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The Microstructure of Composite Slag-Limestone Cements

1. Introduction

Limestone-bearing composite cements have attracted significant research interest recently [1-4]. These systems offer environmental and technical advantages [5, 6]. Several authors have reported on the relationships between composition, hydration and microstructure [6-8] on one hand and on composition and durability [9] on the other. The enhanced hydration and microstructural changes arise from physico-chemical effects.

Limestone influences clinker hydration by providing seeding for C-S-H as well as the space for C-S-H growth [10, 11]. Recent studies have also observed synergy between high alumina SCMs and limestone [3, 4]. The interaction is not fully understood yet. Suggested explanations include enhanced clinker hydration with the attendant higher levels of portlandite [12]. However, the enhanced synergistic effects even at higher limestone levels [13], makes the dominance of the aforementioned mechanism debatable. Higher limestone content potentially increases the limestone-clinker inter-particles spacing [14]. This dilutes the hydrating matrix rather than facilitating C-S-H nucleation. High levels of calcium, potentially arising from limestone dissolution has also been suggested recently [10]. This has implications on the pore solution pH required for SCM reaction.

With regards to the hydrates in limestone containing cements, increased portlandite and C-S-H with high Ca/Si ratios have been reported elsewhere [15]. Additionally, dissolved aluminates react with carbonates to form carboaluminates [4, 16]; preserving ettringite [6, 7]. Irrespective of the limestone content, hemi-carboaluminate forms initially but converts to mono carboaluminates with time depending on the proportions of calcite and aluminates [17]. This conversion is however inhibited at lower limestone content [7].

Alumina availability as a precursor to limestone reaction is well documented [4, 7]. However, the impact of limestone on the supply of aluminates is not fully understood. This paper therefore investigates slag reactivity at varying limestone levels.

2. Experimental program

2.1. Raw Materials

Four binders were investigated: commercial CEM I 52.5 R, according to European standards EN 197-1 (designated as C), a cement-slag blend (CS) and cement-slag blends containing either 10% or 20% limestone (CS-10L and CS-20L respectively).

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The composition of the materials obtained through XRF and particle size distribution measured by laser granulometry are shown in **Table 1** and **Figure 1** respectively. The clinker to supplementary materials ratio in the composite cements was 50:50. The sulfate content was also maintained at 3% in all cements by the addition of ground anhydrite. No extra sulfate was however added to the blends without slag. The mixes were blended and homogenized in a laboratory roller ball mill for 3 hours.

Table 1 Chemical composition of raw materials

Compositions	SiO ₂	Al ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	SO ₃	Blaine (kg/m ²)
CEMI 52.5R	20.37	5.56	1.65	62.10	0.65	0.07	3.54	593
Slag	34.87	11.62	5.82	41.82	0.47	0.07	3.13	454
Limestone	2.00	0.08	0.64	53.13	0.10	0	0.07	328

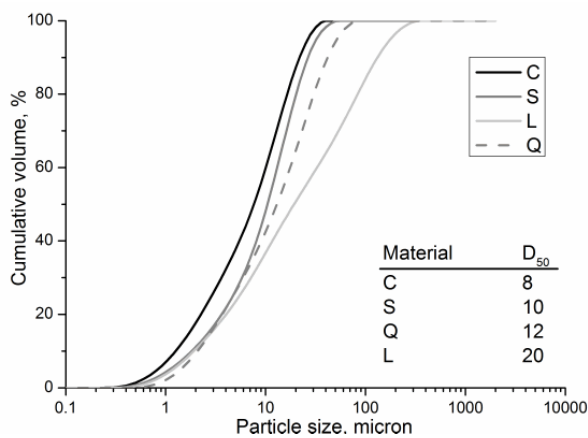


Figure 1 Particle size distribution of constituent materials

In order to isolate the filler effect from actual SCM reactions, parallel calorimetry and chemical shrinkage runs were performed in which the slag and limestone were alternately replaced with quartz of similar particle gradations (**Figure 1**).

2.2. Experimental Process

Compressive strength tests were carried out according to EN 196-1 after 1, 2, 7, 28 and 180 days.

Hydration was followed by isothermal conduction calorimetry, chemical shrinkage, x-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Isothermal calorimetry was conducted on 9g 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 9g of quartz paste also prepared with a 0.5w/b ratio. Chemical shrinkage was assessed according to the method described previously [18, 19]. Specimens for XRD were not hydration stopped while those for SEM were hydration stopped by freeze-drying.

