INFLUENCE OF SLAG COMPOSITION AND CURING DURATION ON THE PERFORMANCE OF SLAG BLENDS IN CHLORIDE ENVIRONMENTS

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Abstract

This study investigated the influence of chemical composition of Ground Granulated Blast Furnace Slag (GGBS) and curing duration on the performance of slag-cement blends; specifically strength and transport properties. Two slags (1 and 2) with Ca/Si ratios of 1.05 and 0.94 respectively, were used to partially replace 30% of a CEM I 52.5R cement. Various tests, including compressive strength, isothermal calorimetry, water absorption, sorptivity, and chloride ingress were conducted on mortar specimens to measure the performance of the slag blends against a CEM I 42.5R cement. The mortar specimens were pre-cured for 7 and 28 days before exposure to a 3% sodium chloride solution. Two different exposure conditions were studied (one in which the samples were submerged completely in the salt solution, and the other in which the samples were subjected to a 6 hr wetting and drying cycle). The results obtained showed similar performance for both slags at longer curing durations; with the more basic slag 1 exhibiting better transport properties than slag 2 for both exposure conditions at shorter curing durations. This suggests that curing duration as well as variation in chemical composition of slags affects the performance of slag blends in chloride environments.

1. INTRODUCTION

Concrete is the most widely used construction material in the world as a result of its ability to resist penetration of water when used in marine environments, good fire resistance properties, versatility in forming various shapes, abundance of raw materials and low manufacturing and maintenance costs [1]. As a consequence of concrete's popularity, the material has a considerable environmental footprint, with the production of Portland cement contributing 5-7% to global CO_2 emissions [2].

In recent years, the use of secondary cementitious materials (SCMs) to partially replace Portland cement (PC) in the making of concrete has become a common practice. This is primarily because SCMs are cheaper and help to reduce the environmental impact associated with construction. They may also improve other properties of concrete such as workability, durability and long-term strength. Ground granulated blast furnace slag (GGBS) is one such SCM which is known to perform excellently when used in combination with Portland cement (PC).

In chloride-rich environments, the use of slag blends has been shown to be beneficial in terms of chloride binding and resistance to the penetration of chloride ions [3-5]. During cement hydration, the calcium hydroxide produced from the hydration of PC activates the slag, which also reacts with water to form calcium aluminates and C–S–H [6]. The formation of these additional hydration products results in a hardened cement paste with fewer large capillary pores and more of very small gel pores. Furthermore, the resulting hardened cement paste is usually more chemically stable than that of ordinary PC in that it contains much less free lime; reducing the likelihood of further reaction products such as ettringite or efflorescence [7].

Several standards concern the use of GGBS, and often these cover properties such as the oxide ratios and other physical properties such as fineness. For example, BS EN 197-1:2011 stipulates that the $(CaO + MgO)/SiO_2$ ratio by mass must exceed 1 [8]. However, work done by several authors has shown that these oxide (basicity) ratios may not be an accurate predictor of slag reactivity and performance. For example, Mantel [9] investigated the hydraulic activity of five different slags and concluded that there was no clear correlation between the basicity ratios and the properties of slag blends.

As use of GGBS becomes more widespread, the impact of slag variability becomes more critical. Also, various studies involving slag blends and other blended systems have shown that prolonged curing enhances performance. However, in practice, structures may often be cured for shorter durations. This work focuses on the influence which a change in slag composition and curing duration has on the performance of slag blends.

2. EXPERIMENTAL PROGRAMME

2.1 Materials

Two slags (S1 & S2) having similar physical properties but different chemical composition were used for the study. Figure 1 shows the particle size distribution of the slags obtained using Mastersizer 2000. Given that both slags were ground under identical conditions, it was also assumed that their morphologies would be similar. Hence it was assumed in this study that any changes in performance were due to changes in the chemical composition of the slags. Both slags were combined with a CEM I 52.5R at 30% replacement level. The performance of the slag blends were measured against a CEM I 42.5R. The chemical composition of the slags and cements, as determined by XRF, as well as other physical properties are shown in Table 1.

2.2 Details of mixes and curing conditions

Mortar and paste samples used for the tests were prepared using a water: binder (w/b) ratio of 0.5. All samples were cured at temperature of 20°C and at a relative humidity of 99%.

