

Influence of exposure environments on the durability of slag-blended cements

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ABSTRACT

Both chlorides and sulphates combine in seawater to affect the durability of reinforced concrete structures located in marine environments. This paper presents the results of an experimental study on slag blended cement systems, cured for 7 days, before exposure to a combined solution of sodium chloride (30 g/L) and sodium sulphate (3 g/L). Two slags of different chemical compositions, designated as slags 1 and 2 were respectively blended with Portland cement CEM I 52.5R at 30 and 70 wt.% replacement levels. Mechanical tests on mortar samples were complemented by microstructural examination and chemical characterisation on paste samples, all using a constant w/b ratio of 0.5, to investigate the influence of exposure environment. The exposure environments include water and ponding in combined chloride-sulphate solution at 20 °C and 38 °C (to reflect temperate and tropical climates). The results show that temperature has a significant effect on the durability of slag blends. Reduced sorptivity at higher temperature led to reduced chloride penetration at early age. This effect is less so at later age. Compressive strength generally improved with increase in chloride penetration. SEM-EDX elemental analysis provided a good basis for following chloride penetration profile. XRD analysis showed the conversion of monosulphate to ettringite, Friedel's salt and Kuzel's salt upon exposure to salt solution, which possibly led to improved sorptivity and mechanical properties.

Keywords: Cement, Durability, Slag, Chloride, Sulphate, Environment.

1.0 INTRODUCTION

As different countries of the world grapple with the problems of maintaining ageing infrastructures against the ever challenging economic realities, the need for delivering durable structures has become increasingly important. This has put pressure on industry and academia to respond positively to this challenge. In order to deliver sustainable and more durable concrete structures, the cement and concrete industry, supported by research, introduced the incorporation of supplementary cementitious materials (SCM) or mineral admixtures in cement production. Many of these SCMs react slowly and contribute to long-term strength and durability of concrete structures. Ground granulated blast

others. These advantages are well documented in the literature (Juenger and Siddique, 2015; O'Connell et al., 2012; Teng et al., 2013).

As durability is primarily concerned with the interaction of materials with their service environment, understanding this interaction provides the basis for the robust durability design and application of construction materials. For instance, slag-blended cements which performed well against sulphate attack under static submersion failed to perform well under cyclic wet - dry condition (Chabreliie, 2010). Other studies have found that the presence of sulphate inhibits chloride resistance of cements (De Weerd et al., 2014; Geng et al., 2015).

Furthermore, most studies dealing with the influence of chloride and sulphate on concrete materials use high concentration test solutions to accelerate laboratory processes, which do not reflect actual field conditions. Such data would need to be complemented with those from actual or near field conditions to meet the increasing demand for durable concrete structures with greater certainty. The present study adopts concentrations of chloride and sulphate in combined solution, similar to typical sea water condition, to extend the previous works of Whittaker (2014) on sulphate attack, and Ogirigbo (2016) on chloride attack of slag-blended cement systems. These previous studies did not consider the combined effects of chloride and sulphate in the attacking solution. The present study investigates

wt.%, depending on the expected performance requirements. Between 55 and 59 wt.% replacement in Portland cement have been found to be optimal for strength performance (Oner and Akyuz, 2007), while higher replacement levels up to 70 wt.% favour chloride ingress resistance of concrete structures (Luo et al., 2003).

The use of slag offers advantages in concrete works, which include: low cost, low CO₂ contribution, low heat of hydration, increased workability, and low permeability with improved resistance to the ingress of harmful chemicals such as chlorides, amongst

the strength development and durability of slag-blended cements in combined chloride-sulphate solution and under different exposure conditions, including a change in temperature.

2.0 MATERIALS AND METHODS

Two slags, (slags 1 and 2), with basicity ratios (C/S) of 1.05 and 0.94 respectively, were each blended with CEM I 52.5R at 30 and 70 wt.% replacement. Blending for 2 hours was performed using a roller ball mill with plastic charges. Table 1 shows the particle size data for the two slags, plus the physical properties of the slags and Portland cement, while Table 2 shows their chemical compositions as received by the supplier. Natural sand sieved to a maximum size of 2.0 mm was used in preparing mortar samples.

