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Influence of limestone on the hydration of ternary slag cements

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ABSTRACT

The hydration kinetics, microstructure and pore solution composition of ternary slag-limestone cement have been investigated. Commercial CEM I 52.5 R was blended with slag and limestone; maintaining a clinker to SCM ratio of 50:50 with up to 20% slag replaced by limestone. The sulphate content was maintained at 3% in all composite systems. Hydration was followed by a combination of isothermal calorimetry, chemical shrinkage, scanning electron microscopy, and thermogravimetric analysis. The hydration of slag was also followed by SEM image analysis and the QXRD/PONKCS method. The accuracy of the calibrated PONKCS phase was assessed on slag and corundum mixes of varying ratios, at different water/solid ratios. Thus, the method was used to analyse hydrated cement without dehydrating the specimens. The results show that the presence of limestone enhanced both clinker and slag hydration. The pore volume and pore solution chemistry were further examined to clarify the synergistic effects. The nucleation effects account for enhanced clinker hydration while the space available for hydrate growth plus the lowering of the aluminium concentration in the pore solution led to the improved slag hydration.

1. Introduction

Recent studies have noted synergies between alumina rich supplementary cementitious materials (SCMs) and limestone in ternary blended systems [1,2]. This interaction has the potential to maximise the respective contribution of all the constituent materials [3–5] to cement performance.

Limestone interacts with the other components of the ternary blend in two ways; as a filler and as an active reactant. As a filler, limestone increases the effective water available for hydration and consequently space [6] for hydrate growth. Secondly, limestone provides nucleation sites during hydration [7,8]. Limestone is also an active participant of the hydration reactions. Calcite present in limestone reacts with alumina to form hemi- and monocarboaluminate phase. This results in the stabilisation of ettringite [9–11], thus reducing porosity and increasing compressive strength.

In composite cement, the alumina content may be higher than in the neat cement paste leading to increased formation of AFm phases [9–12]. This can lead to higher compressive strength as previously reported for fly ash and calcined clay composite cement [4,13]. However, in slag composite cements the positive effect of limestone on the strength may be counter-balanced by the formation of hydrotalcite [14,15], thus

limiting the available alumina. Therefore, since demand for these cement is growing [16,17], understanding the reaction mechanisms of composite cement containing slag and limestone is of high importance.

The impact of calcium carbonate on the hydration of ternary slag-limestone cement is the focus of the present study. A multi-technique approach was applied to study hydration. A PONKCS phase for GGBS was introduced in the Rietveld refinement of X-ray diffraction data (XRD) obtained from freshly ground samples without hydration stopping. XRD was complemented by isothermal calorimetry, chemical shrinkage, thermogravimetry (TG). Additionally, samples were investigated by scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) and supported by image analysis (IA). Microstructure evolution was assessed by Mercury intrusion porosimetry (MIP). The observed changes in reaction kinetics and phase assemblages have been related to the pore structure and pore solution chemistry analysis over the course of hydration.

2. Experimental details

2.1. Materials

The cement investigated were prepared from commercial CEM I

Table 1
Oxide composition of raw materials (% weight).

Material	CEM I 52.5 R [C]	Slag [S]	Limestone [L]
SiO_2	20.37	34.87	2.00
Al_2O_3	5.56	11.62	0.80
TiO_2	0.29	1.11	0.04
MnO	0.05	0.27	0.03
Fe_2O_3	2.49	0.45	0.32
CaO	62.10	41.82	53.13
MgO	1.65	5.82	0.64
K_2O	0.65	0.47	0.10
Na_2O	0.07	0.07	–
SO_3	3.54	3.13	0.07
P_2O_5	0.14	0.02	0.04
LOI	1.99	1.45	42.30
Blaine fineness, m^2/kg	593	454	328

52.5 R, together with slag and limestone. The chemical composition and specific surface area of the materials, determined by XRF and Blaine measurements respectively, is shown in Table 1. The mineralogical compositions of the cement and the supplementary materials are shown in Tables 2 and 3 respectively. The particle size distribution of all the constituent materials, measured by laser granulometry, is shown in Fig. 1. The mix proportions used are detailed in Table 4.

The clinker to SCM ratio was maintained at 50:50, with limestone considered as an SCM where incorporated. Ground anhydrite was added to the composite cement and the binary quartz mix to achieve 3% total sulphate content in each mix. The 1.9% calcite in the CEM I 52.5 R was accounted for in calculating the total limestone content for the ternary blends. The formulated cements were homogenised in a laboratory ball mill for at least 3 h using polymer balls to prevent further grinding of the materials.

2.2. Methods

Paste samples were prepared according to the procedure for mortar preparation, as described in EN 196-1 but without aggregates. Care was taken to ensure homogeneous mixing of paste by additional hand mixing.

