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Influence of slag composition and temperature on the hydration and microstructure of slag blended cements



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HIGHLIGHTS

- Slag composition and curing temperature both influence the hydration of slag blends.
- Curing temperature plays a more significant role than composition.
- The compositional requirements of slags are more exacting at higher temperatures.
- More basic slags are preferred for use in tropical climates.

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ABSTRACT

GGBS is used extensively as a cement replacement material, reducing the carbon footprint of cement while potentially improving technical performance. However, standards consider hydration of slag composite cements only at 20 °C. This may not be applicable for use in tropical climates. This work has investigated the impact of GGBS composition and curing temperature on the hydration, microstructure and subsequent transport properties of such composite cements. Two slags, of differing compositions, were combined with a CEM I 52.5 R at 30% replacement. Paste samples were characterised by calorimetry, TGA, XRD and SEM to follow hydration and microstructural development. Mortar samples were used to follow strength development and water transport properties. All tests were carried out at temperatures of 20 and 38 °C. The higher temperature resulted in an increase in the degree of hydration of the slags, but had a deleterious impact on the microstructure. The more basic slag had higher strengths and greater degrees of hydration especially at the high temperature. The results showed that temperature had a much greater influence on the reactivity of the slags than the difference in chemical composition.

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1. Introduction

GGBS is a by-product from iron manufacture. The molten iron slag from the blast furnace is quenched with water or steam to produce a glassy and granular material, which is grounded to a fine powder to produce GGBS. The material has almost the same fineness and specific surface area as Portland cement [1]. The material is glassy in nature and latently hydraulic [2], and its use in mortar and concrete has been specified by various standards [3,4]. However, the nature of the ore, composition of the limestone flux, coke consumption and the type of iron being made are factors which affect the chemical composition of GGBS [5].

The hydraulicity of GGBS depends mainly on its chemical composition, glass content, particle fineness, alkalinity of the reacting

system and temperature at the early stages of hydration [6]. The hydraulicity increases with the particle fineness [7] and the glass content. Typical glass content of GGBS vary between 85 and 90% [8]. BS EN 197-1:2011 [9] specifies that at least two-third of the mass of the slag must be glassy, although research data show that slag samples with as little as 30–65% glass contents are still suitable [10].

The oxides of calcium, magnesium and aluminium are known to increase the hydraulicity of GGBS, while those of silicon and manganese decrease it [11]. MgO has the same influence as CaO up to about 11% by weight [5]. Increasing the Al₂O₃ content to 13% and above will result in an increase in early strength and a decrease in the later strength [12]. Wang et al. [13] observed a positive correlation between the Al₂O₃ content and the reactivity of the slags, for slags having a CaO content greater than 37%. In another study by Ben Haha et al. [11,14], it was observed that the reactivity of the slags increased with the magnesia content. As they increased the alumina content, the reactivity of the slags was reduced at

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Table 1
Oxide composition of the starting materials.

Property	Unit	CEM I 52.5 R	Slag 1	Slag 2
LOI at 950 °C	%	2.54	(+1.66) ^a	(+0.40) ^a
SiO ₂	%	19.10	36.58	40.14
Al ₂ O ₃	%	5.35	12.23	7.77
TiO ₂	%	0.25	0.83	0.30
MnO	%	0.03	0.64	0.64
Fe ₂ O ₃	%	2.95	0.48	0.78
CaO	%	62.38	38.24	37.9
MgO	%	2.37	8.55	9.51
K ₂ O	%	1.05	0.65	0.55
Na ₂ O	%	0.05	0.27	0.36
SO ₃	%	3.34	1.00	1.47
P ₂ O ₅	%	0.10	0.06	0.02
Sum at 950 °C	%	99.50	99.88	99.43

^a The sample was oxidized with HNO₃ before the determination of LOI.

Table 2
Crystalline phases of the cementitious materials.

Phase	Unit	CEM I 52.5R	Slag 1	Slag 2
Alite, C ₃ S	%	62.1		
Belite, C ₂ S	%	8.9		
Aluminate, C ₃ A	%	9.1		
Ferrite, C ₄ AF	%	8.5		
Calcite	%		0.3	0.5
Anhydrite, AH	%	0.6		
Hemihydrate, HH	%	2.4		
Gypsum	%	1.7		
Merwinite	%		<0.1	2.3
Akermanite	%		0.2	<0.1
Illite	%		0.2	<0.1
Gehlenite	%		<0.1	<0.1
Glass content	%		99.3	97.1
Others	%	5.0		
Total	%	100.1	100	100

Table 3
Physical properties of cementitious materials.

