acid precipitation is generated from the incomplete combustion of fuels which are released into the environment as gases (NO₂ and SO₂) and react with water to form acidic precipitation (nitric and sulfuric acid) [62–66]. Therefore, nitric acid is the focus of the present study. Tahri et al. [67] compared the resistance of alkali-activated fly ash samples with Portland cement samples when exposed to different concentrations of nitric acid. At acid concentrations of 10 and 20%, the fly ash samples performed better in terms of mass loss. On the other hand, when a concentration of 30% was used, the Portland cement samples displayed smaller mass losses than 100% fly ash samples. Shi [68] studied the performance of pastes made with alkali-activated slag and Portland cement when exposed to nitric acid. After 580 days of immersion in nitric acid, the alkali-activated slag and Portland cement pastes were corroded to a depth of approximately 1 and 2.5 mm, respectively. The majority of studies conducted on acid resistance suggest improved resistance to nitric acid for alkali-activated materials when compared with Portland cement materials. However, in general there are a wide range of variables considered and many authors only consider a single deterioration indicator which can provide misleading findings. Rather, a multiscale approach is necessary is better understand the performance of different binders due to acid attack [69]. Therefore, further work is needed in relation to the nitric acid resistance of fly ash/slag blends whilst considering a range of deterioration indicators.

This study investigates the physical and durability properties of alkali-activated fly ash concretes with increasing slag content. The engineering properties examined include compressive strength, tensile strength, flexural strength and modulus of elasticity. Durability was investigated by assessing chloride migration, steel reinforcement corrosion, freeze-thaw resistance and acid resistance. A comparison with a traditional Portland cement mix is also carried out. This study compares the engineering properties and performance in a range of aggressive exposure conditions of the same mixes. This provides insight into the properties that need further work to allow the use of alkali-activated concrete to become more widespread.

2. Experimental programme
2.1 Materials
The fly ash, slag and Portland cement were the same powder binding materials as used in previous studies. Their oxide compositions and loss on ignition (LOI) obtained by X-ray florescence are shown in Table 1. Further details regarding their mineralogy and particle size distribution are available in previous publications [70–72]. The alkali-activated binders were activated by solutions of sodium silicate and sodium hydroxide. The sodium silicate solution contained 25.5% SiO₂, 12.8% Na₂O and 61.7% water. The sodium hydroxide solution was prepared at 30% w/w by the dissolution of solid
commercial grade sodium hydroxide with a 99% purity. The aggregates utilised in this study were 0-5 mm lough sand, 4-10 mm crushed basalt and 10-20 mm crushed basalt. The Lough sand was supplied by Creagh Concrete, Northern Ireland and was considered as fine aggregate. The crushed basalts were obtained from James Boyd & Sons, Northern Ireland and were considered as coarse aggregates. The oven dry particle densities and water absorption of each aggregate at 1 and 24 hours were obtained according to BS 812-2:1995 [73] and are reported in Table 2. Prior to mixing, the aggregates were oven dried at 100 °C for at least 24 hours to remove moisture. They were allowed to cool to room temperature before mixing began.

**Table 1 Oxide compositions (wt %) and loss on ignition (LOI) of fly ash, slag and Portland cement**

<table>
<thead>
<tr>
<th></th>
<th>Fly ash</th>
<th>Slag</th>
<th>Portland cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>46.78</td>
<td>29.38</td>
<td>20.21</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.52</td>
<td>11.23</td>
<td>4.79</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.15</td>
<td>0.36</td>
<td>2.78</td>
</tr>
<tr>
<td>CaO</td>
<td>2.24</td>
<td>43.72</td>
<td>63.01</td>
</tr>
<tr>
<td>MgO</td>
<td>1.33</td>
<td>6.94</td>
<td>1.93</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.51</td>
<td>0.08</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.05</td>
<td>0.67</td>
<td>0.27</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.89</td>
<td>1.05</td>
<td>0.19</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.09</td>
<td>0.93</td>
<td>0.59</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.90</td>
<td>1.76</td>
<td>2.60</td>
</tr>
<tr>
<td>LOI</td>
<td>3.57</td>
<td>2.40</td>
<td>3.16</td>
</tr>
</tbody>
</table>

**Table 2 Oven dry particle density and absorption of aggregates**

<table>
<thead>
<tr>
<th>Aggregate</th>
<th>Oven dry particle density (kg/m³)</th>
<th>Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 hour</td>
<td>24 hours</td>
</tr>
<tr>
<td>0-5 mm sand</td>
<td>2690</td>
<td>0.9</td>
</tr>
<tr>
<td>4-10 mm basalt</td>
<td>2790</td>
<td>1.4</td>
</tr>
<tr>
<td>10-20 mm basalt</td>
<td>2751</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Laboratory reagent grade nitric acid (≥65% HNO₃) was used to prepare the 0.52 mol/L acid solution by mixing with distilled water. For the freeze-thaw tests a 3% w/w NaCl solution was prepared by mixing with distilled water.

2.2 Mix proportions

The concrete mix proportions used in this study are presented in Table 3. Five alkali-activated concretes (F100Ac, F100Bc, F80c, F60c, F30c) and one Portland cement concrete (PCc) were studied. F100Bc was considered suitable for low strength applications with a design strength less than 20 MPa. F100Ac
and F80c were considered suitable for medium strength applications with a design strength between 35 and 50 MPa. The mixes with increased slag content (F60c and F30c) and PCc were considered suitable for applications where strength greater than 55 MPa was required. The alkali-activated concrete mixes are based on mix design optimisation carried out by Rafeet et al. [22,74–76] and Vinai et al. [77] and the Portland cement mix proportions were obtained from work carried out by Kwasny et al. [78–80].

Alkali dosage (M+) and alkali modulus (AM) were the parameters used to determine the quantities of each activating solution used in each mix. M+ is the ratio of the Na₂O and the dry powder component of the binder, expressed as a percentage, whilst AM is the mass ratio of Na₂O to SiO₂ in the activating solutions. The absorption water listed in Table 3 represents the amount of water needed to bring the aggregates to saturated surface dry conditions. The total added water includes the absorption water but does not include the water within the activating solutions. The water to solids ratio was calculated by dividing mass of the mixing water (i.e. mass of water in the activating solutions, mass of total added water reduced by mass of absorption water) and mass of the solid portion of the binder (i.e. mass of the powders used in the binder and mass of solids in the activating solutions). F100A has increased alkaline activator dosages (M+ of 11.5) compared with each of the other alkali-activated mixes which have the same dosages (M+ of 7.5). Therefore, F100B, F80, F60 and F30 can be compared to study the effect of fly ash/slag content as they all have the same activator dosages. PC is used as a reference for comparison with each of the alkali-activated mixes. Acid resistance was studied on equivalent mortar (physical tests) and paste (microstructural tests) samples. The composition of the paste was identical for each paste mortar and concrete mixes. The paste content of all the concrete mixes was fixed at 32.5%. The mortar mixes were prepared with 50% volume of paste and 50% volume of sand. Concrete mixes are labelled ‘c’, mortar mixes are labelled ‘m’ and paste mixes are labelled ‘p’.

