Influence of component fineness on hydration and strength development in ternary slag-limestone cements

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Abstract

The quest for sustainable alternatives to Portland cement has led to the exploration of a range of materials or their combinations, often with the aim of exploiting synergies in reactions or particle packing to maximize performance. Simultaneous optimization of both presents a viable option to increase the efficiency of cementitious materials. The objective of this study was to evaluate the effect of varying the fineness of the constituents in ternary blends of CEM I – granulated ground blast furnace slag (GGBS) - limestone on hydration kinetics and strength development.

Eight (8) ternary cement mixes were tested at 0.5 water/binder (w/b) ratio. Hydration was followed by isothermal conduction calorimetry and setting time. In addition, X-ray powder diffraction, thermogravimetric analysis and compressive strength development up to 180 days of curing were assessed. The efficiency associated with changing the fineness of each component was evaluated in terms of the net heat of reaction and compressive strength. The results show that fine CEM I is critical for hydration at early age, and this is reflected in the compressive strength accordingly. The benefits associated with finer GGBS and similarly limestone depend on the fineness of the other constituents in the blend. Optimization of these should consider the inter-dependencies in terms of kinetics and microstructure development.

Keywords: Low carbon cement; Ternary blended cement; Limestone; Fineness; Hydration

1 Introduction

Ternary composite cements comprising of clinker, an aluminosilicate source and limestone have received considerable attention recently due to synergistic interactions of the various components [1-3]. The quest to improve early age reactivity and mechanical properties of such cements has resulted in attempts to optimize the compositions often based on the material chemistry [3, 4].

In these systems, hydration of the aluminosilicate depends on alkalinity of the medium and hence the pH requisite for dissolution. Meanwhile, the aluminosilicates and limestone provide nucleation sites for C-S-H growth [5] which is beneficial to clinker hydration. Additionally, the slow rate of reaction of the aluminosilicates and limestone means that the effective water available for clinker hydration is increased thus, compensating for the reduced clinker content (i.e. dilution effect) [6]. Further to this, participation of limestone in the hydration process depends on the available alumina dissolved from the aluminosilicate material [3]. Carboaluminates form in the process, offsetting the transformation of ettringite into monosulphate [1,7]. This reduces porosity and hence improves compressive strength at about 5% limestone loading [3, 7, 8].

The effect of composition has also been discussed in the literature. Based on thermodynamic modelling, Matschei *et al.* [9, 10] reported the dependence of carboaluminate precipitation on dissolved Al/CO_3^- and Al/SO_4^- ratios. Mounanga *et al.* [11], however, showed that at a given clinker to supplementary cementitious material (SCM) ratio, altering the GGBS to limestone ratio, had minimal influence on the heat of reaction. We made a similar observation but porosity and kinetic data indicated improved hydration of GGBS at higher limestone loading [3]. Meanwhile the sulphate dosage has been shown to play an equally important role [12], where a too high sulphate content (> 3 wt.%) affects slag dissolution negatively, and hence strength development.

The proportion of limestone which reacts in ternary blended cement mixes is limited to 3 – 4 g per 100 g of cement [3, 13]. The reasons for the limited consumption remain to be clarified. This paper systematically examines the role of component fineness in ternary blends on hydration kinetics, phase assemblages and strength development with the aim of gaining further insight into the limiting factors to component reactivity in limestone ternary cement. Our hypothesis is that for a given composition, increasing the fineness of reactive constituents should offset slower rate of hydration due to increased surface area.

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2   Materials and methods

Composite cements were formulated from CEM I, GGBS and limestone, herein designated as C, S and L. The oxide composition, determined by XRF, and the Blaine fineness of the component materials are shown in Table 1. The reactive components were considered at two Blaine values, resulting in eight (8) mixes, as shown in Table 2. To separate the filler effects from reactive contributions of the SCM, complementary mixes where GGBS or limestone was replaced with quartz of equivalent fineness were prepared. To keep the length of the paper concise, the results presented here is focused on the five mixes highlighted in Table 2.

