Proceedings Paper:

Adu-Amankwah, S, Black, L orcid.org/0000-0001-8531-4989 and Zajac, M (2014) Slag Hydration in composite cements. In: Bernal, SA and Provis, JL, (eds.) Proceedings of the 34th Cement and Concrete Science Conference. 34th Cement and Concrete Science Conference, 14-17 Sep 2014, University of Sheffield, Sheffield, UK. , pp. 321-324.

This is an author produced version of a paper presented at the 34th Cement and Concrete Science Conference.

34th Cement and Concrete Science Conference **Paper Number 164**
14-17 September 2014
University of Sheffield

Slag Hydration in composite cements

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ABSTRACT

Despite reported synergies between alumina rich supplementary cementitious materials (SCMs) and limestone, previous studies have focused on up to 5% limestone content. Slag hydration in the presence of 10% limestone is reported in this paper. Hydration was followed through chemical shrinkage, calorimetry, thermal analysis, electron microscopy and X-ray powder diffraction. The results show that limestone incorporation improves slag hydration.

1. INTRODUCTION

Ternary blended OPC-limestone and alumina rich SCMs have attracted significant research interest recently. These systems offer environmental and technical advantages [1]. Previous studies have however considered up to 5% total limestone content [2, 3].

The hydration mechanisms and performance of Portland cement (PC)-slag and PC-limestone binary cements are well documented [2-5]. Slag is latently hydraulic while limestone is a non-pozzolanic SCM; yet both influence clinker hydration physically and chemically. At early age, SCMs provide nucleation sites for clinker hydration and also increase the effective water/binder ratio. When the particle sizes have been optimized, SCMs also enhance the packing density [6].

Compositionally, carbonates react with aluminates following depletion of sulphates, thus preserving ettringite [2]. Coexistence of ettringite and carboaluminates has been observed in limestone ternary blends [2, 3]. Irrespective of the limestone content, hemi-carboaluminnate has been shown to form initially. The conversion of hemi to mono-carbonaluminates is however inhibited at lower limestone content [7]. It follows that alumina availability is the precusor to carbonate incorporation into hydration products.

	C2	S1	L
SiO_2	20.37	34.87	2.00
Al_2O_3	5.56	11.62	0.80
MgO	1.65	5.82	0.64
CaO	62.10	41.82	53.13
K_2O	0.65	0.47	0.10
Na_2O	0.07	0.07	0
SO_3	3.54	3.13	0.07

Unlike OPC-limestone systems, the aluminate content is both higher and discharge is continuous over a longer duration in composite slag cements. Carbonate incorporation is therefore expected to improve as slag hydrates.

The interaction between slag and limestone content exceeding 5% in composite cements is still unclear. This paper seeks to evaluate the interaction and its effect on slag hydration, using a combination of heat flow, chemical shrinkage, and BS-SEM imaging analysis.

2. EXPERIMENTAL DETAILS

Three binders were investigated: CEM I 52.5 R, CEM I 52.5 R plus slag, and CEM I 52.5 R plus slag and 10% limestone, herein designated C2, C2S1 and C2S1-10L respectively. The clinker to supplementary materials ratio in the composite cements was 50:50, while the sulfate content was maintained at 3% in all cements by the addition of ground anhydrite. No extra sulfate was however added in the blends without slag. The mixes were blended and homogenized in a laboratory roller ball mill.

In order to isolate the filler effect from actual SCM reaction, parallel calorimetry and chemical shrinkage runs were performed in which the slag was replaced with quartz. Particle size distribution and XRF composition of the studied materials are shown in Figure 1 and

Table 1 respectively. Specimens for compressive strength measurement were prepared according to EN 196:1. Specimens were cured in saturated lime solution after removal from moulds and tested at 1, 2, 7 and 28 days.

Hydration was followed by isothermal conduction calorimetry, chemical shrinkage, TGA, XRD and SEM. All hydration studies were conducted on paste samples prepared at 0.5 w/b ratio. Methodology for conduction calorimetry and chemical shrinkage measurements have been described previously [9].