<table>
<thead>
<tr>
<th>Table 3 Mix proportions for alkali-activated and Portland cement concretes.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mix composition</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Fly ash (%)</td>
</tr>
<tr>
<td>Slag (%)</td>
</tr>
<tr>
<td>Portland cement (%)</td>
</tr>
<tr>
<td>Paste content (%)</td>
</tr>
<tr>
<td>Water/solid ratio</td>
</tr>
<tr>
<td>Water/cement ratio</td>
</tr>
<tr>
<td>Alkali dosage (M+)</td>
</tr>
<tr>
<td>Alkali modulus (AM)</td>
</tr>
<tr>
<td>Fly ash (kg/m³)</td>
</tr>
<tr>
<td>Slag (kg/m³)</td>
</tr>
<tr>
<td>Portland cement (kg/m³)</td>
</tr>
<tr>
<td>Sodium silicate solution (kg/m³)</td>
</tr>
<tr>
<td>Sodium hydroxide solution (kg/m³)</td>
</tr>
<tr>
<td>Absorption water (kg/m³)</td>
</tr>
<tr>
<td>Total added water (kg/m³)</td>
</tr>
<tr>
<td>Sand (kg/m³)</td>
</tr>
<tr>
<td>Basalt 4-10 (kg/m³)</td>
</tr>
<tr>
<td>Basalt 10-20 (kg/m³)</td>
</tr>
</tbody>
</table>
2.3 Procedure for mix preparation, samples manufacturing and curing

Concrete specimens were produced using a Croker RP50XD rotating pan mixer. Mortar and paste specimens were produced with a Hobart rotating paddle mixer. The mix procedure summarised in Fig. 1 and is described below:

1. The aggregates were placed into the mixing drum (concretes) or bowl (mortars) along with approximately half of the total water. Aggregates and water were mixed together for 1 minute and then were allowed to absorb moisture for a further 30 minutes (concretes) or 15 minutes (mortars).
2. The appropriate powder binder component of each mix was then added and mixed together with the aggregate for 1 minute.
3. The remaining water and activating solutions (alkali-activated mixes only) were then added and mixing continued for 5 minutes before casting.

The mixes were cast into moulds in two layers and compacted using a vibrating table. They were wrapped in polyethylene film to avoid rapid moisture loss and placed in the appropriate curing conditions. The samples were demoulded after 24 hours and immediately returned to the appropriate curing environment (described below). These curing regimes were established as part of previous research on mix optimisation by the Geopolymer Team at Queen’s University Belfast. Two main curing regimes were employed depending on binder type:

- The 100% fly ash mixes (F100A and F100B) were oven cured at 70 °C for 7 days then placed in constant room conditions (20 ± 2 °C and 55 ± 5% humidity) until testing.
- The fly ash/ slag mixes (F80, F60 and F30) and Portland cement mixes were cured at 20 ± 2 °C and a relative humidity of greater than 90% until testing. 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 [81].
2.4 Testing procedures

A summary of tested properties and details related to samples and testing procedures used are provided in Table 4.

The volume of permeable voids (VPV) was assessed according to the standard procedure given in ASTM C642 [82]. The standard procedure recommends an oven drying temperature of between 100 and 110 °C. In this study, a temperature of 40 °C was employed to avoid excessive drying which can cause changes to binding phases within alkali-activated concrete [83].

The compressive strength of concrete mixes was obtained from 100 mm cubes after 1, 7 and 28 days of curing. A constant load rate of 200 kN/min was applied and the average was calculated from three samples.

Concrete splitting tensile strength at 7- and 28-day was tested according to BS EN 12390-6:2009 [84]. Three cylinders, 100 mm in diameter and 200 mm in height, were tested at each testing age.

Concrete flexural strength was tested at the age of 28 days using three concrete beams (100×100×500 mm) following the two-point loading method specified in BS EN 12390-5:2009 [85].

The tensile strength was determined with the pull-off test, according to BS 1881-207:1992 [86]. For each concrete mix, three 230×230×100 mm slabs were cast. After 14 days of curing, partial coring was taken (to a depth of approximately 40 mm) at two locations at the mould-finished surface of each slab. Then, slabs were returned to their designated curing conditions. At 21-day slabs were moved to a conditioning room and were stored there at 20 ±1 °C and RH of 55 ±10% in order to remove the surface moisture. One day before testing, four 50 mm in diameter metal discs were fixed to the mould-finished surface (two to uncored surface and two to the partially cored surface) using an epoxy resin adhesive.
At 28-day the pull-off apparatus (called Limpet [87]) was attached to the disc and a load was applied at a steady rate of approximately 2.4 kN/min, until the failure occurred (via the disc coming off the concrete sample). The tensile strength was calculated by dividing the failure load by the adhered surface area of the disc. An average of six measurements is reported as the pull-off surface tensile strength (in MPa) for discs attached to both uncored and partially cored surface.

Modulus of elasticity was determined according to BS 1881-121:1983 [88] using three cylinders (100 mm in diameter and 200 mm in height). Fourteen days prior testing, the cylinders’ trowel-finished ends were capped with a thin layer of a fine mortar, in order to create two parallel test planes. On the subsequent day the cylinders were returned to the designated curing conditions. At the age of 28 days three concrete cylinders were tested. The average static secant modulus of elasticity is reported.

To determine the drying shrinkage of concrete, the length change of specimens was measured following ASTM C490-08 [89]. For each concrete mix, three prisms were cast. Between the 3rd and the 5th day after casting, a steel ball was attached to the centre of each end of the prisms, using geopolymer or cement paste. The length of the prisms was measured initially at 7-day after casting and subsequently at convenient dates, i.e. 8, 10, 14, 21, 28, 35, 70, 140, 210, 280 and 364-day after casting (±2% accuracy). After the initial reading was taken, the prisms were placed in a conditioning room, maintained at RH 55 ±5% and 20 ±1 °C, on racks ensuring exposure of all surfaces to this environment. The drying shrinkage for each measurement, expressed in microstrain, was calculated for the nominal gauge length of 250 mm. The change of length was reported as drying shrinkage (average of three measurements). In addition, at each measurement age, the masses of the prisms were recorded to calculate a relative mass change due to the loss of evaporable water.