Table 1. Physical properties of binders.

Property	Unit	CEM I 52.5R	S1	S2
Blaine	cm ² /g	7357	5995	5540
Density	g/cm ³	3.16	2.93	2.91
D10	µm	2.94	2.27	2.87
D50	µm	9.43	11.56	12.91

Table 2. Chemical compositions of binders (as supplied).

Property	Unit	CEM I 52.5R	S1	S2
SiO ₂	%	20.50	36.58	40.14
Al ₂ O ₃	%	5.43	12.23	7.77
TiO ₂	%	0.29	0.83	0.30
MnO	%	0.05	0.64	0.64
Fe ₂ O ₃	%	2.51	0.48	0.78
CaO	%	63.43	38.24	37.90
MgO	%	1.51	8.55	9.51
K ₂ O	%	0.79	0.65	0.55
Na ₂ O	%	0.17	0.27	0.36
SO ₃	%	3.43	1.00	1.47
P ₂ O ₅	%	0.14	0.06	0.02
LOI 950°C	%	1.37	1.66	0.40
Total	%	99.62	99.88	99.43
Glass content	%	na	99.3	97.1

2.1 Sample Preparations

Mortar Samples

Mortar samples were cast in steel moulds, with water:binder:sand ratios of 1:2:6. Samples were demoulded after 24 hours followed by curing in water for 7 days before immersion in a combined chloride-sulphate solution.

Paste Samples

Paste samples for XRD and microstructural analysis were cast in 14 mm ϕ x 50 mm plastic vials using w/b ratio of 0.5. The fresh samples were sealed and rotated in a sample rotator at 20 rpm for 24 hours to prevent bleeding. Hydration of paste samples was stopped using isopropanol solvent replacement method, at specified ages.

Exposure Conditions

Samples were exposed to either water (X1) or a salt solution (X2), containing sodium chloride (30 g/l) and sodium sulphate (3 g/l) (Table 3). The concentrations are typical of chlorides and sulphates in sea water (BS EN 12390-11, 2015; El-Hachem et al., 2012). All samples were exposed in parallel at either 20 °C or 38 °C, after initial curing for 7 days in water. The paste samples were kept sealed and stored in controlled temperature water baths, and were only demoulded for exposure to the salt solution.

Table 3. Exposure conditions.

Code	Initial curing	Exposure environment	Exposure temperature
X1	7 days in water	Ponding in water	20°C or 38°C
X2	7 days in water	Ponding in combined chloride-sulphate solution	20°C or 38°C

2.2 Test Methods

Free Chloride Penetration Depth in Mortars

50 mm mortar samples were exposed to combined chloride-sulphate solution for up to 90 days before free chloride penetration depths were measured after splitting and spraying with 0.1 M silver nitrate solution, to form a colour boundary. 6 measurements were obtained from 2 adjacent sides of the split sample, while the average is reported as chloride penetration depth in mm.

Total Chloride Penetration Profile in Mortars

This was performed on triplicate 160x40x40mm mortar prism samples (Ogirigbo and Black, 2017). Prior to ponding, samples were coated using epoxy resin on all sides except one square face to allow only unidirectional diffusion. The sample was exposed in salt solution for up to 90 days with the solution renewed monthly. Total or acid soluble chloride was determined in line with the RILEM TC 178-TMC (2002) method on ground mortar slices, to build a chloride concentration profile from the exposed surface progressing inwards up to a depth of 50 mm.

Chloride Penetration Profile in Pastes

Chloride penetration depths were also measured by SEM-EDX analysis using samples cured for 7 days, then exposed for a further 21 days. Samples were epoxy resin mounted and polished paste discs. Elemental spot analysis was conducted at x1000

magnification. Analysis was performed at 0.5mm intervals from the outer surface, radially down to 5mm total depth.

Sorptivity

The rate of capillary water absorption or sorptivity was measured using 28 mm ϕ x 50 mm mortar samples. The schematic of the test set-up is shown in Figure 1. Prior to measurement, samples were conditioned to constant weight in an oven at 40 °C, according to BS EN 13057 (2002).

