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Effect of Limestone Addition on the Early Age Hydration and Microstructure Evolution of Composite Slag Cements

Adu-Amankwah S[1]*, Black L[1], Zajac M[2]

1. Institute for Resilient Infrastructure, School of Civil Engineering, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
2. Heidelberg Technology Center GmbH, Rohrbacher Str. 95, 69181 Leimen, Germany

Abstract
Limestone and slag exert physico-chemical effects on cement hydration and the resultant microstructure. In limestone containing cements, the carbonate species interact with the dissolved aluminates to form carboaluminates, thus stabilizing ettringite. Reaction of slag mainly produces additional C-S-H and a hydrotalcite phase; refining the pore structure. Recent literature suggests an enhancement of the carbonate-aluminate interactions in ternary systems of OPC, limestone and alumina-rich SCMs such as fly ash and slag. Both limestone and SCM exert a filler effect on the cement clinker. However, insufficient information exists on the threshold of limestone-slag combination which maximizes the physico-chemical benefits. Optimizing the limestone-slag content offers the additional benefit of lowering the clinker and/or SCM contents in composite systems.
In this paper, the impact of higher limestone contents upon slag hydration and microstructure up to 90 days is presented. Hydration was followed by isothermal conduction calorimetry and chemical shrinkage while microstructure evolution was examined by scanning electron microscopy, x-ray powder diffraction and thermal analysis. The clinker to SCM ratio was kept at 50:50 while the sulfate content in all mixes was 3%. The results show the consumption of limestone in the course of hydration. Limestone, in addition to providing nucleation sites for clinker hydration, also enhances slag hydration.
With respect to the hydrates formed, ettringite was also stabilized while hemi-carboaluminate was observed in all mixes after two days. Coexistence of hemi- with mono- carboaluminnate was observed after 28 days in the limestone composite cements. The data shows an increased degree of clinker and slag hydration with increasing limestone content. The possible reasons for the observations, including nucleation, availability of space for hydrates to grow and the effect of the interplay between aluminates, sulphates and carbonates on the microstructure will be discussed.

Originality
The present study further examines the synergy between carbonates and aluminates in ternary blends. However, previous studies have considered limestone contents of around 5%. Previous studies have also mainly considered fly ash as the alumina source due to alumina being more abundant in this material than in slag. This paper has also considered considerably higher limestone levels, i.e. 10% and 20%. Using a combination of advanced characterization techniques it has been possible to examine the degree of hydration of each of the components within the blends, thus shedding light on the interactions within the ternary blend. The benefit at these levels of limestone is to harness the combined filler effect on clinker hydration as well as the synergy between the extra aluminates dissolved from slag and carbonates from limestone. This work shows that, the interaction between carbonates and alumina significantly affects the porosity and phase assemblages in ternary blends with slag. The observed improvement in slag hydration in the presence of limestone is novel. These results demonstrate that the limestone exercise the filler effect not only on the cement clinker but on slag as well.

Keywords: Al-adsorption on AFm, Hydrotalcite, Hydration, Slag, Limestone

1. Introduction

Ternary blended OPC-limestone and alumina rich SCMs have attracted significant research

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[1] **Corresponding author: s.adu-amankwah@leeds.ac.uk, Tel +44113432103**

interest recently (De Weerdt *et al.,* 2011a; De Weerdt *et al.,* 2011b; Menéndez *et al.,* 2003; Tennis *et al.,* 2011). These systems offer environmental and technical advantages (Kandasamy and Shehata, 2014; Lothenbach *et al.*, 2011).

Several authors have reported on the relationships between composition, hydration and microstructure (Lothenbach *et al.*, 2011; Whittaker *et al.*, 2014; Zajac *et al.*, 2014) on one hand and also composition and durability (Ghirci *et al.*, 2007) of limestone containing composite cements on the other. The mechanisms leading to the enhanced hydration, strength development and reduced porosity in limestone composite cements have been attributed to physico-chemical effects. Generally, SCMs enhance clinker hydration through the provision of nucleation sites, space for C-S-H growth, enhanced packing density and also increased effective water/binder ratios (Gutteridge and Dalziel, 1990a; Gutteridge and Dalziel, 1990b; Lawrence *et al.*, 2003; Soroka and Setter, 1977). By virtue of being softer, shearing of particles during mixing potentially increase the limestone particles available for nucleation.