The chloride migration coefficient was determined by carrying out the chloride migration test based on the NT Build 492 [33] test method. This test was carried out on disk samples (50 mm thick and 100 mm in diameter) which were cored from concrete slabs and then cut to size. The test involved subjecting three samples from each mix to an electrical potential to facilitate the transfer of chloride ions through the concrete. The concrete disc was positioned between two cells containing testing solutions, on one side a 10% NaCl catholyte solution and on the other a 0.3 M NaOH anolyte solution. Cathode (stainless steel) and anode (mild steel) perforated plates were positioned inside the cells on either side of the sample. A sample was pressed into a silicone sleeve (to ensure no leakage during the test) and the two cells were tightened together with bolts. Immediately after the cells were filled with adequate solutions, an initial electrical potential of 30 V was applied between the electrodes. Initial current was measured and, based on recommendations given in the standard, it was used to estimate electrical potential and duration of the test. When the test was completed (between 6 and 96 hours depending on test conditions), the samples were removed from the apparatus and split. Silver nitrate solution (0.1 M AgNO₃) was then
applied to the freshly split sample to obtain the chloride penetration depth. The presence of chloride is identified by a white/silver precipitate formed due to a chemical reaction between chloride and silver nitrate. The chloride penetration depths were more difficult to identify for the alkali-activated concretes than for the Portland cement concrete. A total of 7 readings were collected at 10 mm intervals from 20 to 80 mm along the 100 mm length of each split specimen. Additional information was also collected before and after the test procedure, including sample dimensions, the anolyte and catholyte temperature. These were used alongside the average chloride penetration depth to calculate the chloride migration coefficient according to Eq. 1.

\[
D_{\text{NSSM}} = \frac{0.0239(273 + T)L}{(U - 2)t} \left( x_d - 0.0238 \sqrt{\frac{(273 + T)Lx_d}{U - 2}} \right)
\]

where:

- \(D_{\text{NSSM}}\) = non-steady-state migration coefficient \((\times 10^{-12} \text{ m}^2/\text{s})\)
- \(T\) = average value of the initial and final temperatures in anolyte solution (°C)
- \(L\) = specimen thickness (mm)
- \(U\) = applied voltage (V)
- \(t\) = test duration (hour)
- \(x_d\) = average value of penetration depths (mm)

The electrical resistivity was obtained for each concrete mix before and after the chloride migration test according to the two probe method. The sample was placed between two conductive plates and moist sponges were used as contact media. A current was applied between the two plates and the potential was measured. The equipment used was a Tinsley prism instrument - 6451 LCR Databridge.

The corrosion of steel reinforcement was investigated by casting steel bars inside concrete slabs and ponding the slabs with NaCl solution. Six slabs were cast for each mix. The slabs were cast with a 15 mm rim around the outside of the ponding surface to contain the NaCl solution as shown in Fig. 2. Three 16 mm diameter carbon steel bars were cast inside each slab at depths of 15, 25 and 40 mm from the ponding surface. Three slabs were cast for each mix and the position of the bars inside the slabs were altered for each slab i.e. the bar cast at a depth of 15 mm was on the left, middle and right in one of each of the three slabs. The layout of the steel bars is shown in Fig. 3. Prior to placement inside the concrete and casting of concrete, the steel bars were cleaned with a wire brush and the mass of each bar was recorded. The slabs were stored at room conditions (20 ± 2 °C and 55 ± 5% humidity) and ponded with 3% NaCl solution every 7 days. After 24 hours, the remaining ponded solution was removed with a sponge. Therefore, the samples experienced wetting (1 day) and drying (6 days) cycles. This procedure was continued for a duration of 1 year (52 ponding cycles). After 6 months (26 cycles) and 1 year (52
cycles) the steel bars were extracted from three slabs and inspected visually for signs of corrosion. Subsequently, the steel bars were cleaned with a wire brush and their mass was recorded. The results were reported as percentage mass losses of steel bars from the initial mass after 26 and 52 ponding cycles. The average depth of chloride penetration into each concrete slab was measured by applying AgNO\(_3\) solution onto the split surface and measuring the depth of penetration from the ponding surface. A portion of each concrete slab from just below the ponding surface was taken for X-ray diffraction (XRD) analysis to determine if any chloride binding salts were formed.

Fig. 2. Photograph of concrete slab for ponding test.
Cross section A-A

Slab with bars at location A
- Ponding mould-finished surface
- Reinforcing bar Ø16x170 mm
- 3 coats of epoxy resin
- Concrete slab 100x230x230 mm

Slab with bars at location B

Slab with bars at location C

Top view

Side view

Fig. 3. Layout of steel reinforcement embedded inside three concrete slabs.
The freeze-thaw resistance of the concrete mixes was determined by performing a scaling test similar to DD CEN/TS 12390-9:2006 [90]. The test was carried out on 100 mm thick cores with a diameter of 100 mm obtained from concrete slabs and the test setup is shown in Fig. 4. The lateral surface of the cores were coated with epoxy resin to ensure scaling only took place on the test surface. A rubber seal was also placed on the top surface to avoid any moisture build up and deterioration. Three samples were tested for each mix and two different freeze-thaw mediums were used (water and 3% NaCl solution). After 21 days of curing the samples were placed on 10 mm supports inside the polyethylene containers along with the appropriate freeze-thaw medium at 20 ± 2 °C. The container was filled to a depth of 15 mm with the appropriate freeze-thaw medium. This allowed saturation of the samples with the freeze-thaw medium before freeze-thaw cycles began. After 7 days, the freeze-thaw medium was replaced and the 24 hour freeze-thaw cycles were started according to the limits displayed in Fig. 5. After 7 cycles the scaled material was collected by filtration, oven dried and its mass recorded. The freeze-thaw medium was replaced and the samples were returned to the freeze-thaw chamber immediately. This process was repeated after every 7 cycles until 56 cycles or until the samples had lost more than 25% of their original mass by scaling.

Fig. 4. Freeze-thaw experimental setup.
Acid resistance was tested based on the general guidelines provided in ASTM C267 [91] and exactly the same procedure as previous studies [70–72]. To summarise, acid resistance was studied by immersing four 50 mm mortar cubes into a 0.52 mol/L solution of nitric acid for 8 weeks. The mass was recorded and the acid solution replenished each week. After 8 weeks of acid exposure, the compressive strength of three of the exposed samples was obtained for comparison with control samples stored in water. The fourth cube was used to assess the apparent depth of acid penetration. It was split and sprayed with phenolphthalein solution to highlight the pH distribution. XRD and SEM were used to assess the effect of nitric acid exposure on 50 mm paste cubes exposed to the sample cyclic exposure regime for 3 weeks.