The composite cements were prepared based on weight percentage at a clinker-GGBS-limestone proportion of 50:40:10 respectively. The clinker and limestone contents were calculated to account for the limestone contained in CEM I as a minor additional component. In addition, ground anhydrite was added to achieve 3 wt. % total sulphate content. The formulated cements were homogenized in a laboratory ball mill for at least 3 hours, using polymer balls to prevent further grinding of the materials.

Paste samples were prepared at 0.5 w/b ratio, and mixing performed on a vortex mixer for 2 minutes. Isothermal conduction calorimetry, thermogravimetric analysis (TGA) and X-ray powder diffraction (XRD) were combined to investigate kinetics and phase assemblages. Isothermal calorimetry was measured on an 8 channel TAM Air instrument with quartz samples prepared at 0.5 liquid/solid ratio as reference. The 9 g pastes were cast into plastic ampoules and observed for 7 d. Samples for XRD and TGA were cast into 10 ml vials and kept in a water bath maintained at 20 °C until testing. The XRD measurements were performed on freshly ground samples in a PANalytical MPD Pro operated at 40 kV and 40 mA. TGA was measured on hydration stopped samples using a Stanton 780 analyser in a nitrogen purged atmosphere. Details of the hydration stopping protocol and data collection are described elsewhere [3]. The data was normalized to 100 g of the anhydrous binder.

Setting time was measured on the cement pastes prepared according to a methodology based on EN 196-3 [14], but at 0.5 w/b ratio. An auto-Vicat apparatus operated with a drop interval of 15 minutes was used for setting time measurements. The paste was cast into a conical test mould on a Perspex base plate. The assembly was then submerged in a recirculating deionized water bath which was maintained at 20 °C throughout the test. Initial set was taken as the time from initial mixing with water until the non-penetrable depth was 6 ± 3 mm and final set at 40 ±0.5 mm. Compressive strength was performed on mortar samples according to EN 196-1 [15] using 40 × 40 × 160 mm samples. These were cured in saturated lime solution after demoulding and tested after 1, 2, 7, 28 and 180 days.

3   Results and discussion

Figures 1a and 1b show the rate of heat evolution and the cumulative heat released from the cement mixes highlighted in Table 2. The heat evolved due to the silicate reaction (labelled as I) in C2S1-L1, i.e. the blend containing fine cement was nearly twice that of the equivalent mix containing coarse cement (C1S1-L1). Meanwhile, onset of the silicate reaction was accelerated when the finer limestone was blended with the coarser slag, S1, than S2. Similarly, the rate of silicate reaction was higher when the coarse GGBS, rather than fine, was blended with fine limestone, but the overall silicate reaction peak was comparable for all C2 blends except with combined S1L1 mix. The main aluminate reaction peak (II) was also accelerated in the C2 blends. The second aluminate peak (III), which is associated with sulphate depletion [16], also occurred sooner in the blends prepared with C2 and showed further dependence on the fineness of other constituent materials. Both peaks were accelerated and the reactions intensified in the finer GGBS (S2) blends. For example, blending C2 with S2 instead of S1 accelerated the appearance of sulphate depletion peak by 6 hours. The finer limestone amplified slightly both the silicate reaction peak (I) and the first aluminate peak (II). However, the second aluminate peak (III) was much more intense, particularly for the finer GGBS blends, as also reflected in the cumulative heat (see S1 in Figure 1b).

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

Composition	SiO_2	Al_2O_3	MgO	CaO	K_2O	Na_2O	SO_3	LOI	Blaine (kg/m^2)
CEM I [C1, C2]	20.37	5.56	1.65	62.10	0.65	0.01	3.54	2.2	383; 593
GGBS [S1, S2]	34.87	11.62	5.82	41.82	0.47	0.01	3.13	2.93	454; 749
Limestone[L1,L2]	2.00	0.08	0.64	53.13	0.10	-	0.07	42.3	328; 700
Anhydrite [s]	2.04	0.60	1.45	38.32	0.16	-	52.24	-	472
Quartz [Q1,Q2,Q3,Q4]	99.68	0.07	-	-	-	-	-	-	300; 450; 700; 760

Table 2. Mix identification.