Carbonates interact with silicates and aluminate phase assemblages in clinker (Kuzel and Pöllmann, 1991; Matschei *et al.*, 2007; Ramachandran and Zhang, 1986). Increased portlandite and C-S-H with high Ca/Si ratios have been reported elsewhere (Ramachandran and Zhang, 1986). Additionally, in the presence of limestone, dissolved aluminates react with carbonates to form carboaluminates (De Weerdt *et al.*, 2011b; Hoshino *et al.*, 2006); preserving ettringite (Lothenbach *et al.*, 2011; Zajac *et al.*, 2014). Irrespective of the limestone content, hemi-carboaluminnate forms initially but converts to mono carboaluminates with time depending on the proportions of calcite and aluminates (Matschei *et al.*, 2007). This conversion is however inhibited at lower limestone content (Zajac *et al.*, 2014). It follows that, alumina availability is the precursor to carbonate participation in reactions. However, some literature also suggests shorter interparticle spacing outweighs aluminate availability with respect to limestone reaction (Berodier and Scrivener, 2014; Vance *et al.*, 2013). In the presence of alumina rich SCMs, the effect of limestone is similar to that on C_3A. The dissolved aluminates react with calcite to form carboaluminates rather than sulfates in ettringite. Ettringite is thus stabilized, leading to higher compressive strength (De Weerdt et al., 2011a; De Weerdt et al., 2011b; Moesgaard et al., 2012).

In this paper, the hydration of composite cements containing up to 20% limestone is investigate in order to assess the impact of limestone addition on slag hydration.

2. Experimental
2.1. Raw Materials
Four binders were investigated: commercial CEM I 52.5 R, according to European standards EN 197-1, and separately blended composite cements formulated from CEM I 52.5 R plus slag with or without limestone. The mixes are herein designated C, CS, CS-10L and CS-20L. The composition of the materials, obtained by XRF, plus the particle size distributions are shown in **Table 1** and **Figure** 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 added to the blends

without slag.   The limestone contained in CEM I was taken into consideration in the mix design.   The proportioning of constituents to yield the prescribed clinker to SCM ratios are shown in **Table 2** alongside with their relevant compositional ratios.

The mixes were blended and homogenized in a laboratory roller ball mill for 3 hours.

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**).

Table 1   Chemical composition of raw materials

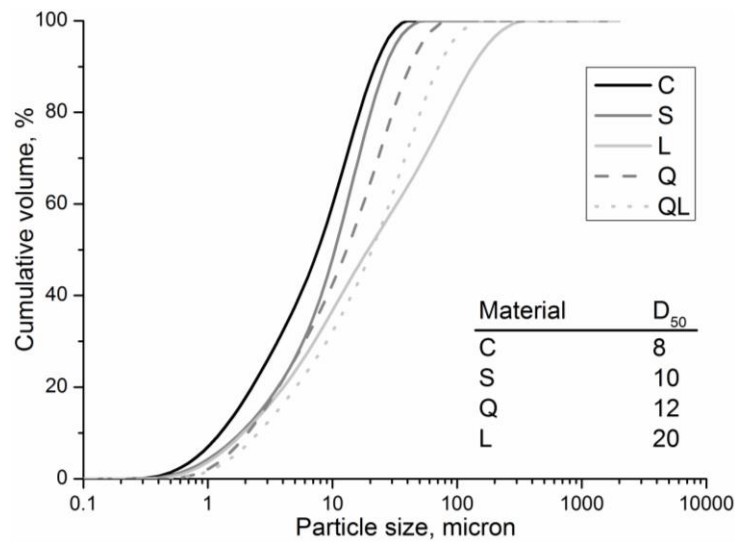| Compositions	SiO$_2$	Al$_2$O$_3$	MgO	CaO	K2O	Na$_2$O	SO$_3$	Blaine (kg/m^2)
CEM I 52.5R	20.37	5.56	1.65	62.10	0.65	0.07	3.54	593
Slag	34.87	11.62	5.82	41.82	0.47	0.07	3.13	454
Limestone	2.00	0.08	0.64	53.13	0.10	0	0.07	328

