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# Effects of Temperature and Curing Duration on the Stability of Slag Cements in Combined Chloride-Sulphate Environments

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## ABSTRACT

This experimental study investigates the effects of temperature and curing duration on the stability of slag blended cement systems exposed at 20 °C and 38 °C to combined sodium chloride (30 g/L) – sodium sulphate (3 g/L) solutions. Two slags, designated as slag 1 and 2, having CaO/SiO<sub>2</sub> ratios of 1.05 and 0.94, were respectively blended with Portland cement CEM I 52.5R at 30 wt.% replacement level. Mortar prisms and cubes with w/b ratio of 0.5 and binder/aggregate ratio of 1:3 were then prepared for length and mass changes. The samples were cured in lime water for either 7 or 28 days before ponding for a total exposure period of 544 days. Analogous paste samples were also prepared to follow changes in the hydration products using x-ray diffraction (XRD). The results showed that curing at 38°C resulted in less expansion and prolonged curing generally reduced expansion except for slag 1 blend at 20 °C. Also, mass-change was minimal at 38 °C compared to 20 °C, and curing up to 28 days further improved mass stability. There was a positive correlation between mass change and length change for the period of investigation.

**Keywords:** Cement, Slag, Sulphate, Chloride, Curing, temperature.

## INTRODUCTION

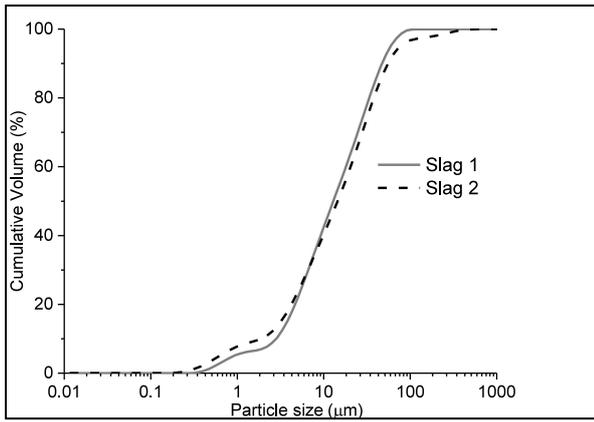
Excessive volumetric changes in concrete structural elements, whether through shrinkage or expansion, can lead to cracking and spalling of the concrete, and so can pose serious threats to the durability of concrete structures. Slag cements have been associated with early age shrinkage (Darquennes et al., 2008). Hence, there is a need to investigate their stability in service environments. Apart from the cement's autogenous tendency to shrink or expand in volume during hydration, exposures to certain environments such as sea water can add to the problems of excessive volumetric changes. Sea water contains chlorides and sulphates amongst others. Chlorides are associated with the corrosion of embedded steel reinforcement (Galan and Glasser, 2015), while exposure of cement materials to sulphate solutions has been known to cause expansion and mass loss in the hydrated cements. The sulphate ions react with calcium hydroxide and the hydrated aluminate phase of cement to produce gypsum and ettringite which are associated with expansion (Whittaker and Black, 2015; Yu et al., 2013). Amongst other causes, the composition of the binder in relation to C<sub>3</sub>A content, and curing conditions are factors affecting sulphate attack of cements (El-Hachem et al., 2012). Standards give limiting values of sulphate concentrations for severe exposure conditions ranging from 3000 to 6000 mg/l (BS EN 206, 2013). However, expansive effects of sulphate attack in plain and slag blended cements have been observed at concentrations as low as 3000mg/l, associated with sea water (El-Hachem et

al., 2012; Whittaker et al., 2016). Yet, it is still not clear how the changes occur when there is a simultaneous presence of chlorides and sulphates. Previous studies used high concentrations which do not reflect actual service conditions. Conflicting views had been expressed previously about the influence of chlorides on sulphate attack (Al-Amoudi et al., 1995; Sotiriadis et al., 2013). According to some, the presence of chlorides reduced deterioration of concrete due to sulphate attack (Santhanam et al., 2006; Zuquan et al., 2007). This view seems more acceptable than the contrary, although the effects of changes in environmental conditions and pre-conditioning of slag-blended systems need to be explored further along with their hydration characteristics.