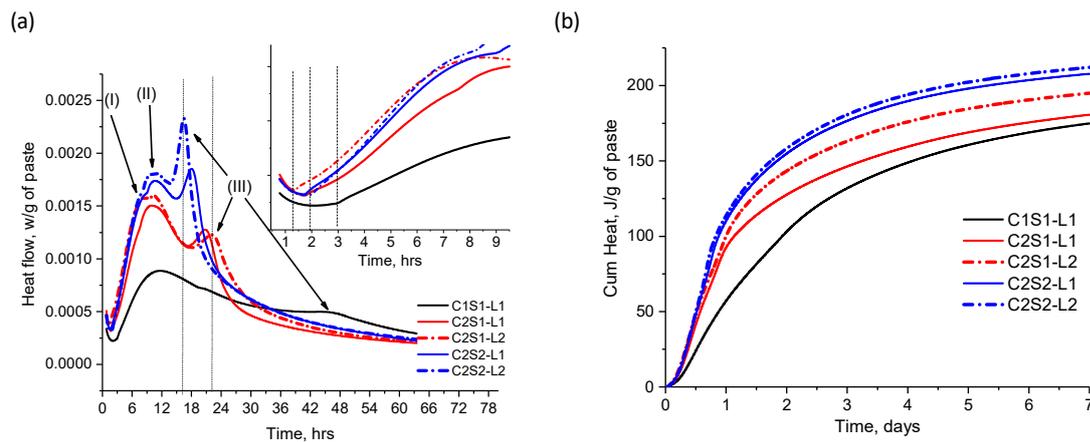| Constituent	S1-L1	S1-L2	S2-L1	S2-L2
CEM I 42.5 R mixes	C1S1-L1	C1S1-L2	C1S2-L1	C1S2-L2
CEM I 52.5 R mixes	C2S1-L1	C2S1-L2	C2S2-L1	C2S2-L2

Figure 1. (a) Heat of reaction of composite cements, as a function of the fineness of CEM I, GGBS and/ or limestone. Insert showing dormant period and time to the onset of silica reaction; (b) Cumulative heat of reaction of composite cements, as a function of the fineness of CEM I, GGBS and/ or limestone.

The onset of the first aluminate reaction (II) was less sensitive to limestone fineness, but sulphate depletion (i.e. III) and perhaps the onset of carboaluminate precipitation [12, 16] was accelerated and the magnitude increased in the finer limestone blends, only when blended with S2.

The rate of reaction plot (Figure 1a) indicated that changing the fineness of CEM I, GGBS or limestone alternately affected the kinetics of silicate and aluminate reactions differently. Figure 1b shows the impact on cumulative heat of reaction. Finer GGBS had a greater impact on the total heat evolution, while the effect of finer limestone was relatively small except when blended with the coarser GGBS (S1). This implies that the accelerated reaction kinetics of silicates and aluminates noticed in the finer limestone mixes did not necessarily increase the overall degree of hydration. A plausible explanation may be the fact that increasing the fineness of the more reactive constituents (i.e. clinker and GGBS) overshadowed the nucleation effect [5] arising from limestone. Additionally, accelerated kinetics may have arisen from the increased shearing due to the fine limestone powder [5, 17]. For a given fineness of CEM I however, acceleration of the silicate reaction peak due to the 10 % fine limestone was comparable to that attained with 40 % finely ground GGBS. This is indicative of the nucleation effect of limestone. Enhanced reaction due to increased GGBS fineness implies more alumina in the pore solution [3]. It is plausible that this promotes carbonate consumption into AFm thus intensifying the aluminate transition peak.

The implications of the component fineness on the initial and final setting times are shown in Table 3. The observed setting time ranges are typical of CEM I paste sample prepared at a similar w/b ratio and are in agreement with the reaction rates (Figure 1). Mix C1S1-L1 had the longest initial and final setting times, due to coarser particle sizes of all constituents. Using C2 in the blend shortened the initial setting time by 2 hours. The calorimetry data (Figure 1) showed enhanced silicate reaction with increasing CEM I fineness and thus suggests faster evolution of connected network of hydrates. It must be emphasized however that, using a finer constituent gives rise to a larger number of individual particles which must be connected to attain setting. In other words, a higher degree of hydration is required to achieve setting in such mixes [18]. Meanwhile, the fine limestone influenced setting time only when there is actively hydrating components in the matrix e.g. fine CEM I or GGBS. The additional silicate reaction associated with fine limestone (L2) had negligible impact on setting time. Meanwhile, blending the coarse limestone (L1) with fine GGBS (S2) significantly reduced the final setting time but the initial set was marginally affected. It seems likely that hydration of the fine GGBS contributed to further densification of the hydrated matrix thus reducing final set time. The C2S2- L2 blend showed much shorter initial and final setting times due to the overall higher surface area of constituents.

