Influence of component fineness on hydration and st

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 v
exploiting synergies in reactions or particle packing to maximize performance. Simultaneous optimization of both presents a viable option t
efficiency of cementitious materials. The objective of this study was to evaluate the effect of varying the fineness of the constituents in ter
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 calorime
time. In addition, X-ray powder diffraction, thermogravimetric analysis and compressive strength development up to 180 days of curing v
The efficiency associated with changing the fineness of each component was evaluated in terms of the net heat of reaction and compressiv
results show that fine CEM I is critical for hydration at early age, and this is reflected in the compressive strength accordingly. The benefits a
finer GGBS and similarly limestone depend on the fineness of the other constituents in the blend. Optimization of these should cons
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

The effect of composition has also been discu
literature. Based on thermodynamic modelling,
al. [9, 10] reported the dependence of carb
precipitation on dissolved Al/CO_3^- and $Al/$
Mounanga et al. [11], however, showed that at a
to supplementary cementitious material (SCM) ra
the GGBS to limestone ratio, had minimal influ
heat of reaction. We made a similar observation
and kinetic data indicated improved hydration
higher limestone loading [3]. Meanwhile the sulp
has been shown to play an equally important role
a too high sulphate content (> 3 wt.%) affects sla
negatively, and hence strength development.

The proportion of limestone which reacts in tern
cement mixes is limited to 3 – 4 g per 100 g of cen
The reasons for the limited consumption rer
clarified. This paper systematically examines
component fineness in ternary blends on hydrat
phase assemblages and strength development v
of gaining further insight into the limiting
component reactivity in limestone ternary co

transformation of ettringite into monosulphate [1,7]. This reduces porosity and hence improves compressive strength at about 5% limestone loading [3, 7, 8].

hypothesis is that for a given composition, increasing fineness of reactive constituents should offset slow 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 past according to a methodology based on EN 196-3 0.5 w/b ratio. An auto-Vicat apparatus operated interval of 15 minutes was used for se measurements. The paste was cast into a conica on a Perspex base plate. The assembly was then in a recirculating deionized water bath which was at 20 °C throughout the test. Initial set was taken from initial mixing with water until the non-penet was 6 ± 3 mm and final set at 40 ±0.5 mm. C strength was performed on mortar samples acco 196-1 [15] using 40 × 40 × 160 mm samples. These in saturated lime solution after demoulding and 1, 2, 7, 28 and 180 days.

3   Results and discussion

Figures 1a and 1b show the rate of heat evolu cumulative heat released from the cement mixes in Table 2. The heat evolved due to the silica (labelled as I) in C2S1-L1, i.e. the blend containing was nearly twice that of the equivalent mix conta cement (C1S1-L1). Meanwhile, onset of the silic was accelerated when the finer limestone was b the coarser slag, S1, than S2. Similarly, the rat reaction was higher when the coarse GGBS, rath was blended with fine limestone, but the ov reaction peak was comparable for all C2 blends combined S1L1 mix. The main aluminate reacti was also accelerated in the C2 blends. The secon peak (III), which is associated with sulphate de also occurred sooner in the blends prepared v showed further dependence on the finenes constituent materials. Both peaks were accelera reactions intensified in the finer GGBS (S2) example, blending C2 with S2 instead of S1 acc appearance of sulphate depletion peak by 6 hou limestone amplified slightly both the silicate reac and the first aluminate peak (II). However, aluminate peak (III) was much more intense, pa the finer GGBS blends, as also reflected in the cum (see S1 in Figure 1b).

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

Composition	SiO₂	Al₂O₃	MgO	CaO	K₂O	Na₂O	SO₃	LOI	Blaine (kg/m²)
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; 7