Fig. 5. Upper and lower limit of temperature at the test surface during freeze-thaw cycles.
<table>
<thead>
<tr>
<th>Property type</th>
<th>Tested property</th>
<th>Sample details</th>
<th>Testing procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td>VPV</td>
<td>100 mm long and 75 mm diameter cylinders taken from 100 mm concrete cubes (six samples for each mix)</td>
<td>Testing procedure according to ASTM C642 [82]. Three samples were tested at the age of 28 and 180 days.</td>
</tr>
<tr>
<td></td>
<td>Compressive strength</td>
<td>100 mm concrete cubes (nine samples for each mix)</td>
<td>Three samples were tested at the age of 1, 7 and 28 days.</td>
</tr>
<tr>
<td></td>
<td>Tensile strength</td>
<td>200 mm long and 100 mm diameter concrete cylinders (three samples for each mix)</td>
<td>Test procedure according to BS EN 12390-6:2009 [84]. Three samples were tested at the age of 7 and 28 days.</td>
</tr>
<tr>
<td></td>
<td>Flexural strength</td>
<td>100 x 100 x 500 mm concrete beams (three samples for each mix)</td>
<td>Test procedure according to BS EN 12390-5:2009 [85]. Three samples were tested at the age of 28 days.</td>
</tr>
<tr>
<td></td>
<td>Tensile pull off strength</td>
<td>230 x 230 x 100 mm concrete slabs (three slabs for each mix)</td>
<td>Test procedure according to BS 1881-207:1992 [86]. At the age of 28 days two cored and two uncored measurements were taken for each slab.</td>
</tr>
<tr>
<td></td>
<td>Modulus of elasticity</td>
<td>200 mm long and 100 mm diameter cylinders (three samples for each mix)</td>
<td>Test procedure according to BS 1881-121:1983 [88]. Three samples were tested at the age of 28 days.</td>
</tr>
<tr>
<td></td>
<td>Drying shrinkage</td>
<td>250 x 75 x 75 mm concrete prisms (three samples for each mix)</td>
<td>Test procedure according to ASTM C490-08 [89]. Initial measurement taken at 7 days after casting and subsequently measurements up to the age of one year.</td>
</tr>
<tr>
<td>Chloride</td>
<td>Electrical resistivity</td>
<td>50 mm long and 100 mm diameter discs taken from concrete slabs (three samples for each mix)</td>
<td>Three samples were tested at the age of 28 days.</td>
</tr>
<tr>
<td>migration</td>
<td>Chloride migration coefficient</td>
<td>50 mm long and 100 mm diameter discs taken from concrete slabs (three samples for each mix)</td>
<td>Test procedure according to NT Build 492 [33]. Three samples were tested at the age of 28 days.</td>
</tr>
</tbody>
</table>

Table 4 Summary of tested properties and sample details
<table>
<thead>
<tr>
<th>Corrosion of steel reinforcement</th>
<th>Mass loss of steel bars</th>
<th>Steel bars embedded in concrete slabs at depths of 15, 25 and 40 mm (six slabs for each mix)</th>
<th>Slabs were weekly ponded with a 3% NaCl solution for a duration of 12 months. Bars were extracted for mass loss measurements from a set of three slabs after 6 months of ponding and then at one year from the remaining three slabs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride penetration depth</td>
<td>Concrete slabs used for ponding test</td>
<td>AgNO$_3$ solution sprayed on cross-section of concrete slabs following ponding test</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>Powdered samples obtained from below the ponding surface of concrete slabs</td>
<td>Samples collected following 6 months of ponding</td>
<td></td>
</tr>
<tr>
<td>Freeze-thaw resistance</td>
<td>Visual appearance</td>
<td>100 mm long and 100 mm diameter cores taken from concrete slabs</td>
<td>Three samples were assessed after every 7 freeze-thaw cycles up to 56 cycles</td>
</tr>
<tr>
<td></td>
<td>Scaled mass</td>
<td>100 mm long and 100 mm diameter cores taken from concrete slabs (three samples for each mix)</td>
<td>Three samples were assessed after every 7 freeze-thaw cycles up to 56 cycles</td>
</tr>
<tr>
<td>Acid resistance</td>
<td>Strength loss</td>
<td>50 mm mortar cubes</td>
<td>Three samples were assessed after 8 weeks exposure to a 0.52 mol/L solution of nitric acid</td>
</tr>
<tr>
<td></td>
<td>Mass loss</td>
<td>50 mm mortar cubes</td>
<td>Four samples were monitored each week for 8 weeks during exposure to nitric acid</td>
</tr>
<tr>
<td></td>
<td>XRD and SEM</td>
<td>50 mm paste cubes</td>
<td>For XRD, samples were collected from the edges of paste samples exposed to acid. For SEM, samples perpendicular to the exposed face were obtained and polished prior to analysis. Pastes samples were exposed to a 0.52 mol/L solution of nitric acid for 3 weeks.</td>
</tr>
</tbody>
</table>
3. Results

3.1 Physical properties

Fig. 6 shows the VPV for each concrete mix after 28 and 180 days of curing. The error bars represent the standard deviation calculated from three specimens. The largest VPV values were observed for the 100% fly ash mixes which decreased as the slag content increased. This suggests a less porous microstructure as the slag content increased. This is due to the formation of space filling C-A-S-H and C-N-A-S-H gels compared with the more porous N-A-S-H gels formed in 100% fly ash mixes [22,92–94]. The Portland cement concrete had a similar VPV as that of the blend of 30% fly ash and 70% slag. After 180 days the VPV value decreases for each mix. This reduction is more pronounced for the mixes with increased slag content and is likely due to continual development of their microstructure, whereas limited further reactions take place in the 100% fly ash mixes after curing was complete.

Fig. 6. VPV for each concrete mix after 28 and 180 days of curing.

Fig. 7 shows the compressive strength of each concrete mix after 1, 7 and 28 days of curing. The error bars represent the standard deviation calculated from three specimens. The 100% fly ash mixes attain more than 50% of their 28 day strength within the first 24 hours. This is likely due to the high temperature curing employed. F100Ac had a 28 day strength of 48.5 MPa compared with 16.0 MPa for F100Bc which was due to the significantly higher alkaline activator content used in F100Ac. The 100% fly ash mixes displayed their maximum compressive strength after 7 days of curing. It could be related to their removal from high temperature curing after 7 days meaning no further reactions took place beyond 7 days. The slight reduction in compressive strength could be due internal stresses as a result of thermal shock or moisture re-entering the pore structure which had been removed during curing [95–
As content of slag increased the compressive strength also improved to 64.0 MPa after 28 days for F30c. The compressive strength of PCc was 62.5 MPa after 28 days which was similar to that of F60c and F30c.