2.3 Test methods

Unconfined compressive strength (UCS) tests were conducted in accordance with EN196-1:2005 [10]. 40 x 40 x 160mm mortar prisms were cast and split in the middle after a period of 24 hours to produce 40 x 40 x 80mm samples for testing. Mortar samples were cured for either 7 or 28 days, after which they were immersed in a 3% sodium chloride solution so as to investigate the influence of chloride ingress on compressive strength development.

Table 1: Properties of cementitious materials

Property	**Unit**	**C42.5R**	**C52.5R**	**Slag 1 (S1)**	**Slag 2 (S2)**
LOI 950°C	%	2.20	2.54	(+1.66)	(+0.40)*
SiO_2	%	19.71	19.10	36.58	40.14
Al_2O_3	%	5.08	5.35	12.23	7.77
TiO_2	%	0.26	0.25	0.83	0.30
MnO	%	0.03	0.03	0.64	0.64
Fe_2O_3	%	2.97	2.95	0.48	0.78
CaO	%	63.16	62.38	38.24	37.90
MgO	%	2.19	2.37	8.55	9.51
K_2O	%	1.08	1.05	0.65	0.55
Na_2O	%	0.06	0.05	0.27	0.36
SO_3	%	2.97	3.34	1.00	1.47
P_2O_5	%	0.20	0.10	0.06	0.02
Total	%	99.90	99.50	99.88	99.43
Glass content	%	na	na	99.3	97.1
Blaine	cm^2/g	3510	5710	4490	4090
Density	g/cm^3	3.23	3.18	2.94	2.95

*The sample was oxidized with HNO_3 before the determination of LOI

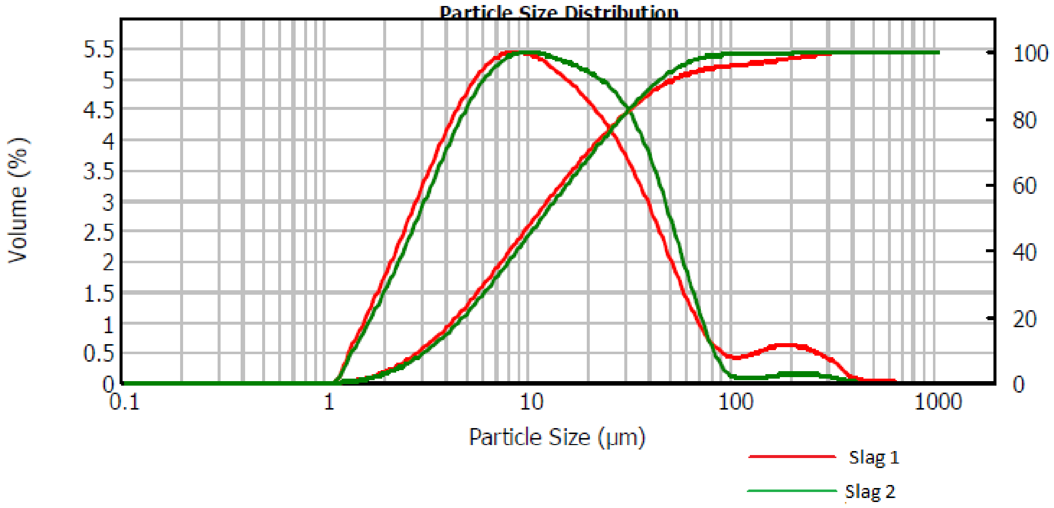


Figure 1: Particle size distribution of slag 1 and slag 2

Table 2: Basicity ratios of slag

Ratio	Slag 1	Slag 2
C/S	1.05	0.94
(C+M)/S	1.28	1.18
(C+M)/(S+A)	0.96	0.99

The heat flow generated during hydration was measured for cement pastes, using a TAM Air calorimeter. 6 g of cement powder and 3g of deionised water was placed in a cup, and mixed for 2 minutes using a vortex shaker. Calorimetric data was recorded for 28 days. In order to determine the contribution of the slags to the heat generated, quartz (Q) was added as filler at the same replacement ratio of the slag blends (Figure 3b).