This study investigates the influence of temperature and curing duration on length and mass changes of slag blended cement mortars in relation to their previously published water absorption and hydration characteristics (Ukpata et al., 2018)

## MATERIALS AND METHODS

This study has used two slags (1 & 2), with CaO/SiO<sub>2</sub> ratios of 1.05 and 0.94 respectively. These were each blended with CEM I 52.5R at 30 wt.% replacement. Blending was carried out for 2 hours using a roller ball mill incorporating plastic charges. The particle size distributions of the 2 slags are shown in Figure 1, while the binders' physical properties and chemical compositions are presented in Tables 1 and 2 respectively.



**Fig. 1.** Particles size distributions of slags 1 and 2.

**Table 1.** Physical properties of binders.

Property	Unit	CEM I 52.5R	Slag 1 (S1)	Slag 2 (S2)
Blaine	cm <sup>2</sup> /g	7357	5995	5540
Density	g/cm <sup>3</sup>	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.

Property	Unit	CEM I 52.5R	Slag 1 (S1)	Slag 2 (S2)
SiO <sub>2</sub>	%	20.50	36.58	40.14
Al <sub>2</sub> O <sub>3</sub>	%	5.43	12.23	7.77
TiO <sub>2</sub>	%	0.29	0.83	0.30
MnO	%	0.05	0.64	0.64
Fe <sub>2</sub> O <sub>3</sub>	%	2.51	0.48	0.78
CaO	%	63.43	38.24	37.90
MgO	%	1.51	8.55	9.51
K <sub>2</sub> O	%	0.79	0.65	0.55
Na <sub>2</sub> O	%	0.17	0.27	0.36
SO <sub>3</sub>	%	3.43	1.00	1.47
P <sub>2</sub> O <sub>5</sub>	%	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

### Sample Preparation, Curing and Exposure

Mortar samples (prisms and cubes) were cast in steel moulds with w/b ratio of 0.5, and aggregate to binder ratio of 3.0. The samples were demoulded after 24 hours before curing. Meanwhile, paste samples were cast in 14 mm  $\phi$  x 50 mm plastic vials with w/b of 0.5. The fresh samples were sealed and rotated in a sample rotator at 20 rpm for 24 hours to prevent bleeding. At specified test ages, hydration was stopped using isopropanol solvent replacement method. Samples could then be stored for subsequent analysis.

The curing and exposure conditions are detailed in Table 3. A salt solution composed of 30 g/l sodium chloride and 3 g/l sodium sulphate was prepared from 99% analytical reagents. Mortars samples were exposed to the solution at either 20°C or 38°C, after initial curing for either 7 or 28 days in saturated lime water to prevent leaching of calcium hydroxide. Pastes samples were kept sealed in water baths and demoulded only for either exposure to the salt solution or for hydration stopping. Parallel reference mortar samples were left in limewater throughout the test period (X1).

**Table 3.** Exposure conditions.

Code	Initial curing	Exposure condition	Exposure temperature
X1	7 or 28 days in lime water	Ponding in lime water	20°C
X2	7 or 28 days in lime water	Ponding in combined chloride-sulphate solution	20°C or 38°C

### Test Methods

Length changes were measured in triplicate using 25 x 25 x 200 mm mortar prisms, in line with ASTM C490 (2011). Readings were taken from each sample face and the average of 12 measurements from the 3 samples were used as in Equation 1.

$$\delta_L = \frac{(L_x - L_i)}{L_i} \times 100\% \quad 1$$

Where:  $\delta_L$  = length change (%),  $L_x$  = Measured length at a given age,  $L_i$  = initial baseline length for the same sample.

Mass changes were measured in triplicate on 50 mm<sup>3</sup> mortar samples to 0.01 g sensitivity. Mass change was calculated according to Equation 2.

$$\delta_M = \frac{(M_x - M_i)}{M_i} \times 100\% \quad 2$$

Where:  $\delta_M$  = mass change (%),  $M_x$  = Measured mass at a given age,  $M_i$  = initial baseline mass for the same sample.