![Compressive strength of each concrete mix after 1, 7 and 28 days of curing.](image)

**Fig. 7.** Compressive strength of each concrete mix after 1, 7 and 28 days of curing.

Table 5 shows the tensile strength, flexural strength, pull off strength and modulus of elasticity of each concrete mix. The standard deviation calculated from three specimens is shown in brackets. The trends observed are similar to those observed for compressive strength. The strength values increased as the slag content increased. Interestingly, the 100% fly ash mix with the increased activator dosages performed very well in the tensile and pull off tests. This suggests the increased activator dosages provided an increased bond of aggregate and binder and could be due to the greater viscosity of the mixture.
### Table 5: Tensile strength, flexural strength, pull off strength and modulus of elasticity of each mix.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Tensile strength (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Pull off strength (MPa)</th>
<th>Modulus of elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 days</td>
<td>28 days</td>
<td>28 days</td>
<td>28 days - surface</td>
</tr>
<tr>
<td>F100A</td>
<td>3.7 (0.6)</td>
<td>3.0 (0.1)</td>
<td>3.5 (0.3)</td>
<td>4.7 (0.6)</td>
</tr>
<tr>
<td>F100B</td>
<td>1.2 (0.0)</td>
<td>1.0 (0.1)</td>
<td>1.2 (0.1)</td>
<td>2.0 (0.2)</td>
</tr>
<tr>
<td>F80c</td>
<td>1.8 (0.3)</td>
<td>2.8 (0.2)</td>
<td>2.4 (0.1)</td>
<td>2.2 (0.2)</td>
</tr>
<tr>
<td>F60c</td>
<td>2.8 (0.7)</td>
<td>3.8 (1.0)</td>
<td>3.37 (0.1)</td>
<td>2.9 (0.3)</td>
</tr>
<tr>
<td>F30c</td>
<td>3.5 (0.4)</td>
<td>3.3 (0.6)</td>
<td>3.4 (0.2)</td>
<td>2.8 (0.4)</td>
</tr>
<tr>
<td>PCc</td>
<td>3.2 (0.1)</td>
<td>3.7 (0.4)</td>
<td>4.5 (0.5)</td>
<td>3.9 (0.5)</td>
</tr>
</tbody>
</table>
Fig. 8 shows the drying shrinkage or length change of each concrete mix over a one year period. The error bars represent the standard deviation calculated from three specimens. The 100% fly ash mixes underwent expansion rather than shrinkage. The expansion was likely due to the high temperature curing causing moisture to be removed during the curing period. As moisture re-entered the pore structure, expansion took place. It generally stabilised by 50 days for both mixes with less pronounced expansion observed for the mix with increased activator dosages. This could be due to a combination of its increased mechanical properties and decreased VPV. The shrinkage of the blended fly ash/slag concrete mixes decreased as the content of slag increased. This may be related to the increased mechanical properties. The drying shrinkage for PCc was similar to that of the alkali-activated mix with 30% slag and 70% fly ash (F30c).

![Graph showing drying shrinkage or length change of each concrete mix over one year period.]

**Fig. 8.** Drying shrinkage or length change of each concrete mix over one year period.

### 3.2 Durability

#### 3.2.1 Resistance to chloride migration

Electrical resistivity is an indirect measurement of the transport properties of concrete and as corrosion is an electrochemical phenomenon it has a bearing on the corrosion rate of steel [98,99]. Table 6 shows the electrical resistivity and chloride migration coefficient for each mix. The standard deviation obtained from three specimens is shown in brackets.
The resistance of each concrete mix to chloride migration was investigated using the accelerated NT Build 492 procedure [33]. The cross-section of one sample from each mix at the end of the chloride migration test is shown in Fig. 9. In the case of the 100% fly ash mixes, the depth of the entire cross-section (50 mm) appeared silver in colour suggesting the entire section was penetrated by NaCl. Therefore, it was not possible to calculate the chloride migration coefficient for these mixes as the exact penetration depth was unknown. However, we can conclude that the resistance of the 100% fly ash mixes to chloride penetration is much lower than each of the other mixes studied. If a penetration depth of 50 mm is assumed for F100Ac and F100Bc, the chloride migration coefficient would be 78.3 and $83.4 \times 10^{-12}$ m$^2$/s, respectively. These values are significantly larger than those observed for each of the other mixes. The NT Build 492 test procedure is designed with the aim of ensuring that the front of chloride penetration is between 0 and 50 mm at the end of the test so that a penetration depth can be measured. This may not have worked for the fly ash concretes as the test was originally designed for the testing of Portland cement-based materials. Furthermore, the VPV of the fly ash concretes was larger than any of the other mixes (Fig. 6). Zhu et al. [100] also reported that alkali-activated mixes with high fly ash content were vulnerable to chloride penetration.

As the content of slag increased the chloride migration coefficient decreased to 46.3, 7.1 and $3.9 \times 10^{-12}$ m$^2$/s for F80c, F60c and F30c, respectively (Table 6). The chloride migration coefficient for the PC concrete was $11.1 \times 10^{-12}$ m$^2$/s suggesting it has much better resistance to chloride penetration than F100Ac, F100Bc and F80c but slightly lower resistance to chloride penetration than F60c and F30c. The electrical resistivity results indicate a similar trend with a higher resistivity obtained for the mixes with increased slag content. These findings show good correlation with the VPV for each mix. The VPV decreased with increased slag content. Similarly, the resistivity increased, and chloride migration coefficient decreased as the slag content increased. This indicates that mixes with increased slag content have a greater resistance to chloride penetration due to their reduced volume of voids and increased resistivity. This is likely due to the more dense calcium aluminium silicate hydrate gel present in mixes with increased slag content compared with the more porous sodium aluminium silicate hydrate gel present in fly ash dominant mixes [22,70,93].

<table>
<thead>
<tr>
<th>Mix</th>
<th>Resistivity – 28 days (Ωm)</th>
<th>Chloride migration coefficient ($D_{nssm}$) ($\times 10^{-12}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F100Ac</td>
<td>18.0 (0.7)</td>
<td>&gt;78.3 (1.3)</td>
</tr>
<tr>
<td>F100Bc</td>
<td>13.3 (1.0)</td>
<td>&gt;83.4 (2.5)</td>
</tr>
<tr>
<td>F80c</td>
<td>17.0 (0.1)</td>
<td>46.3 (4.2)</td>
</tr>
<tr>
<td>F60c</td>
<td>69.0 (5.9)</td>
<td>7.1 (0.1)</td>
</tr>
<tr>
<td>F30c</td>
<td>171.9 (6.1)</td>
<td>3.9 (0.3)</td>
</tr>
<tr>
<td>PCc</td>
<td>85.7 (2.1)</td>
<td>11.1 (0.8)</td>
</tr>
</tbody>
</table>
3.2.2 Corrosion of steel reinforcement