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		C2S1-L1	C2S1-L2	C2S2-L1	C2S2-L2

mixes

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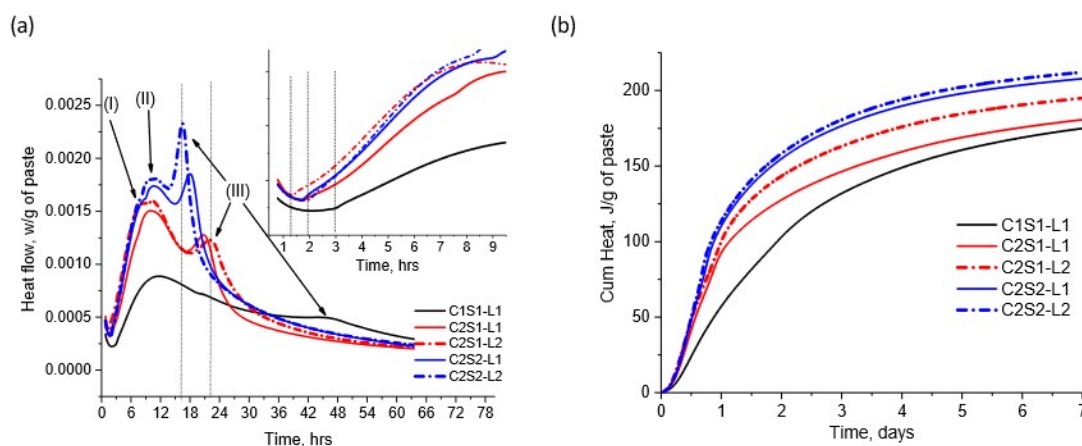
Figure 1. (a) Heat of reaction of composite cements, as a function of the fineness of CEM I, GGBS and/ or limestone. Insert show period and time to the onset of silica reaction; (b) Cumulative heat of reaction of composite cements, as a function of the fineness o and/ or limestone.

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

connected to attain setting. In other words, a hi of hydration is required to achieve setting in such Meanwhile, the fine limestone influenced settin when there is actively hydrating components in e.g. fine CEM I or GGBS. The additional silica associated with fine limestone (L2) had negligibl setting time. Meanwhile, blending the coarse lin with fine GGBS (S2) significantly reduced the final but the initial set was marginally affected. It seen hydration of the fine GGBS contributed densification of the hydrated matrix thus reduc time. The C2S2- L2 blend showed much shorte final setting times due to the overall higher sur constituents.

The XRD patterns in Figure 2, showing the attributable to calcite (Cc) and the main clinker ph and 180 days help to clarify reaction of the components. This information is essential for ide limiting step of the reactions and subsequent e cement performance. There was more residua C_3S, C_2S and C_3A in the C1 blends due to the coars

In the C2 blends, finer limestone enhanced reaction, irrespective of GGBS fineness, potent preferential nucleation on the limestone [5]. Tl were most significant during early stages of hyd levels of residual anhydrous silicates being simila cements at 180d, apart from mix C1S1-L1 where C be noticed. The calcite reflection was weaker an blends and more so in the blend with S2L2, sugges consumption of calcite. These are consisten calorimetry data presented in Figure 1.

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

Mix	C1S1-L1	C2S1-L1	C2S1-L2	C2S2
Initial set (mins)	450	330	330	315

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

(mins)				
Final set (mins)	690	570	570	390

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 limestone fineness combinations show that ble GGBS with coarser limestone (C2S2-L1) favo strength at early age while the C2S1-L2 was co longer hydration times i.e. >28 days. GGBS hydra age explains the higher strength in the S2L1 portlandite reflection peak (Figure 3) is consisten trends. Refinement of gel pores due to additional A-S-H from hydration of GGGBS is well recognize this effect was pronounced with increasin However, the finer GGBS showed marginal in over the coarser one at longer hydration time. It that enhanced early hydration leads to limited : matrix for hydrate growth [19] at later age. Based ternary cement comprising fine limestone, coars CEM I 52.5 R seems more efficient in max nucleation and pore solution effects for clinke respectively.
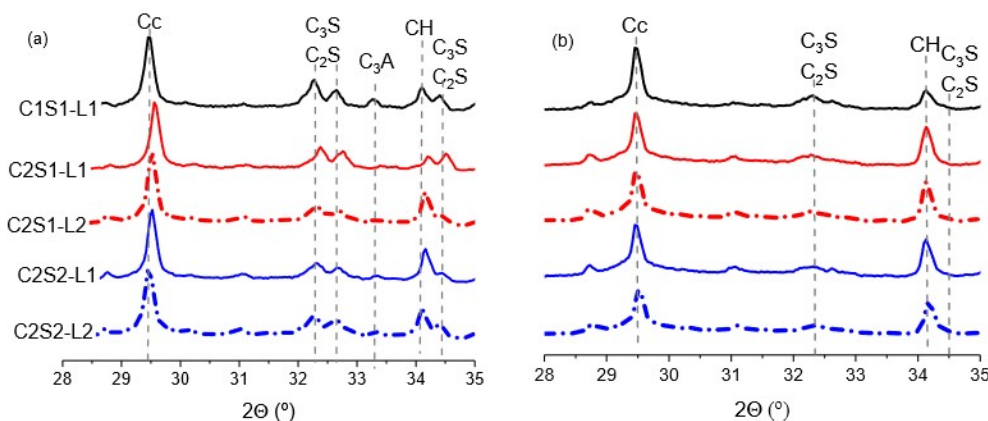

