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Effects of slag composition and temperature on the strength performance of slag blended cement mortars in composite chloride-sulphate environments

Joseph O. Ukpata and Leon Black
School of Civil Engineering, University of Leeds, UK

ABSTRACT

Major structures are often located near marine environments which expose them to attack from sea water containing mostly chlorides and sulphates. The compressive and flexural strength properties of ground granulated blast-furnace slag - blended cement specimens were investigated at temperatures of 20 °C and 38 °C, to assess their performances under typical arid and temperate marine climatic conditions. Slags, having Ca/Si ratios of 1.05 and 0.94, were blended with CEM I 52.5R at 30% replacement levels. The performances of the slag-blended cements were compared with CEM I 42.5R. Mortar samples measuring 40mm x 40mm x 160mm were cast using 0.5 water to binder ratio, pre-cured under water before exposure to combined solutions of chloride and sulphate. Compressive and flexural strengths were determined at specified ages of hydration between 1 and 28 days. Also, x-ray diffraction (XRD) and calorimetry analyses were conducted on paste samples to follow the hydration characteristics of the test binders. The results show that flexural strength increased for samples in combined test solution, and further indicated that the relationship between flexural and compressive strengths could be greatly influenced by temperature changes.

Keywords: Slag, chloride, sulphate, compressive strength, flexural strength.

1. INTRODUCTION

Reinforced concrete is a popular construction material globally. However, the strength and durability of reinforced concrete structures located in marine environments can be adversely impacted by the actions of compounds such as chlorides and sulphates present in sea water. While chlorides are known to cause the corrosion of embedded steel reinforcement bars, sulphates on the other hand tend to attack and weaken the binding property of cement in the concrete matrix due to the decalcification of the C-S-H gel (Bai et al., 2003) and ettringite precipitation. These conditions have grave implications for service life predictions.

The incorporation of supplementary cementitious materials (SCMs) such as ground granulated blast-furnace slag (GGBS or slag) in Portland cement (PC) has become popular due to their advantages in enhancing strength and durability. This is covered in BS EN 15167-1 (2006). Slag reacts with water and calcium hydroxide to produce additional C-S-H gel; contributing to strength development. Also, slag is known to refine the pore structure of concrete causing densification, and thus increased strength and durability. While the advantages of using SCMs to improve concrete strength and durability are well established, the combined influence of chloride and sulphate is still not clear.

Three conflicting views about the interaction between chloride and sulphate concerning sulphate attack have been identified in the literature, i.e. *chlorides accelerate sulphate attack, mitigate sulphate attack or have no significant effect* (Sotiriadis et al., 2013, Al-Amoudi et al., 1995). Sulphates reduce the ingress of chloride into concrete at early ages due to ettringite formation, which give rise to a compact microstructure. This trend is however reversed at later ages, possibly due to excessive formation of expansive ettringite crystals causing cracks that provide channels for rapid ingress of chlorides into concretes (Zuquan et al., 2007, Abdalkader et al., 2015). Frias attributed improved early-age performance to the partial inhibition of Friedel's salt as sulphate reacts with calcium aluminate hydrates preferentially to precipitate non expansive ettringite inside the pores (Frias et al., 2013). However, others have claimed that blending PC with slag results in greater chloride binding capacity due to increased Friedel's salt formation (Maes and De Belie, 2014).

2. Experimental details

2.1 Materials

CEM I 42.5R and 52.5R were used. Two slags, compliant with BS EN 15167-1 (2006), with the same physical properties, but CaO/SiO_2 ratios of 1.05 and 0.94 respectively (Table 1), were used to blend with CEM I 52.5R at 30% replacement. Natural sand sieved to maximum size of 2.0mm was used to prepare mortar samples. Deionised water was used for the mixes. Standard laboratory reagent grade sodium chloride and sodium sulphate were used to prepare test solutions.