Water absorption was measured according to BS1881-122:2011 [11]. 50mm mortar cubes were cured for 28 or 90 days at 20°C, and dried in an oven for 72 hours at 105°C to remove all the evaporable water. After drying, the samples were placed in a desiccator and left to cool for 24 hours at room temperature before testing. The samples were weighed to obtain a dry mass (M_d), after which they were immersed in a water tank with the water level maintained at 25 mm above the samples. The mass of the samples were then recorded at 10, 30, 60 and 120 mins. The water absorbed (W_a) as a percentage was calculated using the following expression:

$$W_a = \frac{K(M_t - M_d)}{M_d} \times 100 \quad (1)$$

where:

M_d dry mass of the sample in g
M_t mass of the sample after time t, in g
K correction factor for the shape of the samples, which is 0.667
W_a water absorption in %

Sorptivity was determined using similar methods as used by Tasdemir [12], and Güneyesi and Gesoğlu [13]. 50 mm mortar cubes were cured for 28 or 90 days at 20°C, and dried to constant mass in an oven at 50°C. The sides of the samples were coated with paraffin and placed in a trough of water, with the water level kept at about 5mm from the base of the samples. The mass of the specimens were recorded at predetermined times (1, 4, 9, 16, 25, 36, 49 and 64 mins). At each of these times, the mass of water adsorbed by each specimen was obtained, and from this the sorptivity coefficient (k) was calculated using the following expression:

$$k = \frac{Q}{A\sqrt{t}} \quad (2)$$

where:

Q amount of water adsorbed in cm^3
t time in seconds
A cross-sectional area of the specimen that was in contact with the water in cm^2
k sorptivity coefficient in $cm/s^{1/2}$.

The depth of chloride ion penetration was measured by exposing 50mm mortar cubes to a 3% sodium chloride solution after they had been initially cured for 7 or 28 days. Two chloride exposure conditions were used, one in which the samples were continuously immersed in the sodium chloride solution and the other where the samples were subjected to a 6-hr wetting and 6-hr drying cycle. The samples were withdrawn periodically, at 14, 28, 56 and 90 days, to determine the depths of chloride ion penetration. The withdrawn samples were split in half and the surfaces of the freshly split samples were sprayed with a 0.1 M silver nitrate ($AgNO_3$) solution. The presence of free chlorides was indicated by the formation of a white precipitate of silver chloride (AgCl), while in the absence of free chlorides the reaction between silver nitrate and portlandite resulted in a brown coloration, due to the formation of silver hydroxide. Thus, by linear measurements from the edge of the specimen up to the colour change boundary, the depth of free chloride penetration could be determined.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

The results obtained for the compressive strength tests are shown in Table 3 and Figure 2. From Table 3, it is seen that the CEMI 42.5R mix had a higher early strength up to 7 days than the slag blends. However, at later ages, the slag blends had higher strengths. The early age performance could be attributed to the lower pozzolanic reactivity of slag as observed previously by Al-almoudi et al [14]. At early ages, the degree of slag hydration is considerably less than that of the cement clinker. Whittaker et al. [15] recently reported that, in 40% slag blends, approximately 40% of slag had hydrated after 7 days, compared with about 80% of the clinker.

The strength performance index of the slag blends was calculated from the ratio of the strength of the slag blends against that of the CEMI 42.5R at 7, 28 and 180 days, as shown in Table 4. There was no significant difference in the strength performance of the two slags, with the long-term benefits of slag-cements being clear.