The XRD patterns in Figure 2, showing the reflections attributable to calcite (Cc) and the main clinker phases after 1 and 180 days help to clarify reaction of the crystalline components. This information is essential for identifying the limiting step of the reactions and subsequent evaluation of cement performance. There was more residual anhydrous C_3S, C_2S and C_3A in the C1 blends due to the coarser clinker.

In the C2 blends, finer limestone enhanced the silicate reaction, irrespective of GGBS fineness, potentially due to preferential nucleation on the limestone [5]. These effects were most significant during early stages of hydration, with levels of residual anhydrous silicates being similar among the cements at 180d, apart from mix C1S1-L1 where C_2S could still be noticed. The calcite reflection was weaker among the C2 blends and more so in the blend with S2L2, suggesting greater consumption of calcite. These are consistent with the calorimetry data presented in Figure 1.

Table 3. Setting time of composite cements, as a function of component fineness

Mix	C1S1-L1	C2S1-L1	C2S1-L2	C2S2-L1	C2S2-L2
Initial set (mins)	450	330	330	315	285
Final set (mins)	690	570	570	390	360

The trends in reaction kinetics were also reflected in the hydrated phase assemblages. As show in Figure 3, the ettringite contents were similar among the cements after 1d but clear differences in the crystalline hemi-carboaluminate could be noticed; being present in the C2 blended mixes but not in the C1 blends. This is in line with the sulphate depletion observed in the calorimetry data (Figure 1) and consistent with the calcite dissolution as noticed in Figure 2.

At longer hydration times (i.e. 180 days), ettringite was clearly stabilized due to the presence of limestone [1, 7] while mono-carboaluminate was the dominant AFm phase. The trends were independent of the fineness of constituent materials.

The compressive strength development is shown in Figure 4. The blends prepared with C2 were consistently stronger than the equivalent C1 blends, in good agreement with a faster hydration (Figure 1) and evolution of the hydration products (Figure 3). Among C2 ternary blends, however, strength gain associated with fine limestone was within the measurement error until after 7 days where increased strength was observed, especially in the coarse GGBS blend.

Comparison of the rate of strength gain for GGBS and limestone fineness combinations show that blending finer GGBS with coarser limestone (C2S2-L1) favoured higher strength at early age while the C2S1-L2 was comparable at longer hydration times i.e. >28 days. GGBS hydration at early age explains the higher strength in the S2L1 blend. The portlandite reflection peak (Figure 3) is consistent with these trends. Refinement of gel pores due to additionally formed C-A-S-H from hydration of GGGBS is well recognized [3, 19] and this effect was pronounced with increasing fineness. However, the finer GGBS showed marginal improvement over the coarser one at longer hydration time. It is probable that enhanced early hydration leads to limited space in the matrix for hydrate growth [19] at later age. Based on strength, ternary cement comprising fine limestone, coarse GGBS with CEM I 52.5 R seems more efficient in maximizing the nucleation and pore solution effects for clinker and GGBS respectively.
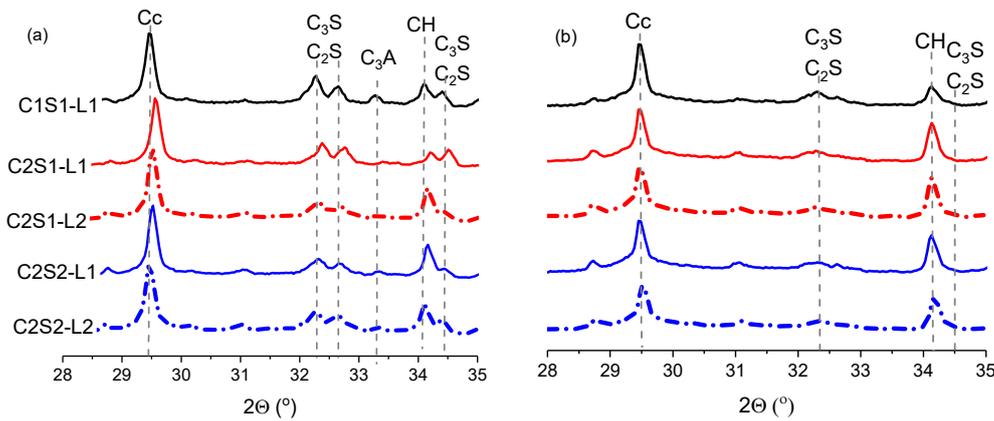