3. Results and discussion

Results from compressive strength tests on the investigated binders are shown in **Table 1**. As expected at early age, strength development was slower in the composite

cements compared to the reference cement. At later ages (≥ 28 days), compressive strength in the composite cements containing up to 10% limestone were comparable to the 100% CEM I system. This is consistent with the literature [4, 20].

The rates of heat flow of the investigated mixes normalized to the clinker content are shown in **Figure 2**. Shortened induction and enhanced alite hydration was observed in all mixes other than the CEM I. The second set of peaks, attributable to the reaction of the aluminate phases was clearly influenced by the presence and composition of the SCMs [6, 21].

Table 1 **Compressive strength development over time**

Age (Days)	C	CQ	CS	CS-10L	CS-20L
	MPa				
1	33.5	11.0	16.6	17.3	15.6
2	43.7	15.9	23.4	24.2	22.9
7	49.5	22.1	38.9	40.1	35.4
28	59.6	26.2	55.3	55.7	48.0
180	62.0	30.3	66.9	63.4	56.3

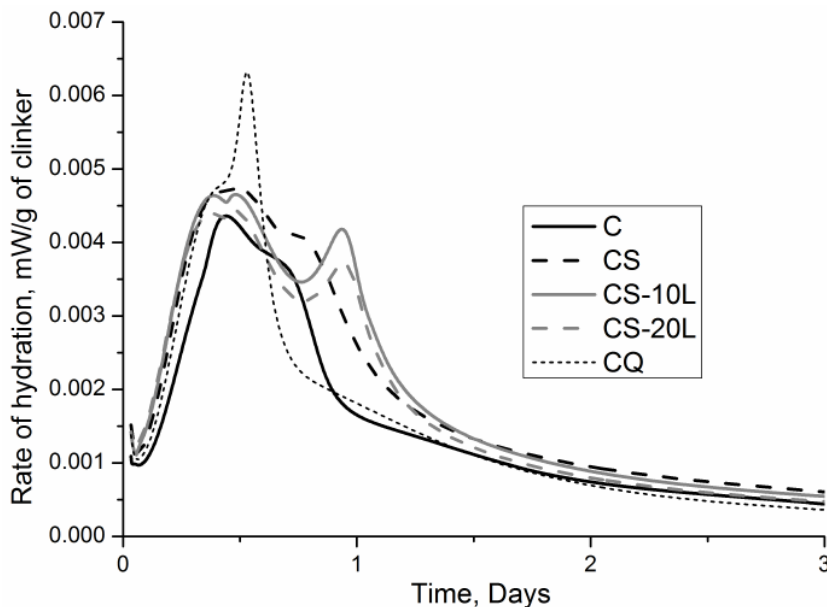


Figure 2 **Effect of limestone on the heat flow (normalized by the clinker content)**

A comparison of the XRD patterns of the investigated systems is shown in **Figure 3**. The diffractograms have been presented focussed on $8-13^\circ 2\theta$. This was chosen to highlight the differences in the AFt and AFm phases for the investigated mixes. Ettringite (AFt) was observed after 1 day with similar reflection intensities in all investigated mixes. The AFt intensities could not be distinguished qualitatively in the

cements containing additional limestone. Moreover, a slight decrease in the ettringite reflection intensities was observed in C and CS after 7 days. These did not however result in the formation of visible sulphate-bearing AFm peaks as additional aluminates dissolved [22, 23]. The formation of hemicarboaluminate was accelerated in the CEM I mix (≥ 1 day). The CEM I contained approximately 2% limestone which was interground with clinker during production. Conversion of hemi to monocarboaluminate was obvious in all composite cements after 7 days. Hemi- and monocarboaluminate reflections dominated the limestone containing blends compared to C and CS. A clear distinction between 10% and 20% limestone blended cements was in the proportions of hemi- and monocarboaluminates formed. The data suggested that, hemicarboaluminate was dominant in the CS-10L system while monocarboaluminate was prevalent when there was 20% limestone present.