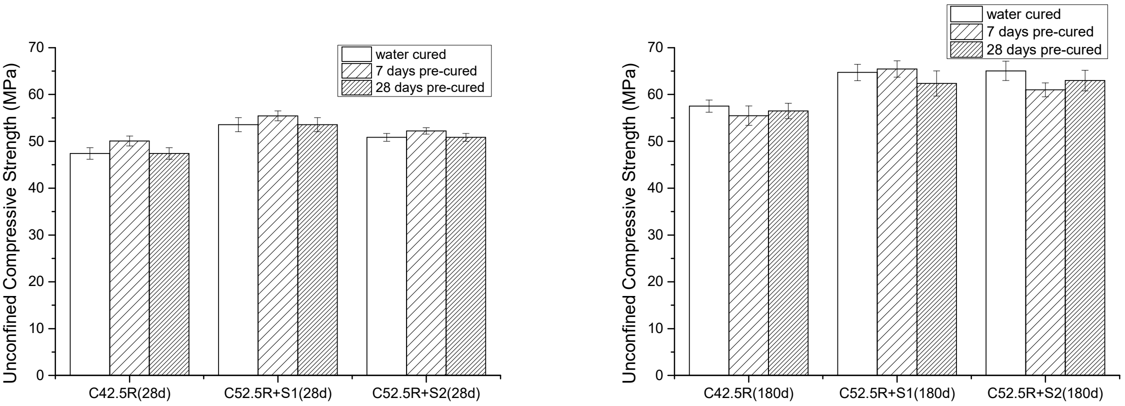
Figure 2 illustrates the impact of immersion in NaCl solution upon compressive strength. Exposure after 7 days of curing led to a slight increase in strength at 28 days, but not at 180 days. In a previous study by Seleem et al. [16], the samples were initially cured for 28 days before exposure. This difference is significant, as in practice structures are often cured for shorter periods of time before exposure to a chloride-rich environment. The early strength gain caused by the chloride ingress could be attributed to the accelerating effect of chlorides on the hydration reaction. Prolonged curing before exposure to the chloride solution didn’t seem to aid strength development as observed for all mixes cured for 28 days before exposure to the chloride solution. This suggests that at 28 days, the microstructure was finer with fewer pores, and thus would be more resistant to chloride ingress.

Table 3: Unconfined compressive strength of samples cured under water at 20°C

Time	C42.5R		C52.5R+S1		C52.5R+S2	
Days	MPa	δ	MPa	δ	MPa	δ
1	18.5	0.3	22.6	0.3	19.0	0.5
2	28.1	0.4	30.7	0.5	26.6	1.1
7	44.2	0.7	40.7	0.9	39.6	0.6
28	47.4	1.2	53.6	1.5	50.9	0.8
90	53.8	0.6	63.1	1.3	60.0	1.6
180	57.5	1.3	64.7	1.8	65.0	2.1

Table 4: Strength performance index of slag blends

Days	C52.5R+S1	C52.5R+S2
7	0.92	0.90
28	1.13	1.07
180	1.12	1.13

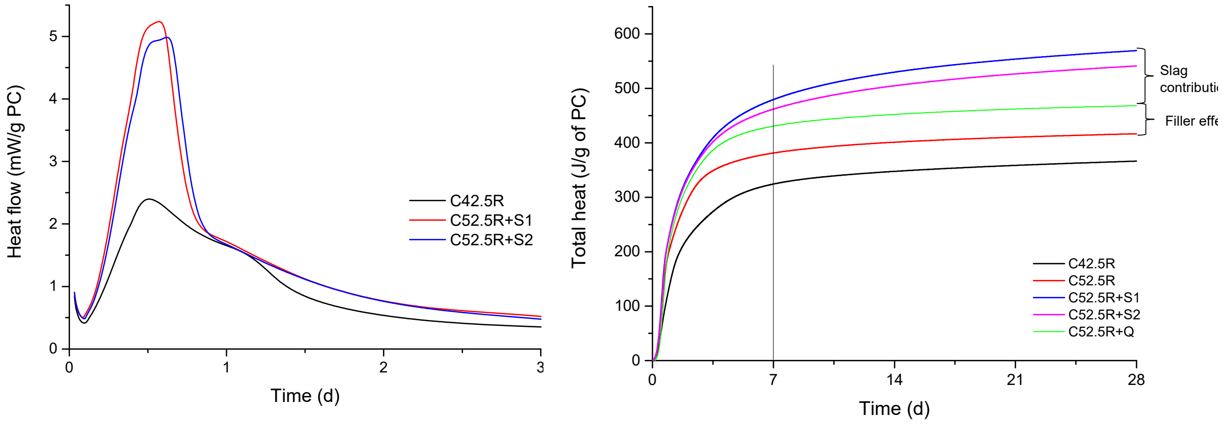


(a) (b)

Figure 2: Influence of chloride ingress on compressive strength development (a) for 28 day old samples (b) for 180 day old samples

3.2 Isothermal calorimetry

Figure 3 shows the heat flow and cumulative heat for the plain cement mix and the slag blends. The more basic slag 1 (Table 2) was expected to be more reactive, and did have a slightly higher heat flow than slag 2 but the difference was minimal. However, the difference in the strength performance index and the calorimetric data did not correlate with the difference in the basicity ratios. This agrees with earlier observations made by Mantel [9].