Figure 1 Particle size distribution of constituent materials

Table 2   Mix design and compositional ratios

Mix ID	CEM I	Slag	Limestone	w/c	w/b	SO$_3$/ Al$_2$O$_3$	CO$_2$/ Al$_2$O$_3$
C	100	-	-	0.5	0.5	0.64	0.31
CS	50	50	-	1.0	0.5	0.36	0.05
CS-10L	50	40	10	1.0	0.5	0.41	0.61
CS-20L	50	30	20	1.0	0.5	0.48	1.43

2.2. Experimental Process

Compressive strength tests were carried out on 40x40x160mm mortar prisms.   Cement, sand and water were to 1:3:0.5 ratios respectively.   Specimens were cured in saturated lime solutions until testing.   Compressive strength testing was carried out on a TONIPACT cube crusher after 1, 2, 7, 28 and 180 days according to the procedure prescribed in EN 196-1.

Hydration was followed by isothermal conduction calorimetry, chemical shrinkage, thermal analysis (STA), and x-ray powder diffraction (XRD). Data up to 90 days hydration are reported in this paper.

Isothermal calorimetry was conducted on 9g of paste prepared with 0.5 w/c ratio. Cement and water were weighed into a plastic ampoule and mixing was carried out using a vortex mixer for 2 minutes. 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 (Geiker, 1983; Kocaba *et al*., 2012). Plastic beakers were filled with 15g of paste, mixed by hand at 0.5w/c ratio for 2 minutes. The beakers were gently tapped to expel entrapped air from the cement paste. The beakers were then filled with water to the brim. A rubber bung with a pre-fitted 1mL pipette was carefully fixed to each filled beaker. Water rising through the pipette was topped with coloured oil. Prepared specimens were kept in a water bath maintained at 20ºC. The progress of reaction was followed through automated image acquisition of the oil level. Images were acquired at 3 minutes-40seconds intervals over 28 days. The images were analyzed using Carl Ziess 'axiovision' analyzer.

Specimens for TG and XRD were prepared as described for chemical shrinkage; cast into plastic vials and stored in a water bath maintained at 20ºC until testing. Sample preparation for XRD measurement and hydration stopping for TG were undertaken in a glovebox to minimize the potential for carbonation.

Specimens for XRD were not hydration stopped. These were manually ground and back loaded for data acquisition. Settings for the scan acquisition were the same as those described elsewhere (Whittaker *et al*., 2014) using an automatic divergence slit.

Samples for thermal analysis were hydration stopped by solvent-exchange. The protocol involved grinding in IPA for 20 minutes, and filtering off the IPA under gravity. The residue was rinsed in ether before drying at 40ºC on a pre-heated glass plate for 20 minutes. Following hydration stopping, samples were stored in mini-grip resealable bags until analysis. Thermogravimetric analysis was carried out under nitrogen on 16-18mg of additionally ground powder using a Stanton 780 Series Analyzer. The heating range was 20-1000∘C at a rate of 20∘C/minute. The bound water and calcium hydroxide contents were computed between 50 - 550∘C and 400 - 500∘C respectively.

3. Results and Discussion
3.1. Hydration kinetics
The rates of heat flow of the investigated mixes normalized to the clinker are shown in **Error! Reference source not found.** for the first 3 days of hydration. The composite cements showed shorter induction periods and slightly higher alite peaks (Whittaker *et al*., 2014). These were similar in the composite cements containing up to 10% limestone as well as the reference quartz-blends. An increase in the limestone content to 20% resulted in slight reduction of the alite peak. The second set of peaks, attributable to the reaction of the aluminate phases is influenced by the filler and composition of SCMs (Bullard *et al*., 2011; Lothenbach *et al*., 2011). In the slag blends, two distinct aluminate peaks were apparent while a single but intensified aluminate peak was seen in the quartz blends. The latter is similar to the effect of fillers on aluminate reaction reported previously (Le Saout and Scrivener, 2006). The first aluminate peak in CS was less distinct, appearing to be merged with the alite peak. The possibility of accelerated slag hydration accounting for the above