Table 1. Properties of test Portland cements and slags

Property	**Unit**	**CEM I 42.5R**	**CEM I 52.5R**	**Slag 1 (S1)**	**Slag 2 (S2)**
LOI 950°C	%	2.12	1.37	(+1.66)	(+0.40)*
SiO_2	%	20.17	20.50	36.58	40.14
Al_2O_3	%	5.33	5.43	12.23	7.77
TiO_2	%	0.29	0.29	0.83	0.30
MnO	%	0.05	0.05	0.64	0.64
Fe_2O_3	%	2.65	2.51	0.48	0.78
CaO	%	63.01	63.43	38.24	37.90
MgO	%	1.45	1.51	8.55	9.51
K_2O	%	0.76	0.79	0.65	0.55
Na_2O	%	0.14	0.17	0.27	0.36
SO_3	%	3.33	3.43	1.00	1.47
P_2O_5	%	0.12	0.14	0.06	0.02
Total	%	99.42	99.62	99.88	99.43
Glass content	%	na	na	99.3	97.1
Density	g/cm^3	3.14	3.16	2.93	2.91
Blaine fineness	cm^2/g	3490	7357	5995	5540
D50	µm	16.29	9.43	11.56	12.90

2.2 Sample preparation and curing condition

Mortar prisms (40mm x 40mm x160mm) with binder to aggregate ratio of 1:3, and water to binder (w/b) ratio of 0.5 as shown in Table 2, were cast for compressive and flexural strengths. Similarly, $50mm^3$ mortar samples were prepared for chloride penetration depth tests. All the samples were demoulded after 24 hours and pre-cured under water for further 6 days followed by immersion in combined chloride (30g/l) and sulphate (3g/l) solution maintained at temperatures of 20°C and 38°C respectively up to test ages.

Table 2. Mix ratios

Mix	W/B ratio	CEM I		GGBS		Water	Sand
		42.5 R	52.5R	Slag 1	Slag 2		
A.	0.5	1	0	0	0	0.5	3
B.	0.5	0	0.7	0.3	0	0.5	3
C.	0.5	0	0.7	0	0.3	0.5	3

Also, paste samples of similar water to binder ratio (0.5) were cast in 8ml plastic vials for XRD analysis. The paste samples were exposed to sulphate and chloride-bearing test solutions as described earlier. Hydration was stopped by isopropanol solvent exchange at ages corresponding to strength tests and then kept under vacuum in a desiccator until analysis.

Hydration was followed by isothermal calorimetry. Paste samples were mixed for 2 minutes using vortex shaker before inserting into the calorimeter. Data was obtained for 28 days at 20 °C and 38 °C.

2.3 Test methods

Compressive and flexural strength tests were conducted in line with BS EN 196-1 (2005). Compressive strengths tests were determined using 500KN Avery Denison/Tonipact compression equipment, while flexural strengths were determined using 25KN Tinius Olsen equipment. Averages of 5 or 6 samples were reported for compressive strength, while flexural strengths were determined in triplicate.

Chloride penetration depths were determined up to 90 days of exposure. At specified periods, the mortar cube samples were split in the middle and sprayed with 0.1M silver nitrate ($AgNO_3$) which reacted with NaCl to form white AgCl. A total of 6 measurements were taken from 2 adjacent sides of one half using a ruler and sliding callipers. The average of 6 measurements was reported as chloride penetration depth (in mm).

3. Results and discussion

3.1 Effects of slag composition

Due to space constraints, only flexural strengths are reported. Figure 1 shows the flexural strength development for the mortar samples exposed to combined chloride – sulphate solution. Figure 2 shows relationship between compressive and flexural strengths. At 20°C, slag 1, the more basic slag with higher alumina content showed higher early strength gain compared to slag 2. This agrees with calorimetry heat flow results shown in Figure 3, and the glass contents and slag activity indices shown in Tables 1 & 3 respectively, in agreement with the literature (Winnefeld et al., 2015).