Figure 2. X-ray diffraction patterns of hydrated composite cements after (a) 1 and (b) 180 days of curing, highlighting the regio residual calcite and clinker phases present in the pastes.

Cc = calcite; C_3S = tricalcium silicate; C_2S = dicalcium silicate; C_3A = tricalcium aluminate; CH = portlandite
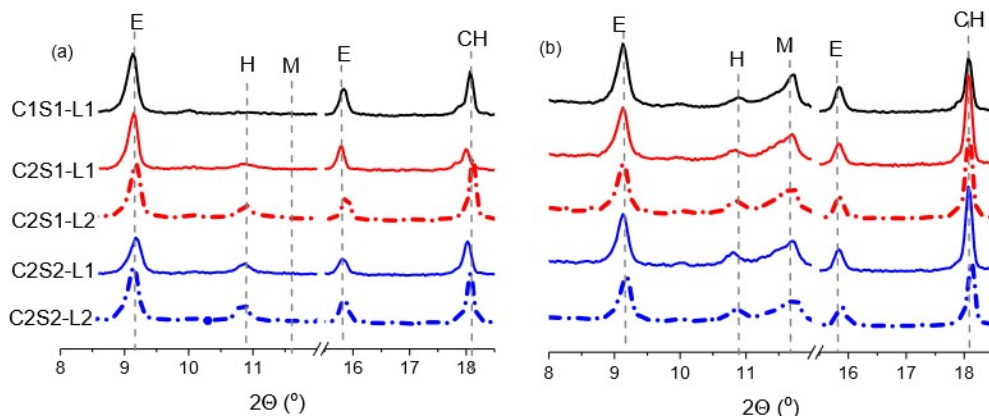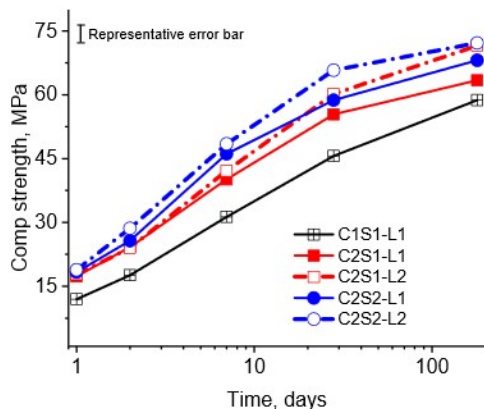

Figure 3. X-ray diffraction patterns of hydrated composite cements after (a) 1 and (b) 180 days of curing, showing the evolution c hydrates in the pastes. E = ettringite; H = hemi-carboaluminate; M = mono-carboaluminate.

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

hydration progressed. The S2L2 blend further p
hydration.   This effect does not emanate
nucleation sites provided by limestone and GG
effects would also be common in the comple
blend.   Instead, the larger surface area of the
renders it more reactive and thus explains the g
evolved. The decelerating efficiency is ascribed t
hydration of C1.
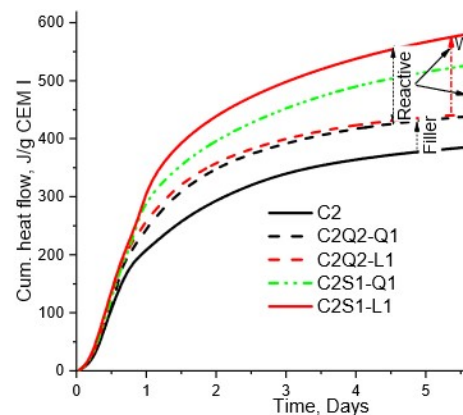
Figure 5. Cumulative heat of hydration normalized to C
showing the filler and reactive contributions fron
limestone in mix C2S1-L1.