Figure 2. X-ray diffraction patterns of hydrated composite cements after (a) 1 and (b) 180 days of curing, highlighting the region showing residual calcite and clinker phases present in the pastes.
Cc = calcite; C_3S = tricalcium silicate; C_2S = dicalcium silicate; C_3A = tricalcium aluminate; CH = portlandite
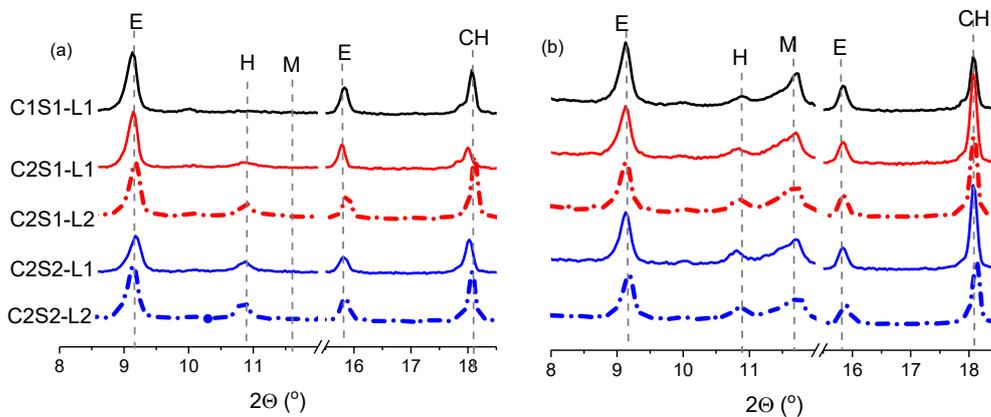

Figure 3. X-ray diffraction patterns of hydrated composite cements after (a) 1 and (b) 180 days of curing, showing the evolution of crystalline hydrates in the pastes. E = ettringite; H = hemi-carboaluminate; M = mono-carboaluminate.
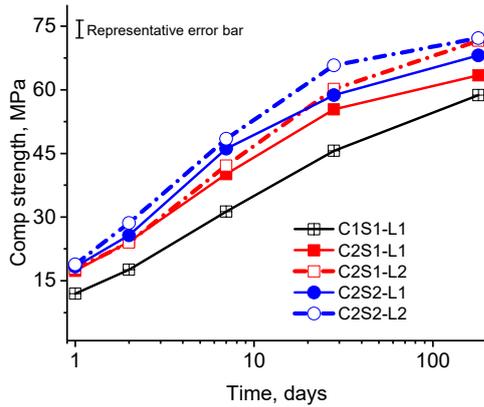
Figure 4. Compressive strength of composite cements, as a function of the fineness of CEM I, GGBS and/ or limestone.