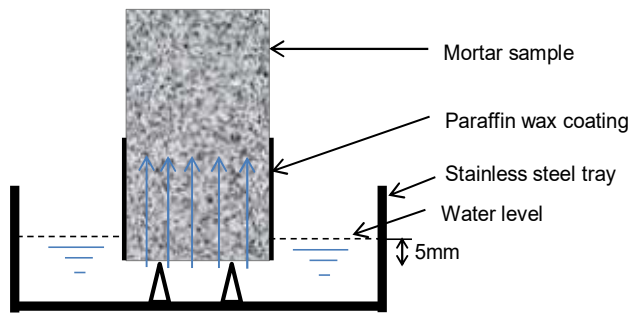


Fig. 1. Schematic set-up for measuring the rate of water absorption in mortar samples.

The samples were then allowed to cool to ambient temperature and the sides coated in paraffin wax to allow only unidirectional ingress of water. Each sample was then suspended on a stainless steel wire mesh in a tray containing deionised water, such that only about 5 mm of the sample was submerged in water. Masses were recorded at 1, 4, 9, 16, 25, 36, 49 and 64 minutes. A similar method was used by many researchers (Guneyisi and Gesoglu, 2008; Sabir et al., 1998). The rate of water absorption was determined from the slope of the plot of cumulative water absorption (g/mm^2) against the square root of time ($\text{min}^{0.5}$), in line with Equation 1.

$$i = K\sqrt{t} \quad (1)$$

Where:

i = cumulative water absorption (g/mm^2),

t = time (minutes), and

k = rate of water absorption ($\text{g}/\text{mm}^2/\text{min}^{0.5}$).

Compressive Strength

Compressive strength was determined from 160 x 40 x 40 mm mortar prisms, in triplicate, according to BS EN 196-1 (2005).

X-Ray Diffraction (XRD)

XRD was performed on hydrated paste samples, ground to fine powder passing 63 μm , using a Bruker D2 phaser. The scan was made from 5 to 70°: 2θ , at 2 s with increment of 0.034°, giving effective total scan time of 4074 s. Sample rotation was 15/min.

3.0 RESULTS AND DISCUSSION

3.1 Free Chloride Penetration Depths

Free chloride penetration data are presented in Figures 2 and 3 for 30 and 70 wt.% slag blends respectively. While there was a degree of scatter in the data, some trends could be discerned. There was little significant difference between the two slag blends, but the high replacement samples generally performed better. At 30 wt% replacement high temperature curing led to increased chloride ingress, while there was no effect of curing temperature when the replacement level was raised to 70 wt%.

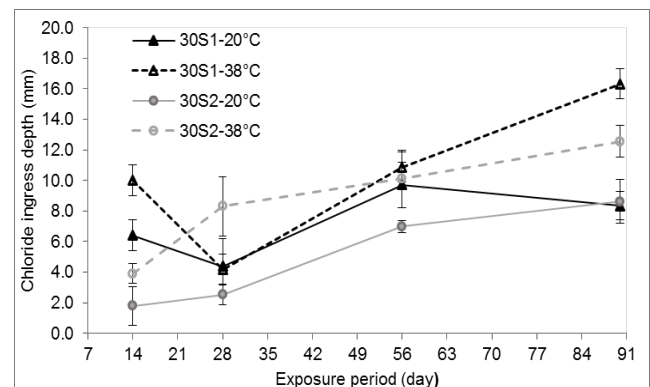


Fig. 2. Free chloride penetration depth for the 30% slag blends.

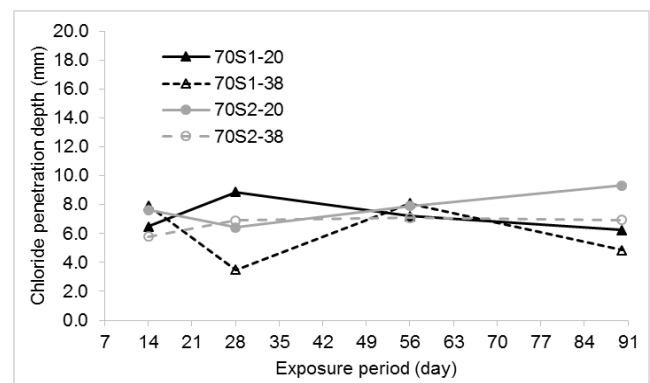


Fig. 3. Free chloride penetration depth for the 70% slag blends.