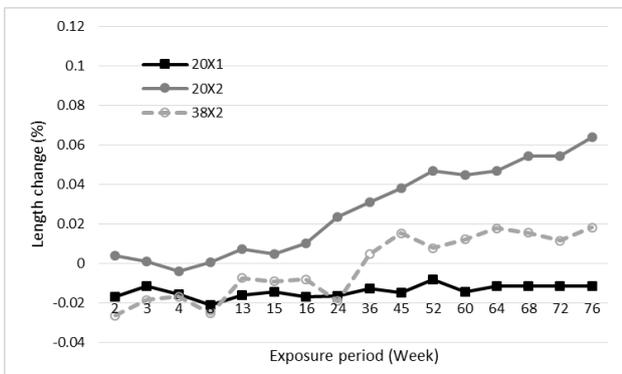
XRD analysis was performed using a Bruker D2 phaser diffractometer on finely ground powder samples passing 63 µm, obtained from hydration stopped samples. Scanning was performed from 5°-70° 2 $\theta$  with a 0.034° step size and a 2s dwell time.

## RESULTS AND DISCUSSION

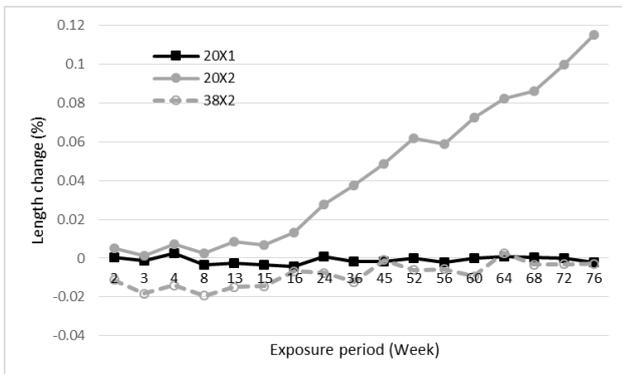
### Length Change

The length change results are presented in Figures 2 to 5. Figure 2a shows length change for the more reactive, slag 1 blend exposed to the salt solution

following 7 days of curing, while Figure 2b shows the results for samples cured for 28 days before exposure. The samples cured for 7 days before exposure showed slight shrinkage, but this disappeared by 28 days. Generally, the reference samples (X1) remained stable, showing minimal length change throughout the test period. Exposure to the salt solution at 38°C led to slight expansion beyond 6 months. However, samples exposed at 20°C showed significant expansion from about 15 weeks' exposure. The samples cured for 28 days before exposure behaved differently. The samples cured at 38°C suffered slight initial shrinkage prior to exposure, but remained stable throughout the test period. Meanwhile, the samples cured and exposed at 20°C from about 15 weeks onwards, with expansion ultimately being greater than for the samples cured and exposed at lower temperature.



**Fig. 2a.** Length change for slag 1 blends cured for 7 days prior to exposure (Error = ±0.06%).



**Fig. 2b.** Length change for slag 1 blends cured for 28 days prior to exposure (Error = ±0.01%).

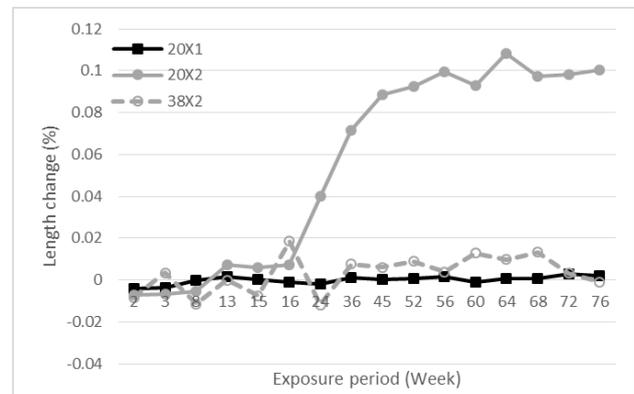
Figures 3 (a & b) show the length change for the less reactive, slag 2 blends. The reference samples showed no expansion, as did the samples cured and exposed at 38°C. However samples cured and exposed at 20°C showed significant length change from about 16 weeks onwards. In this case, expansion was greater for samples cured for 7 days than 28 days.