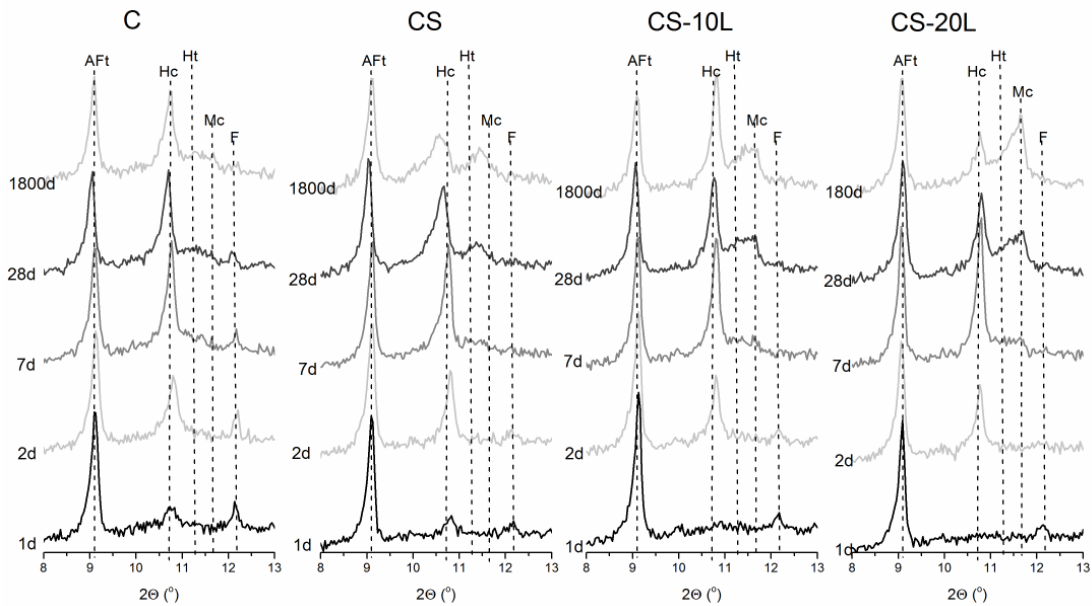


Figure 3 Influence of limestone on composite cements: Ettringite (AFt); hemicarboaluminate (Hc); monocarboaluminate (Mc); hydrotoalcite (Ht); ferrites (F)

The reactivity of slag deduced from chemical shrinkage is shown in **Figure 4**. The filler effects and limestone interaction were discounted in calculating the shrinkage due to slag by only replacing slag with quartz in the corresponding mixes. The results suggest enhanced slag reactivity in the limestone containing cements compared to the OPC-slag cement. This is being quantitatively verified through other techniques.

Elemental ratios between calcium, silicon and aluminum as determined by EDX, from the outer product (Op) C-S-H composition of samples hydrated for 90 days are shown in **Figure 5**. The Ca/Si ratio was taken as the cluster of EDX points farthest to the right on the abscissa while the Al/Si ratio was taken as the slope of a line drawn from the origin and remaining tangent to the cloud of points. The composition of the C-S-H in the CEM I mix clearly differed from that of the composite cements. In addition to a higher Ca/Si ratio (1.92), the CEM I 52.5R cement also showed lower alumina content. Alumina incorporation into C-S-H in composite slag cements have been reported elsewhere [8, 24].

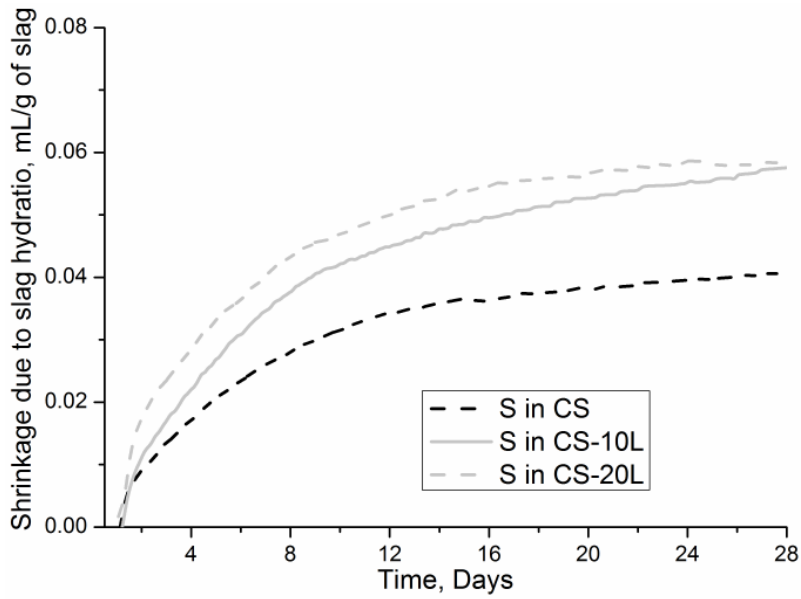


Figure 4 Effect of limestone on slag hydration (from chemical shrinkage measurement)