Figure 6 further indicates that fine GGBS and lime
more efficient from early age. The finer GGBS
more heat in the C2L1 blend, suggesting that fine
C2L2 ternary blend was counter-productive. A s
was noticed with the fine limestone, show
contribution to the heat of hydration in the
compared to C2S2. The contribution of limest
cumulative heat, differed significantly from the
(Figure 5). Consequently, an explanation for the
GGBS and limestone combinations may be rel
nature of hydrates and pore solution effects. Th
contents were similar in all mixes (Figure 3) c
SO$_4$/Al$_2$O$_3$ ratio [10, 12] and hence do not explair
calcite consumption.

Calcite, portlandite and bound water content
from thermogravimetric analysis are shown in Fig
b).   Residual calcite content in the various mixes
with the efficiency data in Figure 6 where increase
fineness in the blend with C2S1 led to m
consumption.   The residual calcite content in th
comparable to the fine GGBS blends after 1d, redu
at longer hydration time. The calcite consume
agree with trends in the AFm signatures, evolvir
C2S1-L2 mix (Figure 3). In contrast, diffused AFn
found in the coarser limestone mixes. The fine
more reactive (Figure 1b) and hence more a
expected in the pore solution.   It is well recogniz
alumina favours calcite consumption [1, 3, 12]. T
more GGBS reacted but the AFm signatures we

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

more GGBS reacted but the AFm signatures we the coarse GGBS mix blended with the fine suggests that the synergy may be initiated by There however seems to exist a threshold cal

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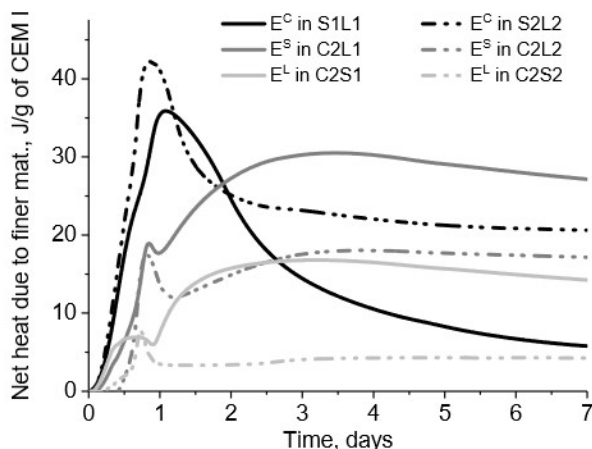
Figure 6. Net heat derived from using finer CEM I, GGBS or limestone in the ternary cements. Note the filler effects were isolated using the corresponding quartz blends.

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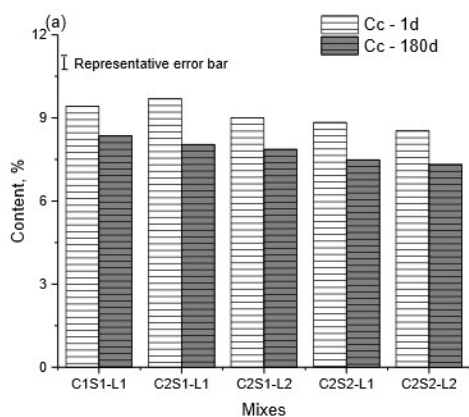
for the limited calcite reaction in our view is a thr content.

The bound water contents (Figure 7b) agree with t portlandite evolution, suggesting more hydrate GGBS or limestone blends. The data further confi I fineness to be more critical at early age and y limestone beneficial in the C2S1 ternary mix.