The effects of curing duration at 20 and 38°C are exemplified in Figures 4 and 5. In almost all cases, the importance of prolonged curing was evident in the 2 slag blends and at both temperatures. More

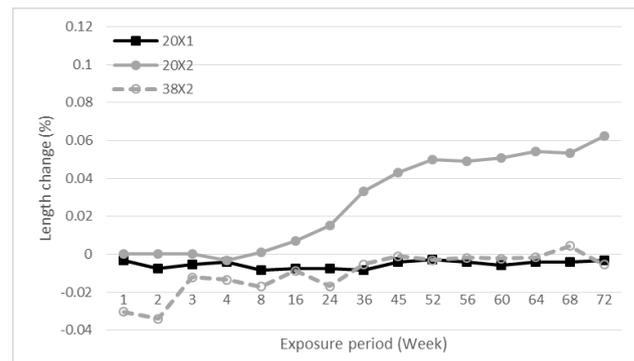
noticeable was the impact of curing temperature, where increased temperatures greatly improved performance. The length changes at 38°C agreed well with water sorptivity data for the same samples, where sorptivity reduced with increased temperature (Table 4). No previous comparable data on the effect of temperature on the expansion of slag cements could be found in the literature. However, the results of expansion at 20°C are consistent with earlier research (Maes and De Belie, 2014).

**Table 4.** 90d sorptivity ( $\text{g}/\text{mm}^2/\text{min}^{0.5}$ )  $\times 10^{-3}$ .

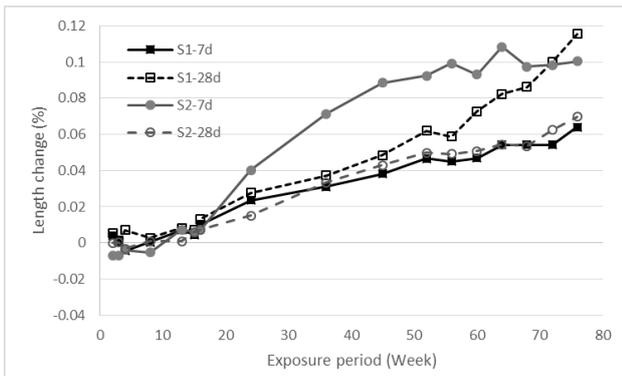
Mix	Exposure	20°C	Std Dev.	38°C	Std Dev.
C2S1	90d (X1)	0.024	0.0017	0.022	0.0034
	90d (X2)	0.044	0.0012	0.048	0.0075
C2S2	90 (X1)	0.037	0.0020	0.028	0.0025
	90 (X2)	0.060	0.0026	0.051	0.0108



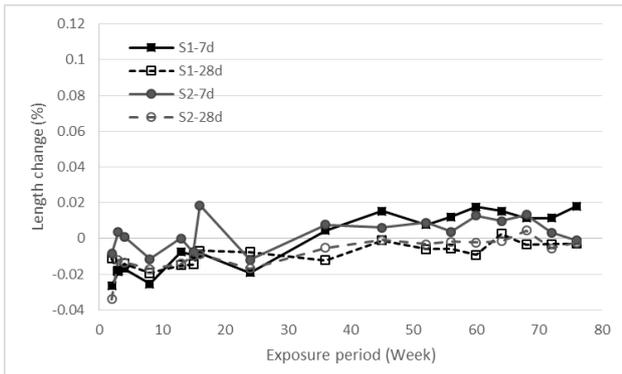
**Fig. 3a.** Length change for slag 2 blends cured for 7 days prior to exposure (Error = ±0.01%).