The slag containing samples were investigated by the experimental program comprising of a study of the hydration kinetics, pore solution concentrations and the microstructure formed. Parallel measurements were performed on mixes in which slag and/or limestone were replaced with quartz of similar fineness. The objective here was to isolate the filler effect from the SCM reaction as in [18].

Isothermal calorimetry was conducted on 9.0 g of paste prepared with 0.5 w/b ratio. The heat of reaction was measured continuously for 28 days at 20 °C using an 8-channel TAM Air calorimeter. Reference channels were filled with ampoules containing 6 g of quartz mixed with 3 g of deionized water.

Samples for XRD, TG, MIP and SEM were cast into 15 ml plastic vials, sealed and rotated for the first 12 h to prevent bleeding. Samples were then stored in a water bath which was maintained at 20 °C until testing or hydration stopped. XRD scans were performed on freshly ground samples aged 0.5 to 180 days without hydration stopping. Specimens for thermal analysis and MIP were hydration stopped using a modified solvent removal technique [12], while those for scanning electron microscopy (SEM) were hydration stopped by freeze-drying. The solvent exchange regime involved grinding or crushing the

Table 3
Mineralogical composition of supplementary materials (% weight).

Phase	Calcite	Quartz	Dolomite	Amorphous
Slag (%)	2.4	0.1	–	97.5
Limestone (%)	96.6	0.4	1.0	2.0
Quartz (%)	0.5	99.5	–	–
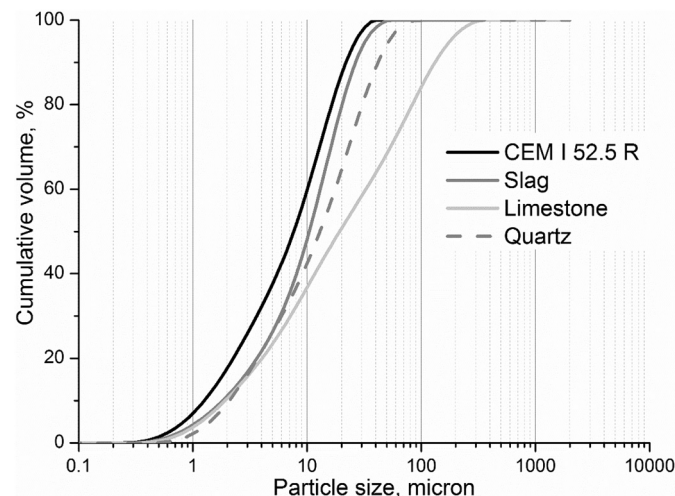
Fig. 1. Particle size distribution of constituent materials, determined by laser granulometry. Note: quartz* substituted for limestone as appropriate.

Table 4
Composition of mixes investigated (%).

Mix designation	CEM I 52.5 R	Slag/quartz	Limestone/quartz	Anhydrite
CS	50.68	47.08	–	2.24
CQ	51.84	48.16	–	–
CQs	50.68	47.08	–	2.24
CS-L	51.18	38.03	8.55	2.24
CS-Q	51.18	38.03	8.55	2.24
CS-2L	51.18	28.53	18.06	2.24

Note: the commercial CEM I 52.5 R cement contained 1.9% calcite and 4.8% calcium sulphate, which were accounted for when maintaining a 50:50 clinker: SCM ratio.

hydrated cement into 1–2 mm particles in isopropanol (IPA) for 20 min, and filtering off the IPA under gravity in a glove-box which was kept free of CO_2 by purging with nitrogen gas. The residue was rinsed with ether before drying at 40 °C on a pre-heated glass plate for 20 min. Following hydration stopping, samples were stored in mini-grip bags in the glove-box until analysis.

XRD data were acquired on a PANalytical MPD Pro using a CuKα anode operating at 40 kV and 40 mA equipped with a X'Celerator detector, over a range of 5–80 °2θ using a step size of 0.0334°. Automatic incident divergence and fixed anti-scatter slits were used together with a 10 mm incident beam mask. The continuous scan mode was adopted for all data acquisition. The data analysis was performed on TOPAS Academic software v4.2.

A first order Chebyshev polynomial background function was adopted for calibration purposes. The fundamental parameter approach was used to model the slag phase. This approach combined instrument and sample contributions to all peaks [19]. The slag phase was

Table 2
Clinker content of CEM I 52.5 R (% weight).

Phase	$C_3S[M3]$	β-C_2S	C_3A	C_4AF	Calcite	Anhydrite	Bassanite	Others
Content (%)	58.1	14.3	9.2	6.7	1.9	1.7	3.0	5.1