These differences may be explained by changes in pore structure development upon hydration. Microstructural investigations into the pore structure are ongoing. At 30 wt.% load, hydration was dominated by the clinker, for which hydration at a higher temperature is known to result in a more porous microstructure (Lothenbach et al., 2007; Ukpata et al., 2018). This behaviour is reversed with higher slag load where the dominant effect of elevated temperatures is the increase in slag hydration.

3.2 Total Chloride Profiles

Figures 4 and 5, show the profiles for unidirectional chloride diffusion into mortar prisms at 30 and 70% slag load respectively. There was very little

difference in the results, but chloride penetration was slightly greater in the 30% slag systems, and occurred to a greater depth. Penetration was only 10mm in the 70% slag samples while in the 30 wt.% slag blends chloride penetration about 18 mm depth.

At 38°C, the chloride penetration of the 30% slag blends was less than the values reported elsewhere (Ogirigbo and Black, 2017) for comparable samples, which were exposed to pure sodium chloride solution of similar concentration. This can be explained by the formation of pore-filling ettringite due to sulphate presence, leading to reduced penetration of chloride (Frias et al., 2013). However, the chloride penetration in this study was higher at 20°C. This is consistent with the changes in sorptivity and also agrees with the expansion behaviour of the slag systems discussed in a related paper for the same conference.

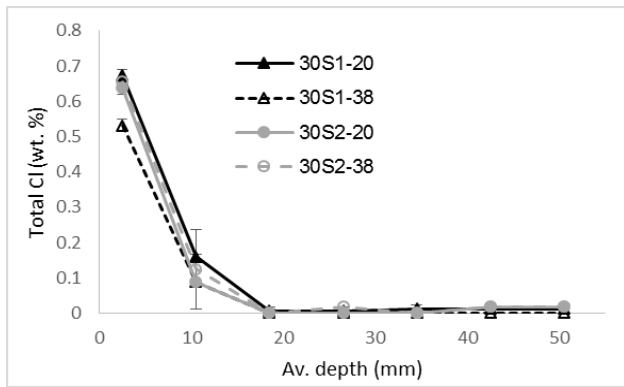


Fig. 4. Total chloride penetration profile for 30% slag blends

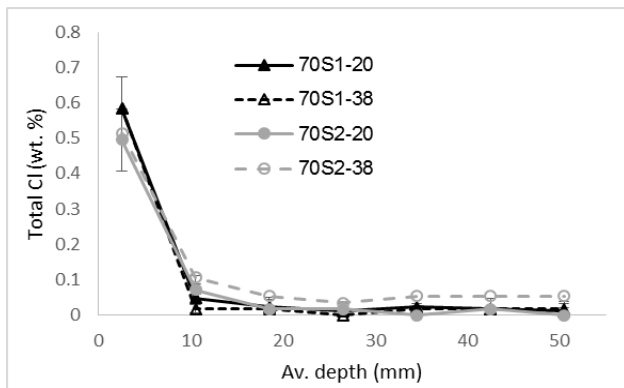


Fig. 5. Total chloride penetration profile for 70% slag blends.

3.3 SEM-EDX Chloride Penetration Profiles

Scanning electron microscopy with EDX analysis allowed further investigation into chloride penetration at the microstructural scale (Figure 6). From the profiles, pastes cured and exposed at 38°C generally showed less chloride penetration than those exposed at 20°C. Also, the slag 1 systems generally performed better with respect to chloride penetration resistance except for the 30% slag at

20°C. Increasing slag load from 30 to 70% also reduced chloride penetration significantly, consistent with the literature (Luo et al., 2003). The differences in the amount of penetrated chloride reduced with increasing depth of penetration, approaching convergence by around 5mm depth.