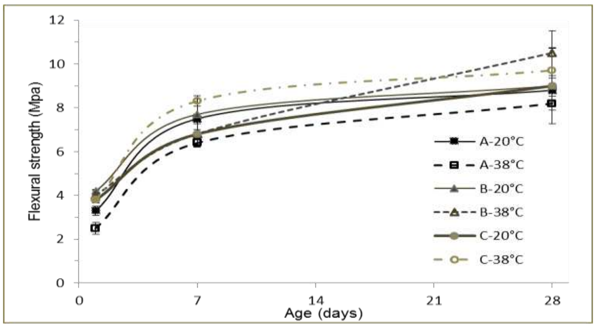

Figure 1. Flexural strength development at 20°C and 38°C for plain CEM I (A), CEM I + 30% Slag 1(B), and CEM I + 30% Slag 2 (C).

Table 3. Slag activity indices

Mix	Slag content (%)	Slag activity index (%)		% increase
		7 days	28days	
CS1	50%	80.4	95.1	18.28
CS2	50%	77.2	85.1	10.28

C = CEM I 52.5R, S1 = Slag 1, and S2 = Slag 2

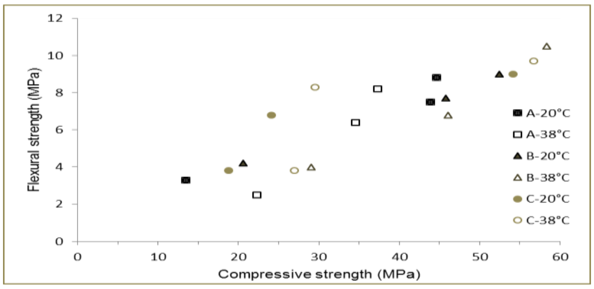

Figure 2. Relationship between Flexural strength and compressive strength.

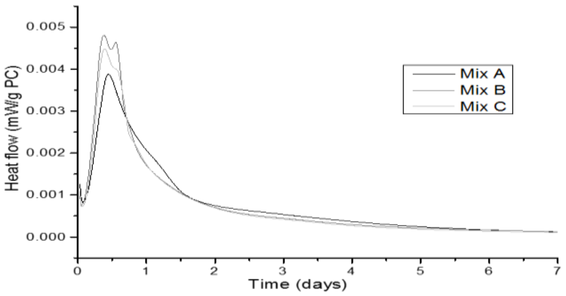

Figure 3. Calorimetry heat flow relationships of different mixes.

3.2 Effects of Temperature

The effects of increased temperature from 20°C to 38°C can be seen in Figures 1 & 4. It appears that increased temperature has a positive influence on strength of slag-PC mortars. A similar result was reported by Ogirigbo and Black (2015).

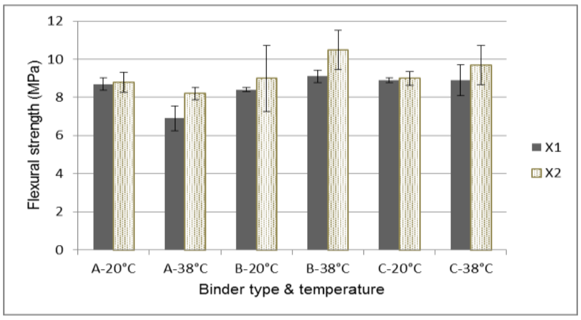

Figure 4. Comparison between 28days flexural strengths for samples cured under water (X1) and submerged in chloride-sulphate solution(X2).

3.3 Effects of exposure to composite chloride-sulphate solution.

Figure 4 compares 28-day strength at 20°C and 38°C for mortar samples submerged in test solution from age 7 to 28 days, and those left under water through the same period. There is a consistent trend in the flexural strengths, with samples exposed to chloride-sulphate solutions showing greater strengths than those in water. This suggests a synergy between chloride and sulphate in refining the microstructure of the matrix resulting in densification and increased strength as reported in Frias et al. (2013). It remains to be seen what effect will be seen at later ages.