Fig. 10 shows photographs of the surface of each concrete mix after 6 months and 1 year of ponding with NaCl solution. The 100% fly ash mixes appear to have suffered some damage to the surface via scaling of paste and exposure of aggregates. A white coloured deposit on the surface is also visible and likely to be recrystallization of NaCl. The exposed surface of the blends of fly ash and slag concrete appear unaffected by ponding of NaCl solution after 6 months of ponding. After 1 year of ponding cracks have emerged on the ponding surface of F60c and F30c at the location of the steel reinforcement with 15 mm cover. The Portland cement concrete appears relatively unaffected by the ponding cycles.
Following 6 months of NaCl ponding, the slabs were split and the depth of chloride penetration was measured by applying AgNO₃ solution to the cross-section of each mix. Fig. 11 shows a photograph of the cross-section of each mix following the application of AgNO₃. The chloride ingress starts from the top of each sample and the front of chloride penetration is marked by a dashed red line. The average measured depth of chloride penetration is also shown. The chloride solution penetrated through the entire cross-section of F100Ac and F100Bc. This is similar to the chloride migration test where these samples were also fully penetrated. This is likely due to the large VPV (Fig. 6) and a well-connected pore network allowing rapid ingress of chloride ions. As the content of slag rose, the average chloride
penetration depth decreased to 65, 20 and 9 mm for F80c, F60c and F30c, respectively. The average chloride penetration depth for PCc was 5 mm, similar to that of F30c. This is similar to the VPV results which also decreased as the slag content increased and PCc also had a similar value as that of F30c (Fig. 5). This suggests that the chloride penetration depth is related to the VPV and pore network. It is worth noting that the chloride penetration depth measured is the average from a number of points. Therefore, the maximum chloride penetration depth would be larger [31].

![Fig. 11. Photograph of the cross-section of each mix following the application of AgNO3.](image)

The steel bars were removed from the slabs and inspected following 6 months and 1 year of ponding with NaCl solution. They are shown in Fig. 12. The steel bars from F30c and PCc had very little visible corrosion. Conversely, the steel bars from the other mixes had areas of brown/orange coloured corrosion. This known as pitting corrosion and is caused by a breakdown of the protective oxide film on steel reinforcement allowing chloride ions to attack [101]. Some of the bars also had grey coloured paste attached. The paste and corrosion product were removed carefully using a wire brush before measuring the mass of each bar. This cleaning process was also applied to the steel bars before placement inside the concrete to ensure the cleaning procedure caused no additional mass loss [102].
Fig. 12. Steel bars extracted from concrete slabs (before cleaning) following 6 months and 1 year of ponding with NaCl solution.
Fig. 13 shows the mass loss of steel bars embedded in each concrete mix at depths of 15, 25 and 40 mm after 6 months and 1 year of NaCl ponding on the concrete surface. The mass losses shown are averaged from three bars embedded in three different slabs at each depth. It is worth noting that the mass losses observed are relatively small (<0.6%) after 6 months. Angst et al. [26] suggested that ideally a significant amount of corrosion should have taken place in such tests if the mass difference is to be detected. After 1 year a significant increase in the mass loss of the steel bars was observed. For each mix the mass loss decreases as the depth of concrete cover increases except for PCc as no mass loss was observed at any depth. The other exception is F100Bc after 1 year which is perhaps because the slab was fully penetrated at all depths for a significant period of time allowing as much or more corrosion to occur at depths of 25 and 40 mm. As the slag content increased the mass loss of the steel bars generally decreased. Particularly for the steel bars with 25 and 40 mm of concrete cover. On the other hand, after 1 year the bars in the 100% fly ash mixes were all significantly corroded regardless of the depth of concrete cover. The corrosion of the steel bars values are in agreement with the chloride penetration depths shown in Fig. 11. The mixes which result in the largest steel bar mass losses (F100Ac, F100Bc and F80c) at depths of 25 and 40 mm allowed chloride to penetrate the furthest after 6 months (Fig. 11). On the other hand, the steel bars embedded in F60c and F30c at 25 and 40 mm had much smaller mass losses. PCc had superior performance than any of the alkali-activated concrete mixes. The steel bars suffered no mass losses even with cover of only 15 mm.
Fig. 13. Mass loss of steel bars embedded in each concrete mix after a) 6 months and b) 1 year of NaCl ponding on the concrete surface.

According to several authors [103–105], the use of fly ash and slag as supplementary materials significantly improves the chloride binding capacity of Portland cement based concretes. This is due to the increased aluminium content in both slag and fly ash, particularly fly ash. However, in Portland cement materials there is ample supply of calcium which is also needed to form chloride binding salts such as Friedel’s salt. There is less calcium available in the alkali-activated concrete mixes. Fig. 14 shows the XRD patterns of each concrete following the ponding test. The samples were collected from directly below the ponding surface. The majority of the phases present were due to aggregate particles. They are clinochlore, muscovite, albite and quartz. Ettringite and calcium hydroxide were also identified.
in PCc but the peaks are small because the patterns are dominated by the peaks from aggregate particles. The only phases observed that can be related to chloride penetration are Friedel’s salt in PCc and halite (NaCl) in PCc. The binding of chlorides due to the formation of Friedel’s salt likely slows down the rate of chloride penetration and explains why PCc performed much better in the steel corrosion ponding test, than the chloride migration test. The chloride migration test described in the NT Built 492 is accelerated over 24 hours so the ability of the concrete to bind chlorides would be largely negated. On the other hand, during the ponding test the binding of chlorides by Friedel’s salt in PCc would have meant less chloride was available to penetrate the concrete and initiate corrosion. In F100Bc, halite was observed which is a NaCl mineral. This suggests that sodium chloride recrystallized in the pores of the sample. This could be due to suitable sodium concentrations available in the pore solution. Halite was also observed by Ismail et al. [31] in 100% fly ash mixes following chloride ponding. Monticelli et al. [106] also reported that chloride binding in fly ash mixes took place via sodium chloride salts instead of Friedel’s salt. There were no chloride binding minerals found in the fly ash/slag mixes (F80c, F60c and F30c) suggesting their ability to protect steel reinforcement is purely dependent on their porosity and pore connectivity.
3.3.3 Freeze-thaw resistance

Fig. 15 shows the visual appearance of each concrete mix following exposure to 56 freeze-thaw cycles in the presence of water and 7 freeze-thaw cycles in the presence of 3% NaCl solution. The presence of NaCl resulted in a higher level of deterioration for each mix than water. All of the alkali-activated concrete mixes have experienced the loss of cement paste and the exposure of aggregates. Most significantly damaged are the mixes with 100% fly ash. The damage to the 100% fly ash mixes, particularly FA100Bc, was so severe that the test surface was very uneven following exposure cycles. As the content of slag increased the damage to the surface decreased significantly and the test surface remained relatively flat so that it was in contact with the freeze-thaw medium. However, the damage was still much greater for the alkali-activated concretes compared with the damage observed for PCc.
Fig. 15. Visual appearance of each concrete mix following exposure to 56 freeze-thaw cycles (water) and 7 freeze-thaw cycles (NaCl).