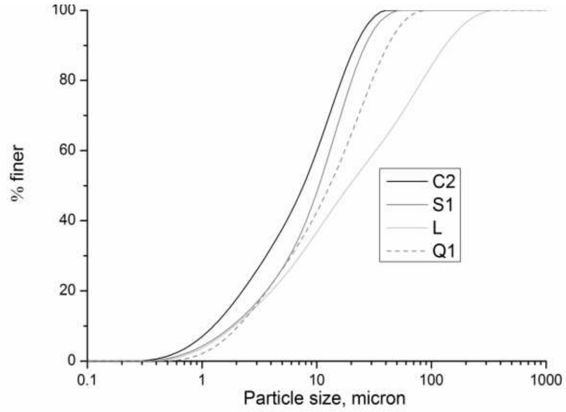

Figure 1 Particle size distribution of materials

	C2	S1	L
SiO_2	20.37	34.87	2.00
Al_2O_3	5.56	11.62	0.80
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Table 1 Chemical composition of materials

XRD was conducted on freshly ground samples without hydration stopping, using a PANanalytical MPD Pro diffractometer in a Bragg-Brentano configuration and CuKα radiation.

Samples for SEM analysis were freeze-dried. Those for TGA were hydration stopped by solvent exchange [7]. The solvent exchange regime was carried out in a CO_2 free environment and involved 10mins of grinding in isopropanol followed by 10mins rinsing in ether. The process was completed by drying samples for 20mins on a preheated glass slide at 40ºC. TG measurements were made on 15-18mg powder at a heating rate of 20ºC/min.

3. Results

3.1. Kinetics of hydration

Figure 2 shows heat flow recorded from each sample. The composite cements showed shorter induction periods and accelerated alite hydration. The alite peak intensity (I) is similar in the two composite cements as well as the reference quartz-blends. The second set of peaks (II and III) attributable to the reaction of the aluminate phases is influenced by the filler and composition of SCMs. In the slag blends, two distinct aluminate peaks are apparent while a single but intensified aluminate peak is seen in the quartz blends. The first aluminate peak in C2S1 is less distinct, appearing to be merged with the alite peak. The secondary aluminate peak (III) is not present in the quartz blends but conspicuous in the presence of slag-limestone blend. This effect however seems to be associated with the limestone-sulfate interaction on the aluminate reaction. Similar observations have been reported for OPC-15% limestone mixes [7].

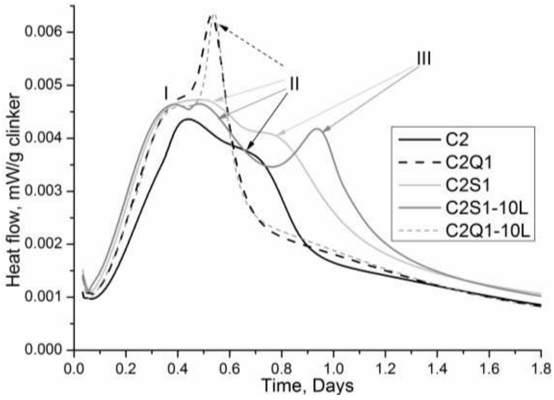

Figure 2: Heat flow rate of the investigated cements, per gram of clinker

It follows from the above that, hydration of composite cements differ from 100% OPC systems in two regards; the filler effect on clinker hydration and the reaction of the SCM plus limestone with clinker hydrates. Finer slag and limestone particles provide heterogeneous nucleation sites for the growth of cement hydrates [8]; explaining the accelerated alite hydration in the composite cements. Limestone and slag also accelerate hydration of both C_3A and C_4AF [3]. In OPC-limestone systems, additionally dissolved aluminates react with carbonates rather than sulphates bound in ettringite. The uptake of carbonates may be enhanced by the availability of aluminate species which emanate from slag hydration.

3.2. Degree of hydration

Chemical shrinkage and isothermal conduction calorimetry were used to extract heat and volumetric contributions from slag in the composite cements. Backscattered SEM images meanwhile were analyzed to quantify the degree of hydration of clinker.

SEM image analysis (**Error! Reference source not found.**) showed clinker hydration to be accelerated at early age in the composite cements, as reported previously [2, 3], e.g. at 2 days the proportion of hydrated clinker was measured to be 74%, 80% and 84% in C2, C2S1 and C2S1-10L respectively. However, at 28days, approximately 90% of clinker has hydrated in all three mixes.