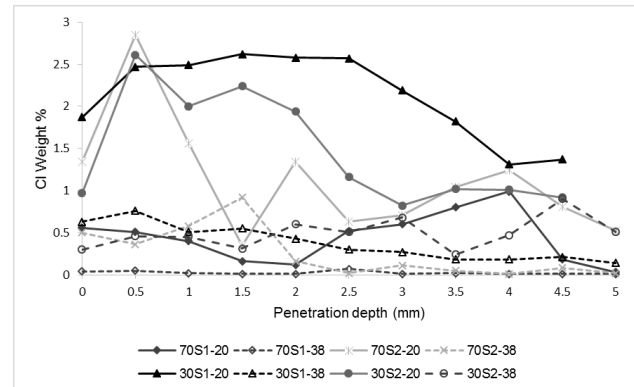


Fig. 6. SEM-EDX chloride penetration profile

3.4 Sorptivity

The results of sorptivity at 28 and 90 days are presented in Figures 7 and 8 for exposures at 20 and 38 °C respectively. Sorptivity was reduced at higher temperature, the difference being more prevalent at 28 days than 90 days. Samples exposed to the test solution (X2), showed reduced sorptivity at 28 days but less so at 90 days. Increasing slag content also caused a decrease in sorptivity, though not very clear at 90 days.

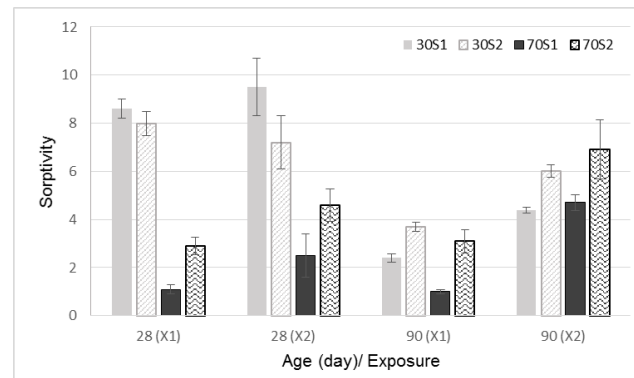


Fig. 7. Sorptivity at 20 °C (g/mm²/min^{0.5}) x10⁻⁵

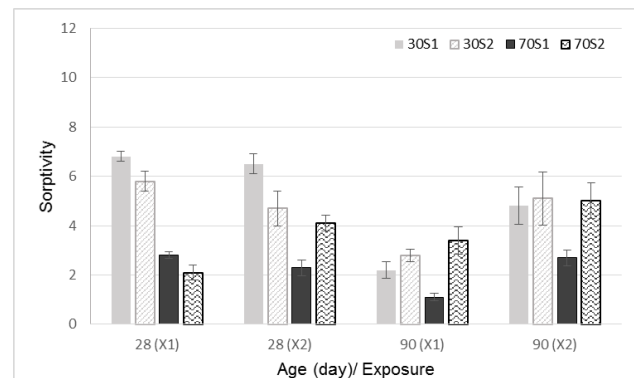


Fig. 8. Sorptivity at 38 °C (g/mm²/min^{0.5}) x10⁻⁵

3.5 Compressive Strength

The development of mortars' mechanical properties are shown in Figures 9 (slag 1) and 10 (slag 2). The results show both the strength development during the 7 days' curing and during subsequent immersion in either water (X1) or the combined chloride-sulphate solution (X2). Samples only exposed to water showed the expected strength development over time, whereby 30 wt% slag samples developed

slightly higher compressive strengths than the 70 wt% slag samples when cured at 20°C, but the higher slag content blends performed better when cured at 38°C. Curing at elevated temperatures improved early-age strength, but at the expense of later age performance, consistent with the results reported elsewhere (Ogirigbo and Black, 2016; Soutsos et al., 2017). This behaviour was similar for both slag blends and irrespective of slag load.

The accelerating effects of the salt solution in hydration and strength development reported earlier (Ukmeta et al., 2018), were evident soon after immersion, but were not clearly evident at later ages.

It is worth noting that, while the 70% slag blends showed lower strength development at 20°C, chloride ingress was minimal.