Fig. 16 shows the cumulative scaled mass percentage of concrete mixes during exposure to 56 freeze-thaw cycles in the presence of water and NaCl. The error bars represent the standard deviation calculated from three specimens. In the presence of water F100Bc was significantly damaged after 21 cycles with a scaled mass of 28.2% observed. Each of the other mixes remained intact for the entire 56 cycles in the presence of water. F100Ac had a final scaled mass of 3.2% followed by F80c, F60c and F30c which had final scaled mass values of 0.6, 0.3 and 0.1% respectively. PCc displayed good resistance as no scaled mass loss was observed after 56 freeze-thaw cycles. The presence of NaCl resulted in larger scaled mass values for each mix compared with water. This has been reported for many years in the case of Portland cement concrete [40] and also applies to the alkali-activated concretes investigated in this study. F100Bc suffered significant damage after 14 cycles, while F100Ac and F80c had scaled mass values of greater than 25% after 21 cycles so testing was stopped. F60c, F30c and PCc had scaled mass values of 7.3, 2.6 and 0.2%, respectively, after 56 cycles. Therefore, resistance to freeze-thaw was significantly increased as the slag content increased. This is likely related to the decrease in VPV (Fig. 6) and increase in tensile strength (Table 5) as the slag content increased. It is worth noting that air entrainment was not used in
this study. The effectiveness of air entrainment to improve the freeze-thaw resistance of alkali-activated concrete should be considered in future investigations.

**Fig. 16.** Cumulative scaled mass (%) of mixes during freeze-thaw cycles in the presence of a) water and b) 3% NaCl solution.
3.3.4 Acid resistance

Fig. 17 shows the strength loss for each mortar mix following exposure to a 0.52 mol/L solution of nitric acid for 8 weeks. The compressive strength of unexposed samples is also shown for comparison and the percentage strength loss is also noted above each bar. The error bars represent the standard deviation calculated from three specimens. The mixes with 100% fly ash (F100Am and F100Bm) and 80% fly ash (F80m) suffered the largest percentage compressive strength losses of approximately 60%. As the slag content increased the percentage strength loss decreased to 37% for F30m. A similar percentage strength loss of 41% was observed for PCm.

Fig. 18 shows a photograph of the cross-section of each mortar mix following exposure to a 0.52 mol/L solution of nitric acid for 8 weeks. Phenolphthalein solution has been applied to the cross-section of each sample to obtain an indication of the pH throughout the cross-section of each sample and possible depth of acid penetration. Unexposed samples are also shown for comparison. The mixes with the largest VPV (Fig. 5) appear to have suffered the largest pH change throughout their cross-section (F100Am, F100Bm and F80m). These mixes also suffered the largest strength losses which is likely caused by their larger VPV permitting a greater depth of acid penetration.

![Fig. 17. Compressive strength loss of each mortar mix following exposure to nitric acid for 8 weeks.](image-url)
Fig. 18. Photograph of the cross-section of each mortar mix following exposure to nitric acid for 8 weeks and application of phenolphthalein solution.

Fig. 19 shows the mass change for each mortar mix during exposure to a 0.52 mol/L solution of nitric acid for 8 weeks. The error bars represent the standard deviation calculated from four specimens. Each mix was found to have undergone a decrease in mass due to nitric acid exposure. Throughout the 100% fly ash mixes displayed lower mass loss than each of their counterparts. Additionally, the mass losses observed were similar regardless of the alkali activator content used. Initially the mixes containing both fly ash and slag lost more mass than the PCm. However, the mass losses for the mixes containing both fly ash and slag appeared to decelerate whereas the mass loss for the PCm appeared to accelerate. As a result, PCm had the largest mass loss of 9.3% after 8 weeks exposure. The mixes containing fly ash and slag had mass losses between 6.3 and 7.4%. The mass loss decreased as the slag content increased. The 100% fly ash mixes had mass losses of only 2.6% after 8 weeks exposure. Fig. 20 shows photographs of each mortar mix after exposure to a 0.52 mol/L solution of nitric acid for 8 weeks. Unexposed samples are shown for comparison. Visual examination highlights that the surface of the 100% fly ash mixes is relatively unchanged following nitric acid exposure. On the other hand, the surface of the mixes containing slag and PCm appears damaged with the loss of paste and exposure of sand particles.
Fig. 19. Mass change of each mortar mix during exposure to nitric acid for 8 weeks.

<table>
<thead>
<tr>
<th></th>
<th>F100Am</th>
<th>F100Bm</th>
<th>F80m</th>
<th>F60m</th>
<th>F30m</th>
<th>PCm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unexposed</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Nitric</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 20. Photograph of each mortar mix following exposure to nitric acid for 8 weeks.

Equivalent paste mixes were also investigated and exposed to 0.52 mol/L of nitric acid for 3 weeks. Fig. 21 shows the XRD patterns of F100Ap, F30p and PCp following exposure to nitric acid. Unexposed samples are also shown for comparison. In F100Ap, quartz, mullite and hematite were identified due to unreacted fly ash particles [107]. Following exposure to nitric acid, very little change was observed; quartz, mullite and hematite remained unaffected. The only change being that the broad hump between 15 and 35° 2θ attributed to silicate and aluminosilicate gels shifted to be centred at a lower angle. Centring of the peak in this region is typically observed for unreacted fly ash and may suggest that some of the reacted aluminosilicate phases have broken down leaving behind unreacted fly ash particles [108–110]. This along with the suggested significant acid penetration would explain the larger strength losses observed for the 100% fly ash mixes. In F30p the main peaks identified in the unexposed sample are quartz, mullite and hematite. The intensities are much lower than for F100Ap due to only 30% fly ash being present in the binder of F30p. A broad peak centred at approximately 29° 2θ was also observed.
and has been attributed to poorly crystalline calcium silicate hydrate type (C-S-H) gels [111–113]. Following nitric acid exposure this peak was no longer present and a broad hump between 15 and 35° 2θ was observed. This is likely due to the decalcification of C-S-H type gel leaving behind silicate and aluminosilicate gels as well as unreacted fly ash particles which are identified by this broad hump [108–110]. In the unexposed PCp sample ettringite and calcium hydroxide were identified. These were not found after exposure to acid, with calcite being identified instead. This suggests the dissolution of ettringite and calcium hydroxide by nitric acid and explains the significant mass losses observed (Fig. 18).

**Fig. 21.** XRD patterns of F100Ap, F30p and PCp following exposure to nitric acid.

Fig. 22 shows SEM images of the outer edge (approximately 2.5 mm) of F100Ap, F30p and PCp following 3 weeks exposure to nitric acid. F100Ap shows little damage to the outer surface, this is in agreement with the mass loss results which showed very little change for the 100% fly ash mixes. The surface of F30p appears to have suffered damage to the edge and the loss of paste which agrees with the mass losses observed (Fig. 19). However, the region inside the outer edge appears unaffected by acid exposure. This may be due to the more dense microstructure observed and may explain the greater strength retention (Fig. 17) following acid exposure. PCp also seems to have suffered damage to the
edge and cement paste appears close to falling off. PCp also had region which appears depleted and more porous than the undamaged area.