(a)

(b)

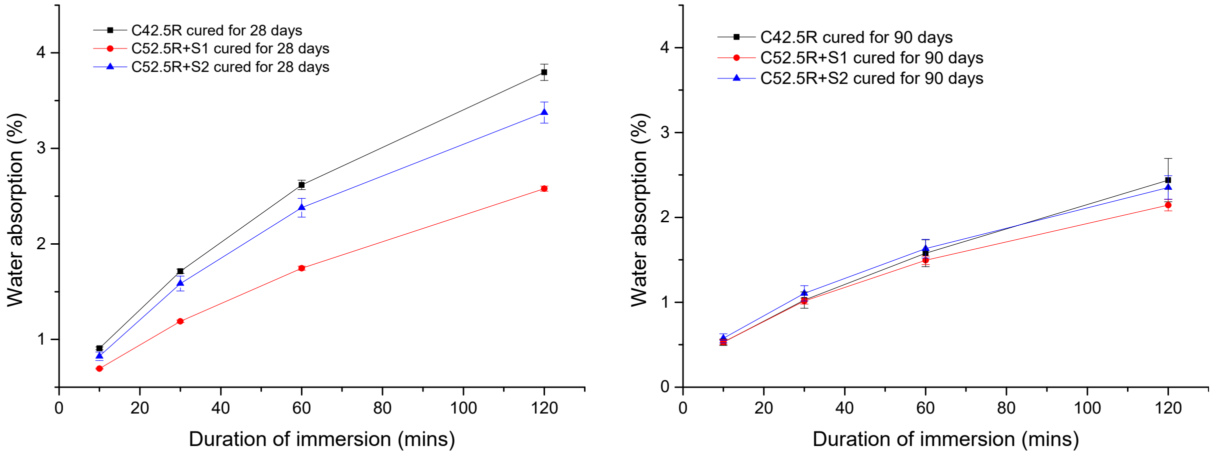
Figure 3: Isothermal calorimetry plot (a) heat flow (b) total heat

3.3 Water absorption and sorptivity

Water absorption curves are shown in Figure 4 while the sorptivity coefficients obtained from 28 and 90 day old samples are shown in Table 5. The results show that, despite the similarities in strength, the slag blends were more resistant to the penetration of water. The water absorption and sorptivity coefficient at 90 days was much lower than that at 28 days, indicating a more refined pore structure. This agrees with results obtained by Güneyesi and Gesoğlu [13], who observed that, water absorption decreases with increasing slag content. It was observed that at 28 days, there was a significant difference in the water absorption and sorptivity coefficient obtained for slag 1 compared to slag 2. However, as the curing duration was increased to 90 days, the difference diminished. This suggests that longer curing duration seem to aid the microstructural development of slag 2.

Table 5: Sorptivity coefficient (k) for 28 and 90 day old samples

	Sorptivity coefficient [k] ($x10^{-3}cm/s^{1/2}$)	
Mix	28 day	90 day
C42.5R	4.12 ± 0.08	2.25 ± 0.05
C52.5R + S1	2.08 ± 0.05	1.37 ± 0.04
C52.5R + S2	3.32 ± 0.09	1.85 ± 0.07