effect has been suggested elsewhere (Lothenbach *et al.*, 2011; Whittaker *et al.*, 2014). However, similarly distinctive aluminate peak has been reported in composite cements without slag (Zajac *et al.*, 2014). The effect of slag fineness can also be discounted on the basis of using the same slag for all composite cements. Therefore the retarded aluminate peak may be attributed to clinker dilution arising from limestone.
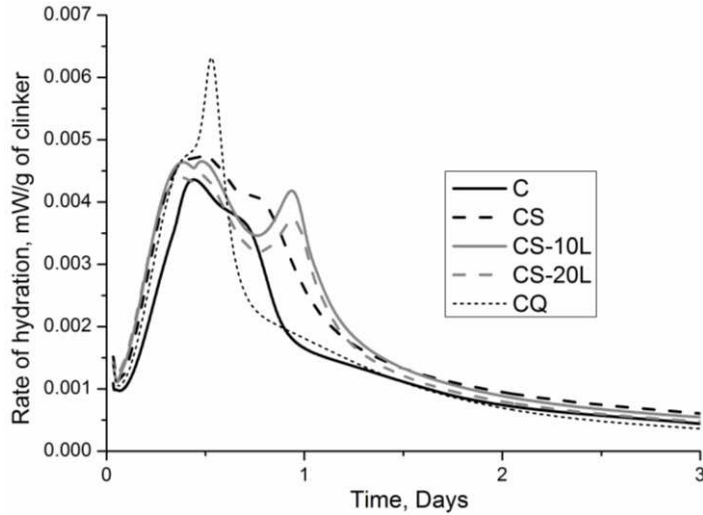

Figure 2 Effect of limestone on the heat flow (normalized by the clinker content)

The bound water and portlandite content of the investigated mixes expressed per cement clinker is shown in Error! Reference source not found. **and** Error! Reference source not found. respectively.
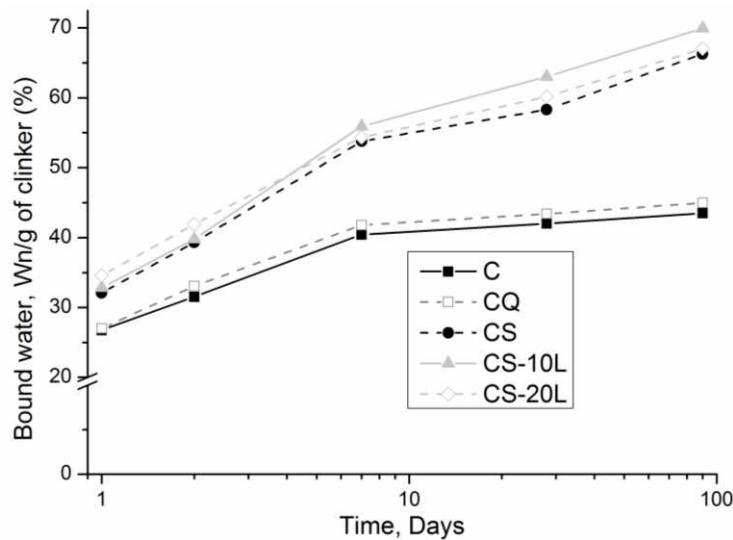

Figure 3 Effect of limestone on the bound water content (normalized per clinker content)

Higher bound water content was observed in the composite cements compared to OPC cement. The presence of limestone also resulted in slightly higher bound water content. The higher limestone content was most beneficial at early age. However, after 7days, the bound water in the 20% limestone cement was comparable to the OPC-slag mix. The portlandite content was higher in the composite cements compared to CEM I. However, in