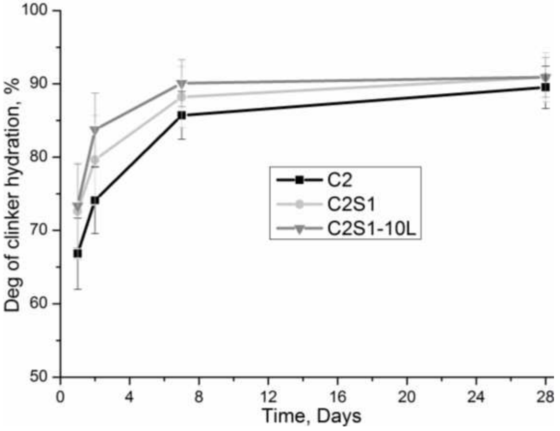

Figure 3 Effect of limestone on clinker hydration: SEM-image analysis

The contribution of slag to chemical shrinkage and the cumulative heat flow are shown in **Error! Reference source not found.** A & B. Similar trends are observed from both techniques. With respect to the clinker content, heat and shrinkage evolution are similar in C2S1 and C2S1-10L. The limestone appears to exert slightly lesser filler effect on clinker hydration compared to quartz. The higher fraction of coarse particles in limestone (Figure 1) may account for the observation. The effect on hydration however becomes clearer upon isolating the filler and normalizing by the slag content (Figure 5). The results suggest enhanced slag hydration in the presence of limestone.

3.3. Hydrates formed

The hydration products were investigated by TG, and XRD. The results obtained are shown in Figures 6-7. DTG and XRD confirm the existence of ettringite (AFt) after one day of hydration in all samples. Figure 3 (A-C) shows that, the addition of 10% limestone increased the amount of C-S-H and AFt formed. This effect was greatest at early age.

Also noteworthy is the absence of carboaluminate in C2S1-10L at 1 day (from both DTG and XRD). This has been attributed to slower dissolution of carbonates compared to sulphates. However, hemi-carboaluminates are observed in C2 and C2S1 suggesting a different mechanism may be responsible. With a constant 3% calcium sulphate in samples, a slightly higher effective SO_3/Al_2O_3 ratio in C2S1-10L may explain the inhibition of hemi-carboaluminates at 1 day [7]. However, slag hydration increases the alumina concentration in the matrix which subsequently combines with the slowly dissolving carbonates.

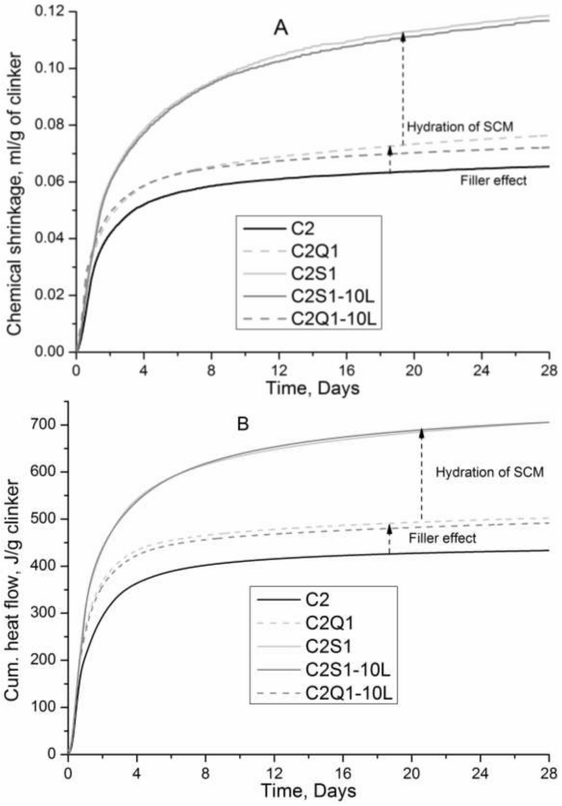

Figure 4 Effect of limestone on composite cement hydration: A – chemical shrinkage, B - calorimetry

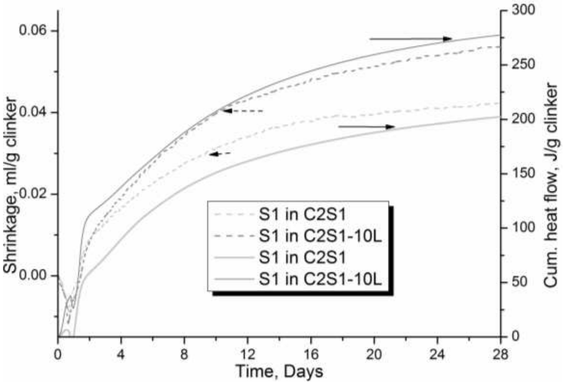

Figure 5 Effect of limestone on slag hydration: chemical shrinkage and calorimetry