With respect to compressive strength, the finer consistently achieved higher compressive irrespective of the fineness of other constituents, early age. However, after 180 days, the C2 b stronger than C1 blends by a similar margin (~ irrespective of other constituents (Figure 8). increasing GGBS fineness yielded moderate impr strength than the coarser mix but the differer smaller at longer hydration time. The blends with showed better early strength. Conversely, the fine consistently improved strength in all combinat C2S1 blends where the early age contribu negligible. A plausible explanation is the domin fine CEM I (C2). Limestone provides nucleatio reacts with dissolved aluminates. The C2S2 m had a high specific surface area, such that the in fine limestone was not significant. Howeve limestone would react readily with dissolved al GGBS and hence the noted contributions at long time.

The above observations may be further explaine that limestone influences CEM I hydration by nu dilution effects [5], while the effect on GGBS hy function of the pore solution chemistry and th space for hydrate growth [3]. Consequently limestone enhanced CEM I hydration and led to gain as observed above. With portlandite as a p increased the pH for GGBS reaction. However, hydration may be counterproductive for GGB since the available space for hydrate grow restricting GGBS hydration. At such stages, the be finer GGBS are no longer realised, as noted in all 180 days.
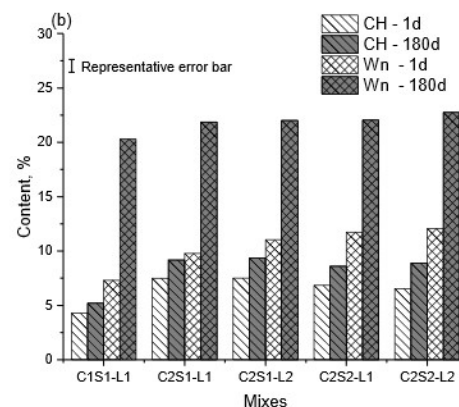
Figure 7. Phase contents of (a) calcite and (b) portlandite and bound water as measured from TGA after 1 and 180 days, showing constituent fineness. Note the results were normalized to 100g of the anhydrous binder.

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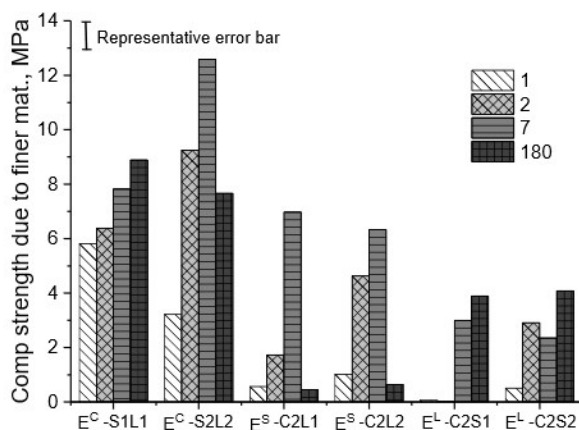
Figure 8. Net compressive strength derived from using finer CEM I, GGBS or limestone in the ternary cements.

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.

References

[1] K. De Weerdt, K.O. Kjellsen, E. Sellevold, H. Justnes, Syr fly ash and limestone powder in ternary cements. Cem 2011(33): 30-38.
https://doi.org/10.1016/j.cemconcomp.2010.09.006

[2] A. Arora, G. Sant, N. Neithalath, Ternary blends conta interground/blended limestone: Hydration, streng structure. Constr Build Mater 2016(102): 113-124.
https://doi.org/10.1016/j.conbuildmat.2015.10.179

[3] S. Adu-Amankwah, M. Zajac, C. Stabler, B. Lothenl Influence of limestone on the hydration of ternary slag Concr Res 2017(100): 96-109.
https://doi.org/10.1016/j.cemconres.2017.05.013

[4] A. Schöler, B. Lothenbach, F. Winnefeld, M. Zajac, quaternary Portland cement blends containing blas siliceous fly ash and limestone powder. Cem Concr Con 374-382.
https://doi.org/10.1016/j.cemconcomp.2014.10.001

[5] E. Berodier, K. Scrivener, Understanding the filler nucleation and growth of C-S-H. J Am Ceram Soc 2 3773. https://doi.org/10.1111/jace.13177

[6] K. Scrivener, B. Lothenbach, N. De Belie, E. Gruyaert, Snellings, A. Vollpracht, TC 238-SCM: hydration and mi⌐ concrete with SCMs. Mater Struct 2015(48):835-862.
https://doi.org/10.1617/s11527-015-0527-4