the limestone containing composite cements, higher portlandite content was prevalent at early age.
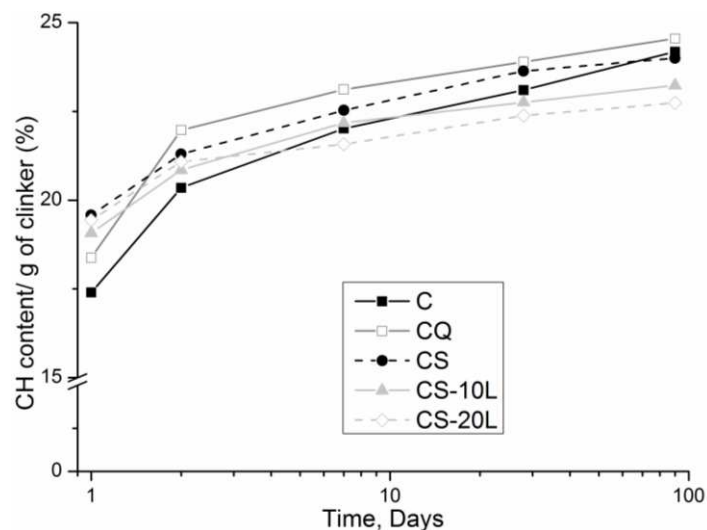

Figure 4 Calcium hydroxide (CH) content of investigated cements (normalized per clinker content)

The differences in the bound water and portlandite contents may be attributed to the effects of limestone on clinker and slag hydration. Alite preferentially hydrate on limestone grains (Berodier and Scrivener, 2014; Ramachandran and Zhang, 1986). The additional nucleation sites provided at higher limestone content facilitates clinker hydration. The possibility of limestone accelerating slag hydration has been reported elsewhere (Hoshino *et al.,* 2006). The enhanced clinker and slag hydrations account for the increased bound water content in the limestone containing cements. The increase in limestone content at the expense of slag would explain the decreased bound water at 20% limestone after 7days.

3.2. Effect of limestone on slag hydration

Chemical shrinkage of the investigated mixes and the corresponding samples in which slag or limestone was replaced with quartz of similar fineness are shown in Error! Reference source not found.. Similar trends were observed from isothermal calorimetry measurements (not shown). The data were normalized to the clinker content (Kocaba *et al.*, 2012). Higher shrinkage per unit clinker was noticed in all composite cements indicative of increased hydration. Similar trends in ternary blended cements have been reported previously (De Weerdt *et al.*, 2011b; Vance *et al.*, 2013). Generally, the magnitude of shrinkage decreased with increasing limestone content. Interpretation of the latter should consider the overall lesser slag content in the ternary blends. These observations suggest that, in addition to the filler effects, limestone contributes to the hydration process in the ternary blend systems (De Weerdt *et al.*, 2011a; De Weerdt *et al.*, 2011b).

Results of shrinkage and heat evolved due to slag hydration in the composite cements are shown in Error! Reference source not found. and **Figure 7** respectively. The filler effects and limestone interaction were discounted in calculating the shrinkage and heat due to slag by only replacing slag with quartz in the corresponding mixes. The results suggest enhanced slag hydration in the limestone containing cements compared to the OPC-slag cement. This

is being verified with other techniques. However, the shrinkage and calorimetry data agree with the bound water and the portlandite contents reported in **Figure 3** and **Figure 4**.
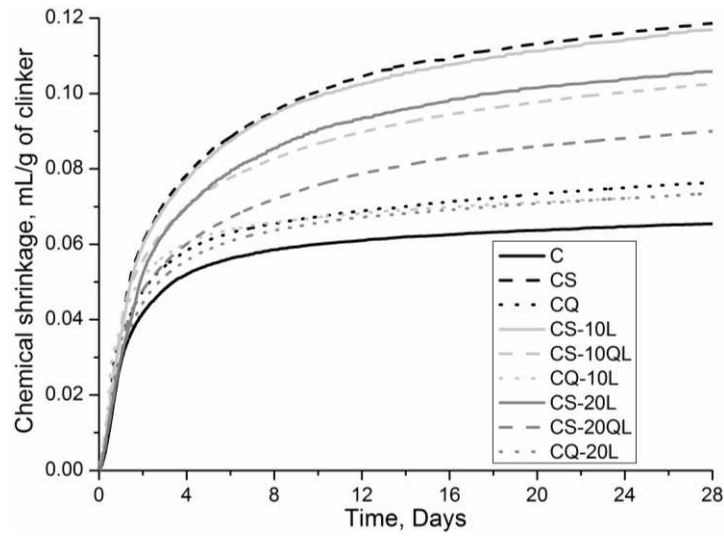