Fig. 22. SEM image of the outer edge of F100Ap, F30p and PCp following exposure to nitric acid.
4. Discussion

The paste content of each corresponding concrete, mortar and paste mix used in this study was identical which allowed comparison between performance in different environments. This provided insight into the performance of alkali-activated binders towards more widespread use as a replacement for traditional Portland cement-based binders. The 100% fly ash concretes (F100Ac and F100Bc) displayed poor resistance to chloride migration as the entire cross-section of the samples became penetrated with chloride. Similarly, the slabs with embedded steel were fully penetrated (Fig. 11) after 6 months of ponding cycles. This performance is likely related to the low electrical resistivity and high VPV. As the content of slag increased the electrical resistivity increased and the VPV decreased. This resulted in a decreased chloride migration coefficient with increased slag content. The penetration depth of chloride into the ponding slabs also decreased, as did the corrosion of embedded steel bars. PCc had a slightly larger chloride migration coefficient than F60c and F30c but was more effective at protecting the embedded steel in the slabs which were ponded. This is likely due to the ability of PCc to bind chloride as Friedel’s salt (Fig. 14) which reduced the chloride penetration depth. This highlights the importance of non-accelerated tests in the assessment of chloride binding capacity.

The freeze-thaw resistance of the 100% fly ash concrete was poor with significant scaling and breakdown of the samples observed. The performance of the mix with the increased alkaline activator dosage was slightly better and was probably due to the increased tensile strength and ability to resist stresses created during freezing. As the slag content increased the performance improved significantly and could be due to the reduced VPV allowing less ingress of the freeze-thaw mediums. Previous work by Provis et al. [114] has shown that mixes with less than 25% slag are dominated by sodium aluminium silicate hydrate gels which do not offer a similar level of pore network obstruction as space filling calcium aluminium silicate hydrate gels found in slag dominant binders. The tensile strength also improved as the content of slag increased which may have increased resistance to tensile stresses created during freezing. The Portland cement concrete had much superior freeze-thaw resistance than 100% fly ash concrete and slightly better freeze-thaw resistance than F30c. The good performance for PCc may be due to its lower sorptivity and advanced pore features such as pore connectivity (which require further investigation) compared with alkali-activated concretes [115,116].

Alkali-activated 100% fly ash mortars displayed approximately a 60% reduction in compressive strength following 8 weeks exposure to nitric acid. As the content of slag increased the decline in strength decreased to 37% for F30m. This is closely linked to the apparent depth of acid penetration which also decreased as the slag proportion increased. Despite the lowered strength and degree of apparent penetration, the 100% fly ash mortars displayed very small mass losses and an undamaged outer surface. This is due to the low calcium content of these binders meaning they are more resistant to decalcification than fly ash/slag blends [70]. The mass losses for the fly ash/slag blends was larger than the 100% fly
ash mixes but decreased as the slag content increased. This decrease can be attributed to the more dense and stronger matrix formed allowing less ingress of acid. PCm suffered larger mass losses than any of the alkali-activated mixes. This is due to the breakdown of ettringite and calcium hydroxide, leaving behind a more porous matrix for further acid attack as observed by SEM (Fig. 22). A porous matrix was not observed at the front of acid attack in F30p due to the formation of silicate rich gel slowing the rate of further decalcification and further mass losses.

In relation to the effect of activator dosages on alkali-activated fly ash concrete. The use of increased activator dosages resulted in enhanced mechanical properties for F100Ac compared with F100Bc. This was due to the increased availability of alkalis to react with fly ash and form a hardened matrix. In turn, this resulted in a decreased VPV and some improvement of durability properties. Albeit the improvement in durability performance may not be large enough to justify the increased cost and environmental impact associated with such an increase in the quantities of activators used.

5. Conclusions
The main findings from this study can be summarised as follows:

- As the slag proportion of alkali-activated fly ash/slag blended concretes increased the mechanical properties also increased and the volume of permeable voids decreased.
- Neat fly ash concretes have poor resistance to chloride penetration due to their large volume of permeable voids. Mixes with increased slag content have similar or better resistance to chloride penetration than that of Portland cement concrete. However, the ability of Portland cement concrete to bind chloride means it is more effective at protecting embedded steel from corrosion than alkali-activated mixes.
- The alkali-activated concretes have lower freeze-thaw resistance than Portland cement concrete. As the slag proportion is increased, resistance to surface scaling is also increased. Further work is needed to investigate the effectiveness of air entrainment on the freeze-thaw resistance of alkali-activated concretes.
- The alkali-activated fly ash/slag blends have increased acid resistance compared with Portland cement binders. This is due to their lower calcium content and the formation of silicate rich gel following the decalcification of calcium aluminium silicate hydrate gel which reduced the rate of further acid ingress and subsequent mass losses.

Alkali-activated concrete mixes consisting of 100% fly ash have numerous barriers to their widespread application including the required curing conditions and need for significant activator dosages to achieve high strength properties. This study has shown that their durability is also a problem. They demonstrated inferior performance in relation to chloride migration, protection of steel reinforcement and freeze-thaw
attack. This is mainly attributed to more open structure when compared with other mixes. However, due to their low calcium content, minimal damage and surface scaling was observed following acid attack. However, the pore structure allowed significant apparent acid penetration which caused a considerable reduction in compressive strength compared with other mixes. Alkali-activated fly ash/slag blends displayed increased performance in relation to chloride migration, protection of steel reinforcement and freeze-thaw attack. This is due to the more dense microstructure formed with less voids available for ion transport. The acid resistance of the fly/slag blends also increased as the slag proportion increased with lower strength and mass losses observed. In comparison with the control Portland cement mix, the alkali-activated concrete with increased slag content displayed comparable performance. The acid resistance was similar while the resistance to chloride migration was superior when using the NT Build 492 procedure. The ability to protect embedded steel was inferior due to the lack of chloride binding that was observed for Portland cement concrete. This requires further investigation, as does the freeze-thaw resistance for which the use of air entrainment techniques may be beneficial.

Acknowledgements
The authors are grateful to the School of Natural and Built Environment, Queen’s University Belfast for provided facilities. The research studentship provided by the Department for the Economy (DfE), Northern Ireland is also gratefully acknowledged. The authors would also like to acknowledge an Invest Northern Ireland funded research project (REF. No.:RDO212970) under which some of the work related to the Portland cement concrete mix was carried out. The authors also appreciate the support received and useful discussions had with Prof. Marios Soutsos.

Author contributions

References


[29] N. Ganesan, R. Abraham, S. Deepa Raj, Durability characteristics of steel fibre reinforced


[33] NORDTEST, NT Build 492 Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady state migration experiments, Espoo, Finland, 1999.