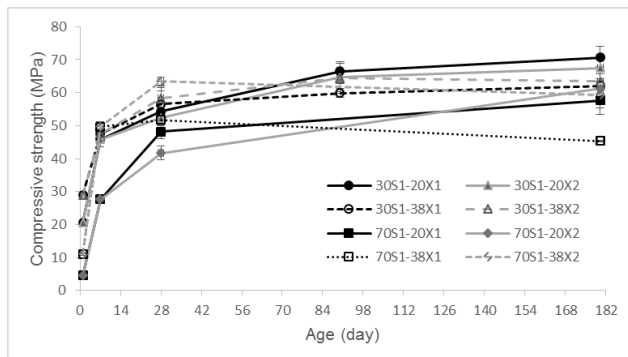


Fig. 9. Compressive strength development for slag 1 blends in water (X1) & salt solution (X2).

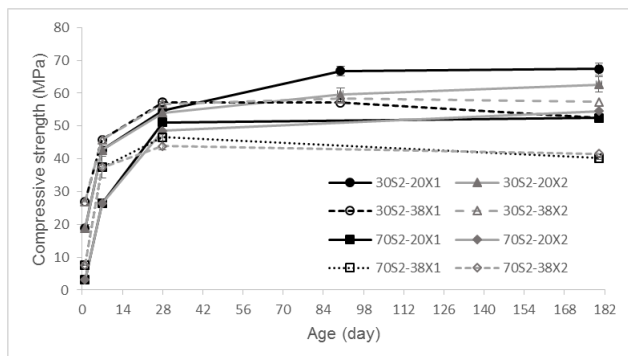


Fig. 10. Compressive strength development for slag 2 blends in water (X1) & salt solution (X2).

3.6 X-Ray Diffraction (XRD) Analysis

XRD patterns of the slag-blend pastes are shown in Figures 11 and 12 for samples cured for 7 days before immersion in either water (X1) or the combined chloride-sulphate solution (X2) to ages of 28 and 90 days respectively. Samples cured only in water showed typical reflections due to ettringite (E), monosulphate (Ms), hemicarboaluminate (Hc) and hydrotalcite (Ht).

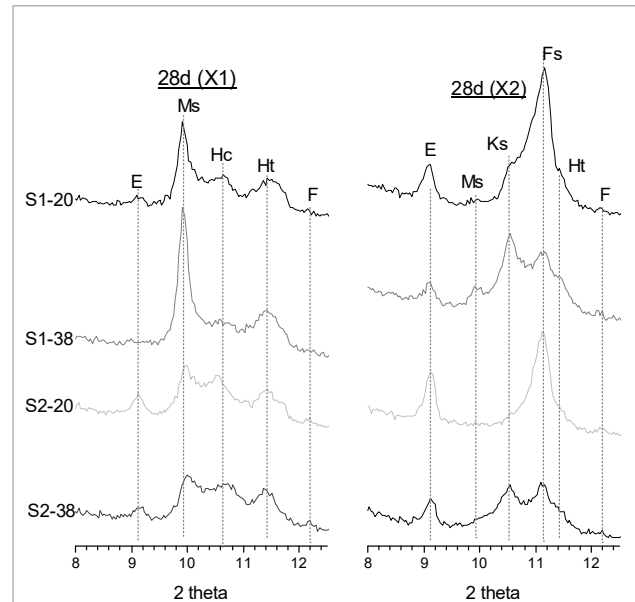


Fig. 11. 28-day XRD patterns for 30 wt.% slag blends exposed to water (X1) or combined solution (X2). (E – Ettringite, Ms – Monosulphate, Hc – Hemicarboaluminate, Ht – Hydrotalcite, F – Ferrite, Ks – Kuzel's Salt, Fs – Friedel's Salt).