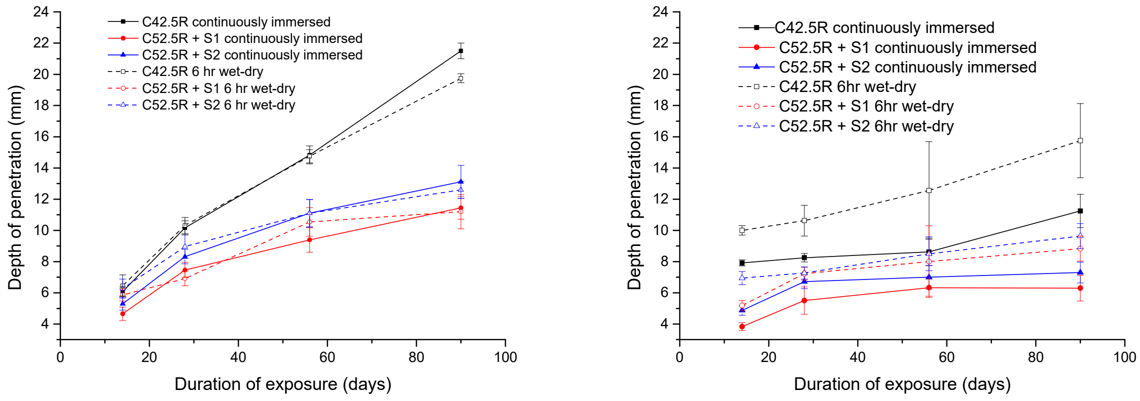


(a) (b)

Figure 4: Water absorption curves for (a) 28 day old samples (b) 90 day old samples

3.4 Chloride penetration

Figure 5 shows the depth of penetration of free chlorides after 14, 28, 56 and 90 days exposure in a 3% sodium chloride solution for mortar samples that were wet-cured for 7 and 28 days. This shows the impact of prolonged curing on the performance of the CEM I system and the slag blends. For both exposure conditions (continuously immersed and wet-dry cycling), prolonged curing prior to immersion led to a reduction in chloride penetration depth. This supports the calorimetric data and previous work by Whitaker et al. [15], that after hydration for 7 days, the degree of slag hydration would be low, and hence the microstructure would still be very porous. However, at 28 days when the microstructure was much more developed, there was less chloride ion ingress. Also, for both exposure conditions, the slag blends performed better than the CEM I system. The difference between the CEM I system and the blends is far greater than the difference between the different blends.



(a) (b)

Figure 5: Depth of chloride penetration for samples continuously immersed in sodium chloride solution and samples exposed to a 6-hr wetting and 6-hr drying cycle after initially wet-cured for (a) 7 days (b) 28 days

Longer curing durations appeared to amplify the effects of the exposure condition on chloride ingress. Samples which were cured for 28 days prior to exposure showed greater chloride ingress depths upon cyclic exposure than when exposed continuously. This effect was more pronounced for the CEM I samples compared to the slag blends. This is similar to results obtained by Ben Fraj et al [17] where they investigated the effect of saturation rate of concrete on chloride ingress by subjecting concrete specimens to wetting/drying cycles at 75% RH and continuously in contact with sodium chloride solution of 30 g/l for 1 month. Some of the samples exposed to the wetting/drying cycles were also sprayed with phenolphthalein to see if there was any form of carbonation. However, the results obtained for samples that had been exposed for 90 days showed no sign of carbonation. This suggests that the increased chloride ingress measured for the wetting/drying cyclic exposure is due to the combined effect of diffusion and capillary suction. For unsaturated concrete exposed to alternate wetting and drying cycles, the chlorides diffuse into the concrete during the wetting period by liquid pressure gradient. In the drying period, only water evaporates from the concrete surface while the salts remain in the concrete leading to an accumulation of chlorides [17], which then increases capillary suction [18, 19].

While the composition of the slag did not appear to have a significant effect on the strength development, it did play a greater role in determining the degree of chloride ingress. Slag 1 had a higher alumina content than slag 2, and was expected to have a higher chloride binding capacity [5, 20] and thus a much lower depth of chloride penetration. This was observed for samples that were cured for 7 days prior to exposure but when the curing duration was increased to 28 days the difference between the two slag blends was minimal. This also applied to the CEM I system. This is in correlation with the result obtained for the water absorption and sorptivity test. At 28 days, the microstructure is more developed and more resistant to the penetration of aggressive ions.

4. CONCLUSIONS

From the results obtained in this study, the following conclusions may be drawn:

- The strength performance of slag blends can surpass that of neat systems at later ages.
- Slag blends have better resistance to the penetration of aggressive ions than neat systems.
- The effect of change in chemical composition of slags on the performance of slag blends is felt more at shorter curing durations. At longer curing durations, there is no much difference in performance.
- Longer curing durations tends to improve the strength and transport properties of slag blends especially slags of lower reactivity.
- Slags of higher reactivity will give a better performance for slag blended systems requiring shorter curing durations.

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