**Fig. 3b.** Length change for slag 2 blends cured for 28 days prior to exposure (Error = ±0.01%).



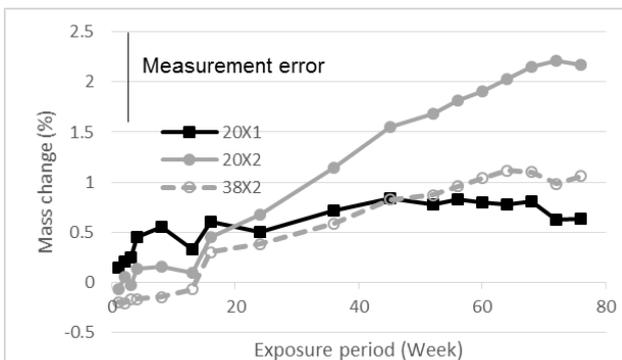
**Fig. 4.** Effect of curing duration at 20°C on length change.



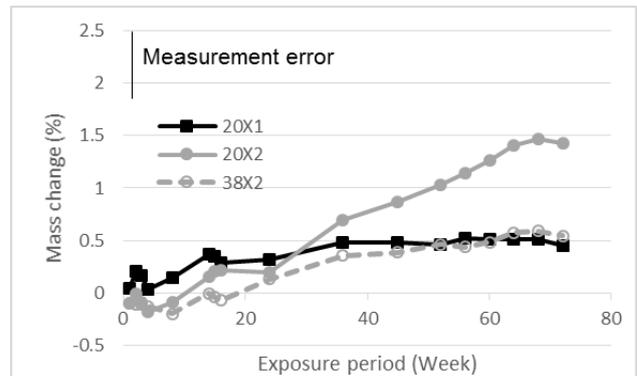
**Fig. 5.** Effect of curing duration at 38°C on length change.

### Mass Change

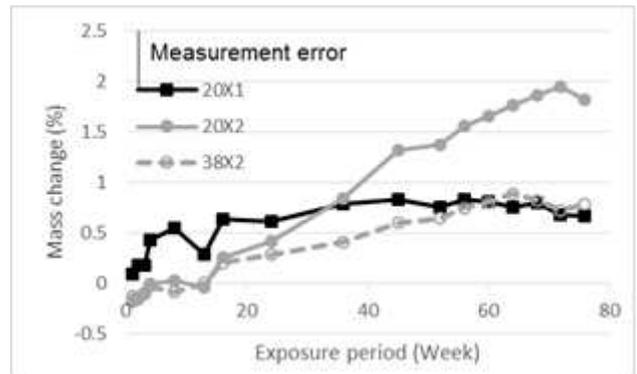
Mass change results are presented from Figs. 6 to 9. Figs. 6 (a & b) show respectively the mass changes for the slag 1 blend initially cured for 7 and 28 days before exposure, while Figs 7 (a & b) show similar results for the slag 2 blends. For both systems, the reference samples (X1) show only slight increases in mass, while the samples exposed to the solution showed mass increases. When cured at 20°C, the increases were considerable from about 24 weeks' exposure. However, the samples exposed at 38°C showed much more modest increases. No spalling of surface material was observed, which possibly explains why no mass losses were yet observed.



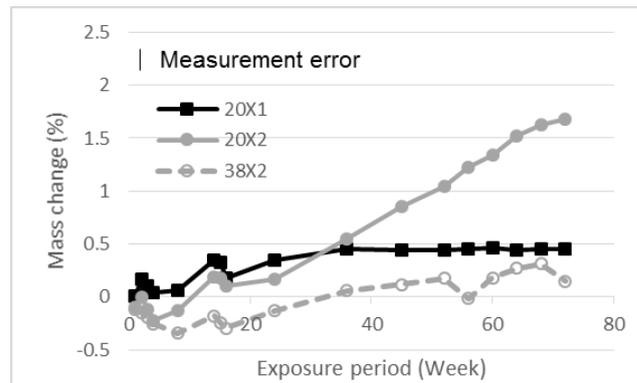
**Fig. 6a.** Mass change for slag 1 blends cured for 7 days prior to exposure.