To clarify the filler and reactive contributions due to increasing fineness of GGBS or limestone, these were replaced in turn by quartz of comparable fineness. This methodology was implemented elsewhere [3, 20]. Figure 5 shows cumulative heat plots normalised to the anhydrous CEM I content for mix C2S1-L1 alongside the complementary quartz blends. The effect of added limestone was negligible when GGBS was replaced by quartz e.g. C2Q2-L1 vs. C2Q2-Q1. It is noteworthy that about 2 % calcium carbonate was already present in the CEM I and hence the nucleation effect on clinker hydration would be comparable with or without the additional limestone. Similarly, using finer quartz in place of GGBS did not impact on the cumulative heat significantly. This indicates that at higher levels of substitution with non or less reactive constituent, dilution effects [6] dominate over the gains arising from nucleation sites as provided by limestone [5]. Conversely, the reactive effect of limestone in the ternary cement was significantly different from the inert filler, evident from comparing C2S1-Q1 to C2S1-L1. Consequently, efficiency derived from using finer constituent materials was further evaluated in terms of the net contribution to heat of hydration and compressive strength after removing the filler effect. The approach to reducing the data is illustrated in Equations 1 − 3. A more positive result indicates that increasing the component fineness was efficient and vice versa.

$$[C_2S_1L_1] - [C_1S_1L_1] = E^C \tag{1}$$

$$[C_2S_2L_1] - [C_2S_1L_1] = E^s \tag{2}$$

$$[C_2S_1L_2] - [C_2S_1L_1] = E^L \tag{3}$$

Where E^C, E^S and E^L denote the efficiency of using finer CEM I, GGBS or limestone.

Figure 6 shows the net or additional heat of reaction derived from using a finer CEM I, GGBS or limestone herein designated E^C, E^S and E^L respectively in the various blends. The results were normalized to the anhydrous CEM I content. The use of finer CEM I, GGBS or limestone in the blends enhanced reaction kinetics but the fineness of other constituents present in the matrix played an important role. Finer CEM I had the greatest effect on heat evolution at early age, consistent with [21]. However, the effect diminished as

hydration progressed. The S2L2 blend further promoted C2 hydration. This effect does not emanate from the nucleation sites provided by limestone and GGBS as such effects would also be common in the complementary C1 blend. Instead, the larger surface area of the C2 particles renders it more reactive and thus explains the greater heat evolved. The decelerating efficiency is ascribed to continued hydration of C1.
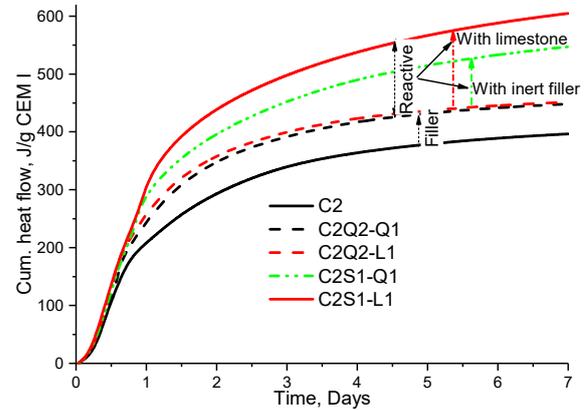

Figure 5. Cumulative heat of hydration normalized to CEM I content, showing the filler and reactive contributions from GGBS and limestone in mix C2S1-L1.

Figure 6 further indicates that fine GGBS and limestone were more efficient from early age. The finer GGBS contributed more heat in the C2L1 blend, suggesting that fine GGBS in the C2L2 ternary blend was counter-productive. A similar trend was noticed with the fine limestone, showing greater contribution to the heat of hydration in the C2S1 blend compared to C2S2. The contribution of limestone to the cumulative heat, differed significantly from the inert filler (Figure 5). Consequently, an explanation for the influence of GGBS and limestone combinations may be related to the nature of hydrates and pore solution effects. The ettringite contents were similar in all mixes (Figure 3) due to fixed SO_4/Al_2O_3 ratio [10, 12] and hence do not explain the limited calcite consumption.