Figure 5 Effect of fillers and SCM hydration on the chemical shrinkage evolution
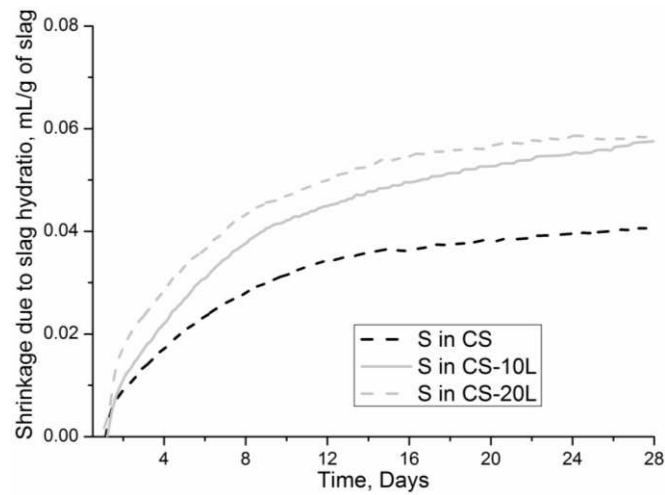

Figure 6 Effect of limestone on slag hydration (from chemical shrinkage measurement)
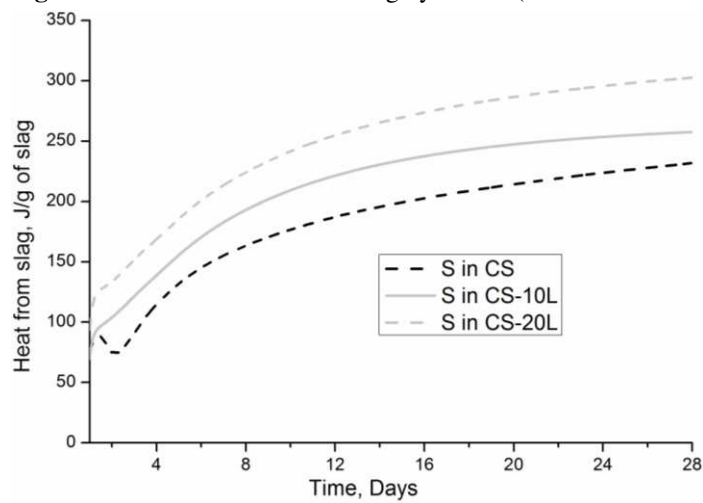

Figure 7 Effect of limestone on slag hydration (from isothermal calorimetry)

3.3. Hydrates formed

The hydrates formed were followed with XRD.

A comparison of the XRD patterns of the investigated systems is shown in **Figure 8**. The diffractograms have been presented focussed on 8-13 $2^0\Theta$ since the main hydration products (i.e. the reflections in AFt and AFm phases) are found in this range.