**Fig. 6b.** Mass change for slag 1 blends cured for 28 days prior to exposure.



**Fig. 7a.** Mass change for slag 2 blends cured for 7 days prior to exposure.

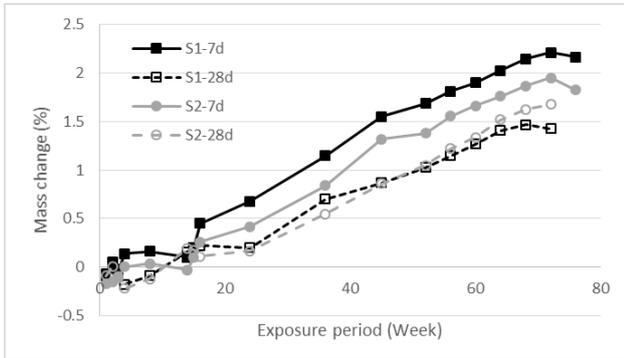


**Fig. 7b.** Mass change for slag 2 blends cured for 28 days prior to exposure.

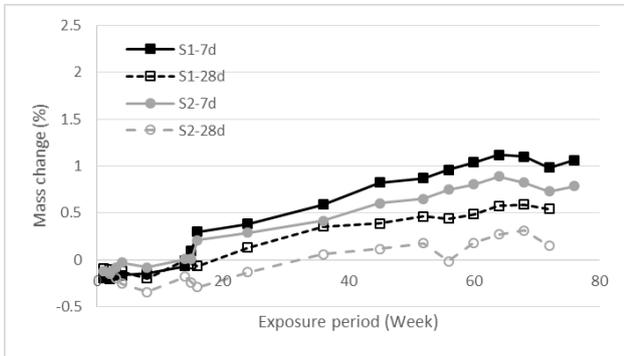
Figs. 8 and 9 show the effects of curing duration on mass change at 20 and 38°C respectively. At both temperatures, prolonged curing before exposure to the salt solution led to lower mass increase compared to exposure following curing for 7 days.

Another important difference was that, despite showing a lower sorptivity (Table 4), the more reactive slag (slag 1) showed a greater mass increase than the less reactive slag 2. This is possibly due to the higher aluminium content of the slag, increasing the potential for AFm, Aft and Friedel's salt formation. Also, slag 2 with greater MgO content showed more expansion than slag 1. This is consistent with the volume-filling nature of MgO hydration (Haha et al., 2011). These findings

underscore the importance of slag composition affecting different performance requirements, which should be carefully considered while using the material.



**Fig. 8.** Effect of curing duration on mass change at 20°C.



**Fig. 9.** Effect of curing duration on mass change at 38°C.

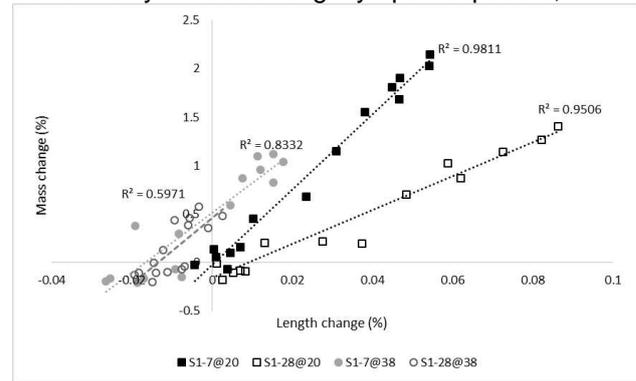
### Relationship between Length and Mass Changes

Fig. 10 shows the relationship between mass change and length change for the slag 1 blended mortars. Irrespective of curing duration or temperature, a positive relation was established between mass change and length change. The positive correlation was stronger for samples exposed at 20 °C than 38 °C, with  $r^2$  values greater than 0.95. Similar mass gain and length increase in 50 wt.% slag blended mortar samples exposed to 50 g/L  $\text{Na}_2\text{SO}_4$  + 50 g/L  $\text{NaCl}$  solution, up to about 600 and 300 days respectively had been reported in a previous study (Maes and De Belie, 2014). Fig. 10 shows that the effect of curing duration was more significant at 20°C than 38°C. This can be explained by the acceleration of slag hydration at elevated temperature.