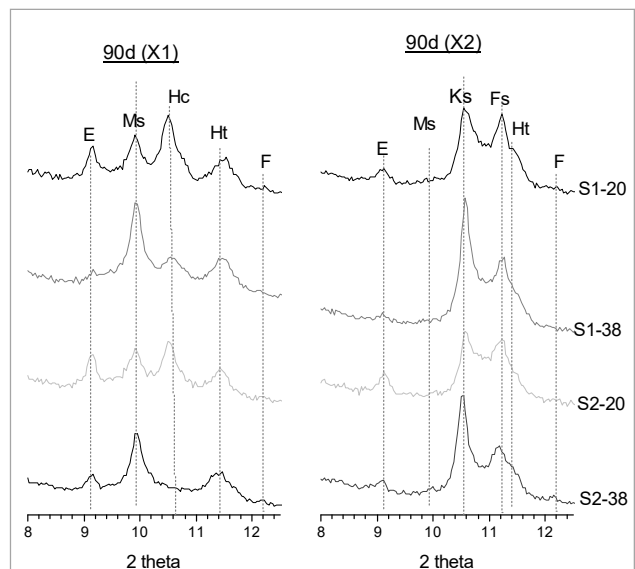


Fig. 12. 90-day XRD patterns for 30 wt.% slag blends exposed to water (X1) or combined solution (X2). (E – Ettringite, Ms – Monosulphate, Hc – Hemicarboaluminate, Ht – Hydrotalcite, F – Ferrite, Ks – Kuzel's Salt, Fs – Friedel's Salt).

At 28 days, monosulphate dominated, with minimal quantities of ettringite present. This was particularly so for the more basic slag 1. Higher curing temperatures led to lower quantities of ettringite and greater quantities of monosulphate. This presumably is due to greater degrees of slag hydration, reflecting accelerated hydration at higher temperature (Kjellsen et al., 1991; Soutsos et al., 2017).

Exposure to the combined solution led initially to the formation of Friedel's salt (Fs), with the formation of Kuzel's salt (Ks) also being evident, particularly at higher temperatures. This was all more prevalent in the alumina-rich and more reactive S1.

In addition, exposure to the combined solution led initially to the formation of ettringite, but this phase was less prevalent at later ages. This is contrary to earlier findings for exposure to pure sodium sulphate solution of similar concentration (Whittaker et al., 2016), and exposure to water (Figures 11 & 12), indicating the effect of concurrent presence of chloride in the solution, reflecting ettringite's increased solubility in chloride solutions. Furthermore, monosulphate was converted to Friedel's salt and Kuzel's salt upon exposure to salt solution consistent with the literature (Balonis et al., 2010). Increasing exposure temperature from 20 to 38°C, led to more intense Kuzel's salt peaks with corresponding decrease in Friedel's salt peaks at both test periods. Similarly, more intense Kuzel's salt peaks were observed from 28 to 90 days of age, with corresponding decrease in peaks due to Friedel's salt.

This finding is consistent with the known preferential reaction of sulphate with monosulphate from the hydration of aluminate phase in the binder to form ettringite or Kuzel's salt (Holden et al., 1983). These reaction products, possibly caused some pore-filling effects that led to the improved sorptivity and compressive strength observed.

4.0 CONCLUSIONS

This study has looked at the effect of exposure environment on the mechanical and durability properties of slag-blended cements. Increase in temperature from 20 to 38 °C accelerated early age compressive strength development but was detrimental at later age. Increasing temperature also reduced sorptivity of the samples. Exposure of the samples to a combined chloride-sulphate solution also improved sorptivity at early age but diminished over longer exposure period, although development of mechanical properties remain improved. This is because sorptivity was generally improved with age, irrespective of the presence of the salt solution.

Unlike the 30 wt% slag cements, samples prepared with 70 wt% replacement showed improved performance when cured at higher temperatures.

This is ascribed to the greatly increased slag reactivity at higher temperatures. The 30 wt.% slag blends meanwhile were detrimentally affected by curing at high temperatures, where the increased slag hydration could not compensate for the previously reported increased porosity in hardened cement paste.

SEM-EDX elemental analysis revealed the extent of chloride penetration. While 30 wt% slag blends, cured at 20°C showed chloride penetration to several millimetres, paste samples prepared with 70 wt.% slag content and exposed to the salt solution at the higher temperature of 38 °C showed drastically reduced chloride levels, falling to background levels within 2.5 mm. Similar results were observed in the mortar samples for total or acid soluble chloride from about 10 mm depth, while in the 30 wt.% slag blends chloride penetration reduced to background levels from about 18 mm depth.

XRD analysis showed that ettringite, Friedel's salt and Kuzel's salt were precipitated when the paste samples were exposed to the salt solution. These had some pore-filling effects, which possibly explains the improved sorptivity and mechanical properties observed.

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