Limestone consumption in C2S1-10L can be seen from Figure 3 (D). Insignificant uptake of carbonates is observed up to 2 days. Hemi-carboaluminate existence in C2S1-10L after 2 days is also evident from the DTG and XRD data. Further carbonate consumption results in the formation of mono-carboaluminates which is noticeable at 28days (**Error! Reference source not found.**). This is in agreement with previously reported thermodynamic data [2, 8].

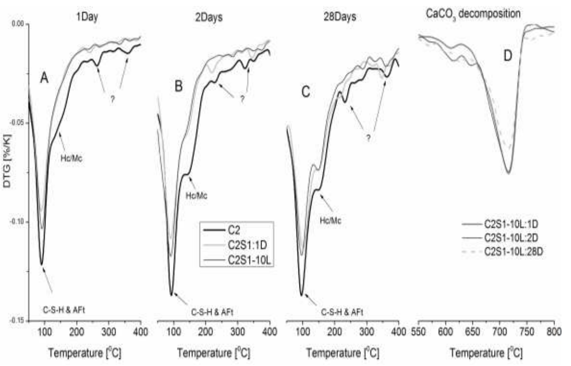

Figure 3 Thermal analysis: Effect of limestone on slag hydration

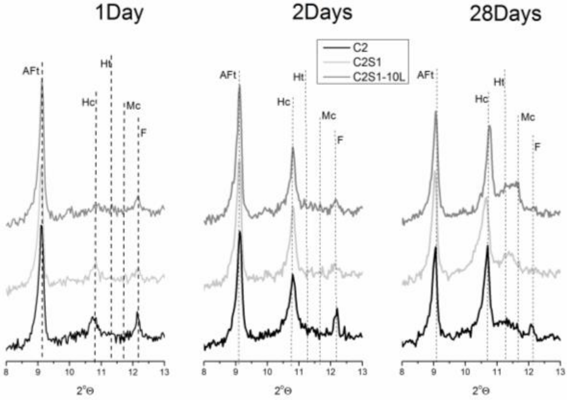

Figure 7 XRD: Effect of limestone on slag hydration

3.4. Compressive strength evolution

The results of compressive strength measurements are shown in **Error! Reference source not found.**. As expected at early age, strength development is slower in the composite cements (C2S1 and C2S1-10L) compared to the reference cement (C2). In the composite cements, a slightly higher compressive strength was observed in C2S1-10L up to 7 days.

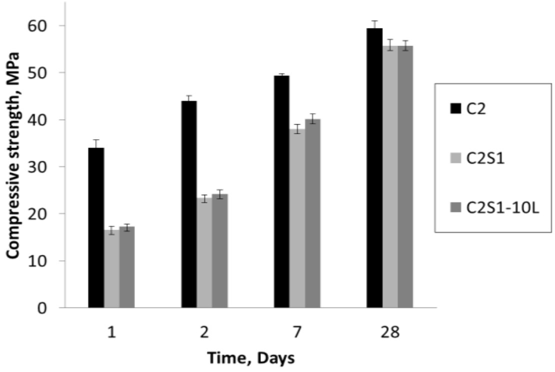

Figure 8 Compressive strength: Effect of limestone on slag hydration

The effect of the 10% limestone addition was less visible at 28 days. The improvement in compressive strength in the limestone ternary blend agrees with the observations from the hydration studies. A slightly higher C-S-H and AFt content, coupled with enhanced clinker and slag hydration may account for the higher compressive strength at early age.

4. Conclusions

The effect of 10% limestone addition on slag hydration has been investigated. Chemical shrinkage and calorimetry data show improved slag hydration while backscattered SEM image analysis show accelerated clinker hydration at early age. Hemi-carboaluminates were only observed in the limestone blend after 2 days of hydration. The higher volume of the preserved ettringite coupled with additional C-S-H gave rise to higher compressive strength in the limestone ternary blend. Thus, the addition of 10% limestone has a positive effect on slag and clinker hydration especially at early age.

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