### X-Ray Diffraction (XRD) Analysis

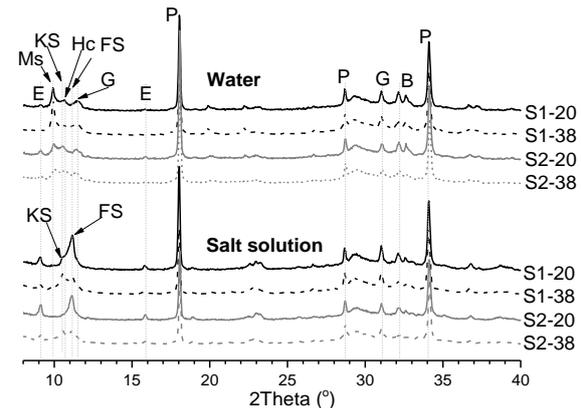
XRD data from paste samples exposed to the combined salt solution are presented in Figures 11 and 12, with Figure 11 showing the data obtained after exposure for 28 days and Figure 12 showing that obtained after exposure for 180 days. The 2

periods represent periods before and after significant mass change or expansion. The ettringite content only increased slightly upon exposure,

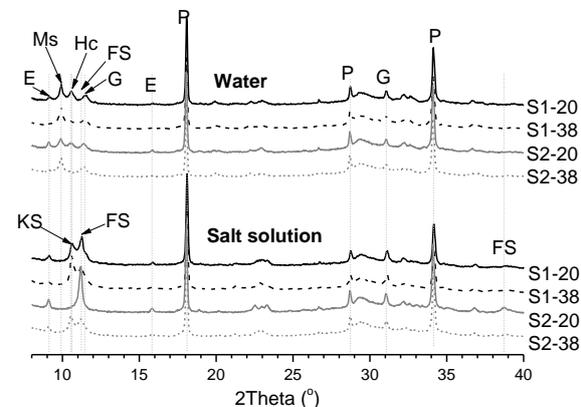


**Fig. 10.** Relationship between mass change and length change for slag 1 systems.

and showed no discernible increase between 28 and 180 days' immersion in the solution. This suggests that the expansion observed in the mortar samples may not be due to ettringite precipitation usually associated with expansion. Monosulphate was converted to Friedel's salt and Kuzel's salt upon exposure to salt solution and their reflections



**Fig. 11.** XRD patterns at 28 days (P: portlandite; B: brucite; G: gypsum; E: ettringite; FS: Friedel's salt; KS: Kuzel's salt; Ms: monosulphate; Hc: Hemicarboaluminate).



**Fig. 12.** XRD patterns at 180 days (P: portlandite; B: brucite; G: gypsum; E: ettringite; FS: Friedel's salt; KS: Kuzel's salt; Ms: monosulphate; Hc: Hemicarboaluminate).

increased with age. For samples exposed at 20°C, there was a significant increase between 28 and 180 days. There were no significant changes for those samples exposed at 38 °C, consistent with the mass and length change behaviours. Portlandite reflections decreased with time at both temperatures reflecting increased slag hydration.

## CONCLUSIONS

The effects of a change in temperature from 20°C to 38°C, and of the duration of initial curing before exposure to an aggressive, combined chloride-sulphate solution have been investigated in 2 slag blended systems. In terms of mass and length changes, curing and exposure at higher temperature generally improved the mortars' resistance to these changes. This may be due a more compact microstructure following improved hydration at higher temperatures, as confirmed in other studies. Except for the length change of slag 1 at 20°C, longer curing, from 7 to 28 days, generally had a positive impact. This is also linked with the slow hydration of slags and the poorly formed microstructure at early age, which allows more ingress of the exposure solution into the mortar matrix. This underscores the need for longer curing periods when mortars and concretes incorporate slags as part of their binders. The need for prolonged curing is more significant at 20°C than 38°C.

Reference samples, which were kept in lime water to prevent leaching of portlandite, did not show any length change but did show a slight increase in mass. This confirms that the observed change in length was due to the ingress of the salt solution. This may be attributed to the formation of Friedel's salt, Kuzel's salt and perhaps, additional ettringite due to the reaction of the aluminate phase with portlandite and the ingressing sulphate from the exposure solution. The slight increase in mass of the reference sample is likely due to water imbibition as explained in literature.

Generally, there was positive correlation between mass change and length change within the period of this investigation.

## Acknowledgement

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