Ettringite 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 7days. These did not however result in the formation of visible sulphate-bearing AFm peaks as additional aluminates dissolved (Bonavetti *et al*., 2001; Kuzel, 1996). Hemicarboaluminate was observed in all mixes after 2 days. The formation of hemicarboaluminate was accelerated in the CEM I mix. The latter contained approximately 2% limestone which was interground with clinker during production hence higher fineness and dissolution (Vance *et al*., 2013). Conversion of hemi to monocarboaluminate was obvious in all composite cements after 7days. Hemi- and monocarboaluminate reflections dominated in 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. Up to 90 days, hemicarboaluminate was dominant in the 10% limestone system while monocarboaluminate was prevalent at 20% limestone.
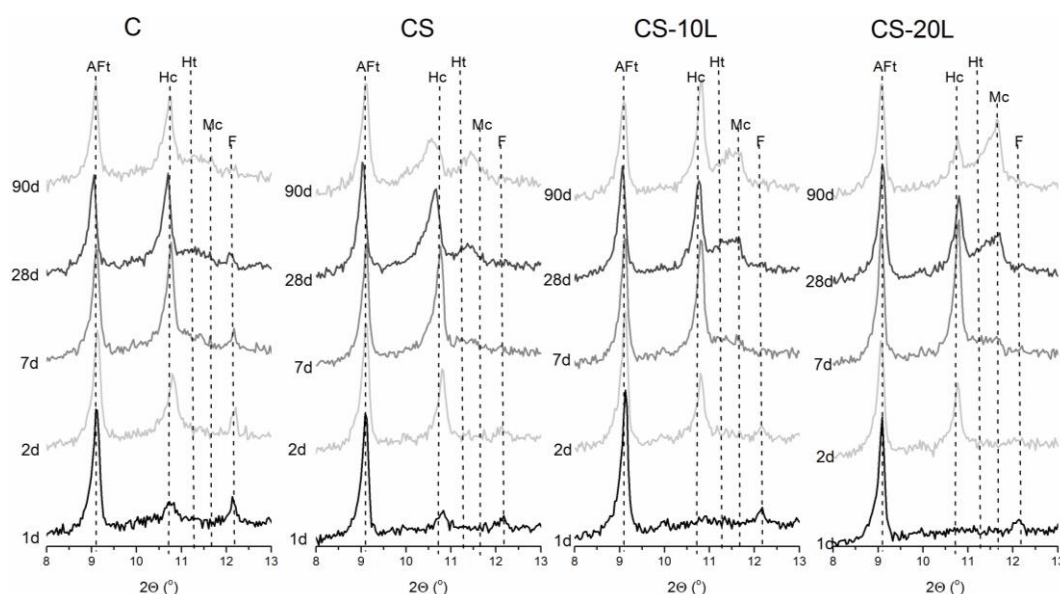

Figure 8 Influence of limestone on composite cements: Ettringite (AFt); hemicarboaluminate (Hc); monocarboaluminate (Mc); hydrotalcite (Ht); ferrites (F)

3.4. Compressive strength

Results from compressive strength tests on the investigated binders are shown in **Figure 9**. As expected at early age, strength development is slower in the composite cements compared to the reference cement (C). Among the composite cements, a slightly higher compressive strength was observed in CS-10L up to 7 days. However, strength was lowest at the 20% limestone content. These results agree with the measured bound water content as well as the calorimetry and chemical shrinkage studies. The strength evolution at 20% limestone

content may appear contradictory to the findings from shrinkage and calorimetry. However, interpretation must consider the reduction of slag content in a given mix.
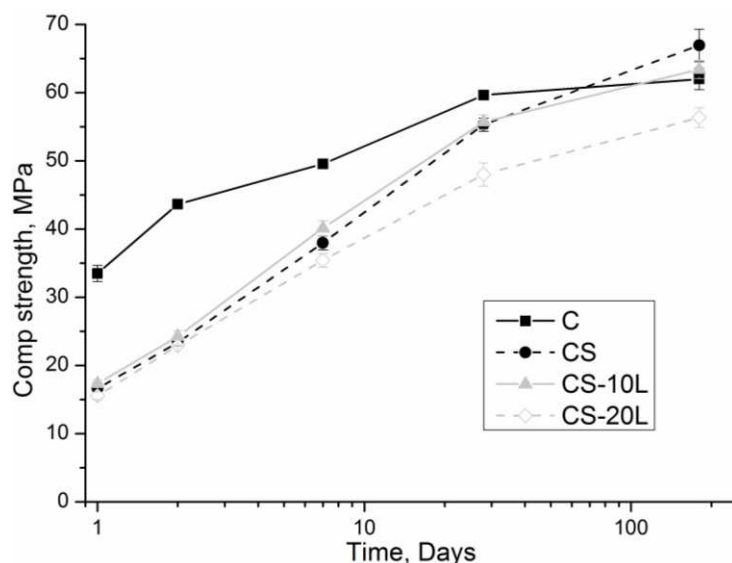

Figure 9 Effect of limestone on compressive strength development

3.5. Conclusions

The effects of limestone content on slag hydration in ternary blended cements have been investigated. Chemical shrinkage and calorimetry data show improved slag hydration in the presence of limestone. Higher limestone content reduced the long term compressive strength due to the reduction of actively hydrating materials. C-S-H, ettringite and carboaluminates were the dominant hydration products. The limestone content affected the proportions of carboaluminates while ettringite was preserved. Alumina incorporation into C-S-H was observed in all slag containing cements.

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