Calcite, portlandite and bound water contents measured from thermogravimetric analysis are shown in Figure 7 (a and b). Residual calcite content in the various mixes is consistent with the efficiency data in Figure 6 where increased limestone fineness in the blend with C2S1 led to more calcite consumption. The residual calcite content in the latter was comparable to the fine GGBS blends after 1d, reducing further at longer hydration time. The calcite consumed generally agree with trends in the AFm signatures, evolving sooner in C2S1-L2 mix (Figure 3). In contrast, diffused AFm signal was found in the coarser limestone mixes. The finer GGBS was more reactive (Figure 1b) and hence more alumina was expected in the pore solution. It is well recognized that high alumina favours calcite consumption [1, 3, 12]. The fact that, more GGBS reacted but the AFm signatures were similar to the coarse GGBS mix blended with the finer limestone suggests that the synergy may be initiated by the latter. There however seems to exist a threshold calcite activity

regardless of the fineness of CEM I or GGBS. It seems probable that, once the threshold is attained, conversion from hemi to mono-carboaluminate is rather favoured. This accounts for the reduced efficiency noted in the fine GGBS and limestone mix.
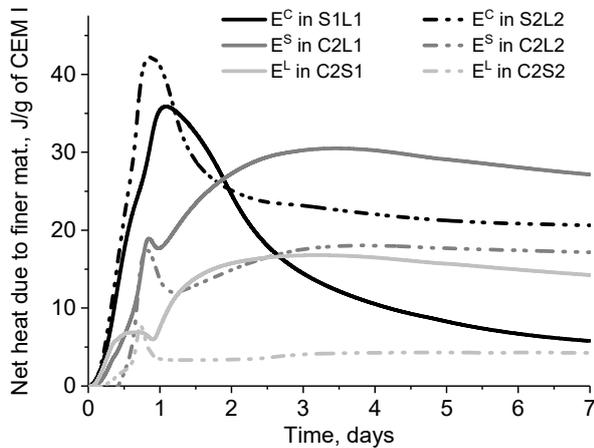

Figure 6. Net heat derived from using finer CEM I, GGBS or limestone in the ternary cements. Note the filler effects were isolated using the corresponding quartz blends.

An inverse relationship between calcite dissolution and pH based on acid-base model has been proposed elsewhere [22]. According to the model, hydroxyl ions selectively adsorb onto calcite forming basic intermediate compounds impeding further dissolution. However, the hydroxyl ion concentrations among the samples reported were not expected to vary considerably [3]. Lower portlandite was recorded in the C1 blend at all hydration times but the differences among the C2 blends were within the error of measurement (Figure 7a). The trends indicate slightly less portlandite in the finer GGBS mixes, attributable to consumption to form calcium bearing hydrates including AFm and C-A-S-H. Depending on the site where they precipitate, AFm formation could possibly explain the lower calcite consumption on the basis of low mobility of the dissolved carbonate ions [23]. However, such an effect should lead to higher calcite consumption in the C1S1 mix but this was not the case. Consequently, a probable explanation

for the limited calcite reaction in our view is a threshold AFm content.

The bound water contents (Figure 7b) agree with the AFm and portlandite evolution, suggesting more hydrates in the fine GGBS or limestone blends. The data further confirm the CEM I fineness to be more critical at early age and yet the finer limestone beneficial in the C2S1 ternary mix.

With respect to compressive strength, the finer CEM I mixes consistently achieved higher compressive strength irrespective of the fineness of other constituents, especially at early age. However, after 180 days, the C2 blends were stronger than C1 blends by a similar margin (~ 6-10 MPa) irrespective of other constituents (Figure 8). Meanwhile, increasing GGBS fineness yielded moderate improvement in strength than the coarser mix but the difference became smaller at longer hydration time. The blends with C2 generally showed better early strength. Conversely, the finer limestone consistently improved strength in all combinations except C2S1 blends where the early age contributions were negligible. A plausible explanation is the dominance of the fine CEM I (C2). Limestone provides nucleation sites plus reacts with dissolved aluminates. The C2S2 mixes already had a high specific surface area, such that the impact of the fine limestone was not significant. However, the fine limestone would react readily with dissolved alumina from GGBS and hence the noted contributions at longer hydration time.