Property	Unit	CEM I 52.5 R	Slag 1	Slag 2
Density	g/cm ³	3.18	2.94	2.95
Blaine	m ² /kg	571	449	409
Particle size, d50	µm	–	11.0	11.9

early ages, but became similar at later ages beyond 28 days. However, of the three slags they studied, the CaO content of the two high alumina slag was less than 37%. For other oxides like P₂O₅, the influence depends on the clinker type and test age, but generally has a positive influence beyond 28 days of curing. Oxides of tin and iron, as well as sulphur, seem not to have any effect [5].

Ratios of these oxides have been used by various standards to assess the hydraulicity of a slag. For example, EN 197-1:2011 prescribes that for GGBS, the (CaO + MgO)/SiO₂ ratio by mass must exceed 1 [9]. Several workers [5,10,15], have also suggested other oxide ratios, some of which have been shown in Table 4. However, previous studies [10,15–17] have shown that these ratios do not necessarily give accurate prediction of a slag's performance. More so, it becomes more complex when other factors like changes in temperature are considered.

The contribution of GGBS to the heat of hydration increases with temperature, due to the accelerating effect of temperature on slag reactivity [18–21], and as a result has been reported to be very beneficial for use in hot weather concreting [5]. For example, Wu et al. [20] studied the influence of temperature on the early

Table 4
Basicity and activity indices of the slags.

	Requirement for good performance	Slag 1	Slag 2
<i>Basicity/hydraulic index</i>			
CaO/SiO ₂	1.3–1.4 [10]	1.05	0.94
(CaO + MgO)/SiO ₂	>1.0 [9]	1.28	1.18
(CaO + MgO + Al ₂ O ₃)/SiO ₂	≥ 1.0 [28]	1.61	1.37
<i>Activity index (%)</i>			
7 day	>45% [3]	58.8	53.6
28 day	>70% [3]	84.3	84.3

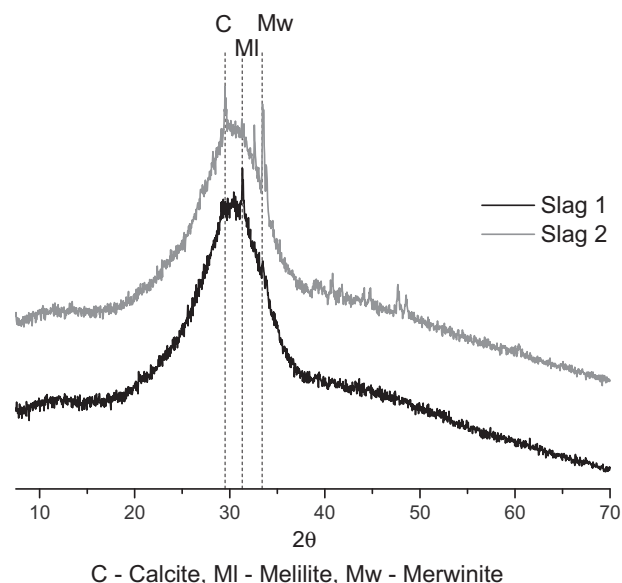
stage hydration of PC slag blends using isothermal calorimetry and chemical shrinkage. They used three different PC slag blends comprising of 40, 50 and 65% of slag. All three blends were hydrated at temperatures of 15, 27, 38 and 60 °C. They observed that the slag reacted more slowly than the PC component at 15 °C and at an accelerated rate at temperatures above 27 °C. Substantial portions of the slag had reacted within the first 24 h at temperatures of 27 °C and above. Similar findings were also reported by others [22–27].

In all these studies, the issue of how changes in temperature affect the hydration process of slags of different chemical compositions was not fully explored. This will be of importance due to the widespread use of GGBS as a cementitious material in tropical climatic regions. This paper looks at how variation in chemical composition of slag coupled with a change in temperature will affect the hydration process of slag blended cements, and how this relates to the microstructure and subsequent transport properties.

2. Experimental programme

2.1. Materials

Two slags were combined with a CEM I 52.5 R at 30% replacement level to produce slag blends designated as S1 and S2 respectively. Both slags had similar physical properties, with different chemical compositions (notably the alumina and silica contents). The oxide and phase composition of the as-received slags and cement are shown in Tables 1 and 2 respectively. The X-ray diffraction showing the amorphous and crystalline phases and the particle size distribution of the slags are shown in Figs. 1 and 2

**Fig. 1.** XRD of the as-received slags.

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