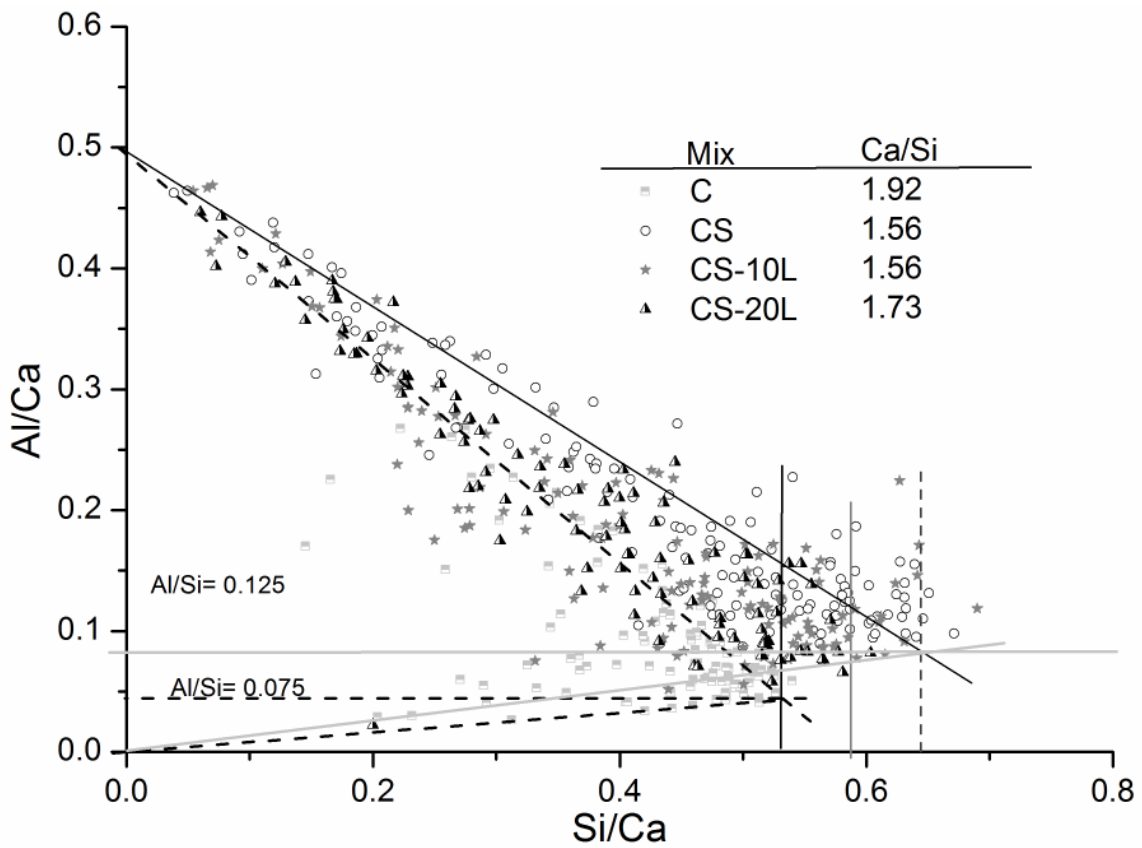


Figure 5 C-S-H composition of investigated cements

The lowering of the Ca/Si ratio and the attendant increase in alumina content in the presence of slag was expected. Dissolved aluminates and silicates from slag in the hydrating cement matrix produce additional C-S-H which incorporates aluminate

species. The increase in the Ca/Si ratio at 20% limestone content may be attributed to enhanced clinker hydration or dissolution of limestone. The alumina incorporation into C-S-H appeared to be solely dependent on slag. This did not change significantly in the presence of limestone.

4. Conclusions

The effect of limestone on the reactivity and microstructure of slag containing ternary blends was studied. The interaction between slag and limestone affects hydration, microstructure and strength development. The results presented here suggest that limestone enhances slag reactivity. Regarding products of hydration, C-S-H with lower Ca/Si but higher alumina content was observed in the composite cements. Ettringite and hemicarboaluminates were also present in all investigated composite slag cements with or without limestone. Mono-carboaluminates were more prevalent at higher limestone content at later ages.

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