[7] K. De Weerdt, M. Ben Haha, G. Le Saout, K.O. Kjellsen Lothenbach, Hydration mechanisms of ternary Por⌐ containing limestone powder and fly ash. Cer 2011(41):279-291.
https://doi.org/10.1016/j.cemconres.2010.11.014

[8] M. Zajac, J. Skocek, S. Adu-Amankwah, L. Black, M. Ber of microstructure on the performance of composite higher total porosity can result in higher strength. Cem 2018(90):178-192.
https://doi.org/10.1016/j.cemconcomp.2018.03.023

[9] T. Matschei, B. Lothenbach, F.P. Glasser, The ro carbonate in cement hydration. Cem Concr Res 2007(3 https://doi.org/10.1016/j.cemconres.2006.10.013

[10] T. Matschei, B. Lothenbach, F.P. Glasser, The AFm pha cement. Cem Concr Res 2007(37):118-130.
https://doi.org/10.1016/j.cemconres.2006.10.010

[11] P. Mounanga, M.I.A. Khokhar, R. Hachem, A. Loukili, In the early-age reactivity of fly ash and blast furnace slag systems using limestone filler. Mater Struct 201 https://doi.org/10.1617/s11527-010-9637-1

[12] S. Adu-Amankwah, L. Black, J. Skocek, M. Ben Haha, N of sulfate additions on hydration and performance c limestone composite cements. Constr Build Mater 2 462. https://doi.org/10.1016/j.conbuildmat.2017.12.1

[13] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Ceme by a combination of metakaolin and limestone. C⌐ 2012(42):1579-1589.
https://doi.org/10.1016/j.cemconres.2012.09.006

[14] BSI, EN 196-3:2016 Methods of testing cement. Det setting times and soundness. 2016, pp. 1 - 18.

[15] BSI, EN 196-1:2016 Methods of testing cement. Part 1: of strength. 2016, pp. 1 - 38.

[16] D. Jansen, F. Goetz-Neunhoeffer, B. Lothenbach, J. N early hydration of Ordinary Portland Cement (OPC): comparing measured heat flow with calculated heat fl⌐ Cem Concr Res 2012(42):134-138.
https://doi.org/10.1016/j.cemconres.2011.09.001

[17] P. Juilland, A. Kumar, E. Gallucci, R.J. Flatt, K.L. Scriv mixing on the early hydration of alite and OPC syster Res 2012(42):1175-1188.
https://doi.org/10.1016/j.cemconres.2011.06.011

https://doi.org/10.1016/j.cemconres.2011.06.011

[18] D.P. Bentz, E.J. Garboczi, C.J. Haecker, O.M. Jensen, Eff
particle size distribution on performance propertie
cement-based materials. Cem Concr Res 1999(2
https://doi.org/10.1016/S0008-8846(99)00163-5

[19] E. Berodier, K. Scrivener, Evolution of pore structure in blended systems. Cem Concr Res 2015(73):25-35.
https://doi.org/10.1016/j.cemconres.2015.02.025

[20] V. Kocaba, E. Gallucci, K.L. Scrivener, Methods for determination of degree of reaction of slag in blended cement pastes. Cem Concr Res 2012(42):511-525.
https://doi.org/10.1016/j.cemconres.2011.11.010

[21] K.D. Weerdt, E. Sellevold, K.O. Kjellsen, H. Justnes, Fly ash–limestone ternary cements: effect of component fineness. Adv Cem Res 2011(23):203-214. https://doi.org/10.1680/adcr.2011.23.4.203

[22] I.V. Dolgaleva, I.G. Gorichev, A.D. Izotov, V.M. Stepanov, Modeling of the Effect of pH on the Calcite Dissolution Kinetics, Theor Found Chem Eng 2005(39):614-621.
https://doi.org/10.1007/s11236-005-0125-1

[23] J. Grandet, J.P. Ollivier. Etude de la formation du monocarboaluminate de calcium hydrate au contact d'un granulat calcaire dans une pate de ciment Portland. Cem Concr Res 1980(10):759-770. https://doi.org/10.1016/0008-8846(80)90004-6