3.4 Relationship between flexural and compressive strength

From Figure 2, flexural strengths showed a positive correlation with compressive strength and fits a power function of the form shown in equation 1, in line with previous studies (Ahmed et al., 2016).

$$f_s = b f_c^n \quad (1)$$

Where: f_s = flexural strength, f_c = compressive strength, b and n are coefficients which vary according to various materials properties as well as age of sample, environmental and curing conditions. From Table 4, b varies between 0.0023 and 0.58, while n varies from 0.70 to 2.51. These variations appear much wider than those reported in Ahmed et al. (2016). This may be attributed to the differences in temperature and materials used in this study. However, the coefficients obtained for the 3 mixes at 20°C tend to agree with the correlation reported in Ghrici et al. (2007), suggesting a similarity in behaviour between plain PC and slag-blended cement.

Table 4. Coefficients of correlation between FS and CS

Mix	Temperature (°C)	b	n	R^2
C	20	0.46	0.76	0.98
C	38	0.002	2.51	0.996
CS1	20	0.38	0.80	0.996
CS1	38	0.042	1.35	0.98
CS2	20	0.58	0.70	0.77
CS2	38	0.29	0.88	0.50

3.5 Chloride penetration in PC and slag blended mortar samples

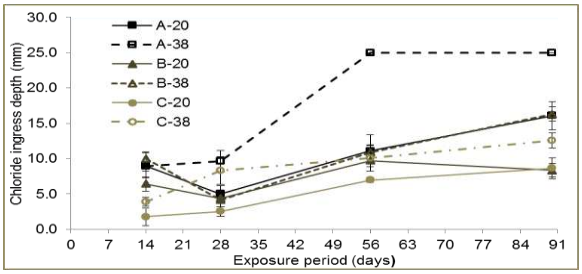

Figure 5. Chloride penetration depths with exposure periods.

Figure 5 presents the chloride penetration depths in 50mm^3 mortar samples up to 90 days' exposure to the combined chloride-sulphate test solution. The results show that slag blended mortars performed better than plain PC. At 20°C slag 2 performed initially better than slag 1. However, slag 1 performed ultimately better than slag 2. The more basic slag 1, with a higher alumina content, is expected to perform better due to its tendency for higher chloride binding capacity (Thomas et al., 2012). In comparison to findings by Ogirigbo and Black (2015) for exposure of similar mortar samples to pure chloride solution, chloride penetration depths from the combined chloride-sulphate test solution were generally less at 20 °C but greater at 38 °C.

3.6 XRD analysis

XRD analysis was performed on paste samples exposed to the combined chloride-sulphate solution compared with those in water to identify reaction products. From the XRD profiles shown in Figure 6, the formation of Freidel's salts and increased ettringite peaks can be observed for samples in the test solution, confirming the synergy of chloride and sulphate in refining the binder microstructure leading to the increased flexural strengths observed. Similar findings have been reported in related previous studies (Frias et al., 2013, Maes and De Belie, 2014).

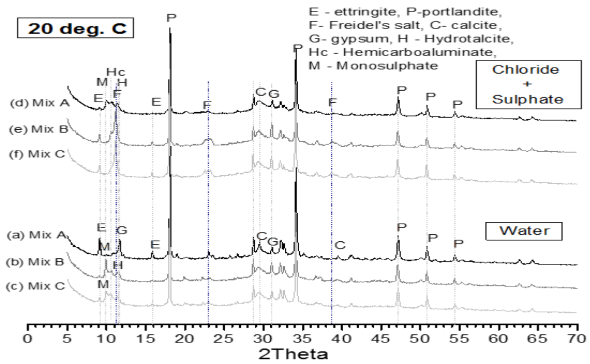

Figure 6. XRD of different pastes at 28 days, immersed in mixed solution of sodium chloride and sodium sulphate after 7 days pre-curing in water, and those left in water throughout.

4. Conclusion

- This study has shown that in composite chloride-sulphate solutions, slag-blended cement mortars generally perform better than plain Portland cement in strength properties and resistance to chloride ingress.
- More basic, alumina-rich slags ultimately showed the best performance.
- Temperature has a greater influence on the relationship between flexural strength and compressive strength than slag composition.
- Chloride ingress is influenced by temperature with higher temperature leading to greater chloride ingress.

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