The above observations may be further explained by the fact that limestone influences CEM I hydration by nucleation and dilution effects [5], while the effect on GGBS hydration is a function of the pore solution chemistry and the available space for hydrate growth [3]. Consequently, the finer limestone enhanced CEM I hydration and led to the strength gain as observed above. With portlandite as a product, this increased the pH for GGBS reaction. However, more CEM I hydration may be counterproductive for GGBS hydration since the available space for hydrate growth reduces, restricting GGBS hydration. At such stages, the benefits of the finer GGBS are no longer realised, as noted in all mixes after 180 days.
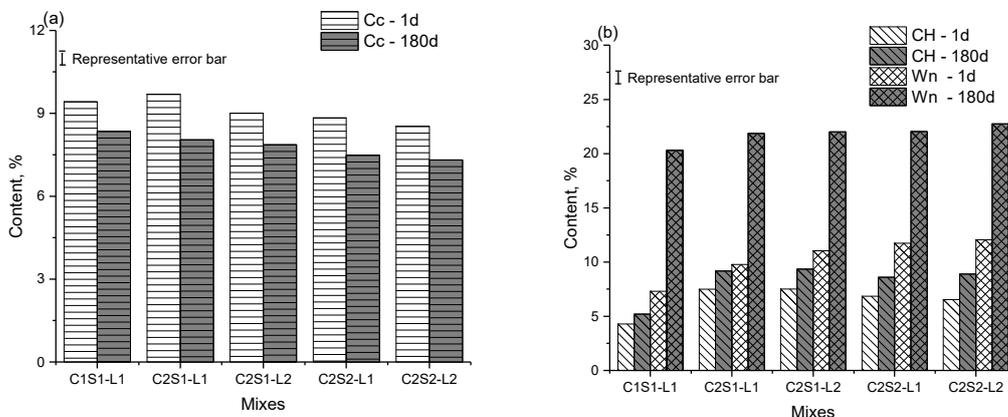

Figure 7. Phase contents of (a) calcite and (b) portlandite and bound water as measured from TGA after 1 and 180 days, showing the effect of constituent fineness. Note the results were normalized to 100g of the anhydrous binder.
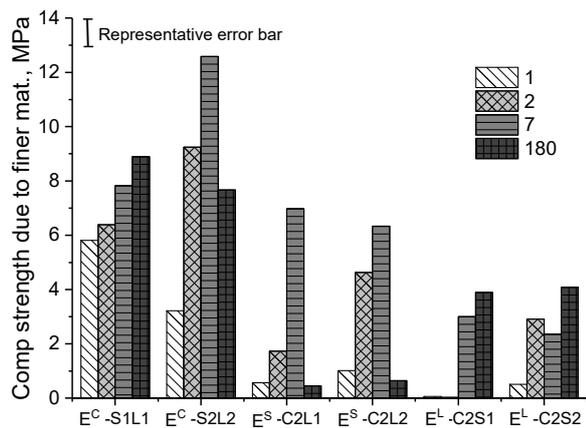
Figure 8. Net compressive strength derived from using finer CEM I, GGBS or limestone in the ternary cements.

4 Conclusions

Ternary blended cements prepared from varying the fineness of CEM I, GGBS and limestone have been studied using a combination of techniques. The results show that optimization of components fineness with respect to hydration, microstructure and performance is imperative for maximizing the efficiency of the components materials in ternary cement blends. The findings are novel in the sense that there is an optimal synergy between specific CEM I/ slag and limestone fineness to maximise their reactivity in ternary blended cements, and it is not the case that finer particles necessarily lead to a greater degree of reaction of ternary cements. This finding is important as it elucidates a pathway for reducing the Portland cement fraction in ternary composite cements, for equivalent reaction kinetics and/or strength, through optimized fineness of components as a function of their chemistry. The key findings are summarised below:

1. The CEM I fineness has the greatest impact on hydration, setting time, phase assemblage evolution and strength development.

2. The limestone fineness affects the heat of hydration and setting time to a smaller extent. However this improves the compressive strength over the entire duration irrespective of CEM I and GGBS fineness. The finer limestone was more efficient when blended with coarser GGBS with respect to heat of reaction and compressive strength.

3. Blending GGBS with coarser CEM I and limestone is not efficient. With finer constituent, the benefits in terms of hydration and compressive strength are realised at early age but diminish at longer hydration times.

4. This study has shown that increasing the fineness of the constituent materials in multi-component cements does not necessarily improve hydration and strength development but requires careful consideration as to the interdependencies between the different components.

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