

# Hydration behaviour of limestone-calcined clay and limestone-slag blends in ternary cement

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\* Anuj Parashar was invited for submission of this letter as an awardee of the RILEM PhD Grant for the 74<sup>th</sup> RILEM Annual Week, 2020

Received: 23 November 2020 / Accepted: 06 March 2021 / Published online: 19 March 2021

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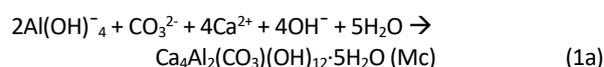
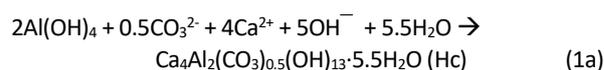
## Abstract

The effect of kaolinitic calcined clay and slag on the hydration of limestone-containing ternary blended cements was investigated. The effect of alumina from different sources of SCMs was considered to activate the formation of carboaluminates. Ternary blends with 50% ordinary portland cement clinker, 45% blends of limestone calcined clay (LC<sup>3</sup>) in 1:2 blend and slag limestone blend (SLS) in 2:1 mix proportion with 5% of gypsum were studied. The hydration behaviour was analysed based on cement mortar compressive strength, heat of hydration using an isothermal calorimeter and bound water measured using thermal gravimetric analysis (TGA). In addition, the degree of hydration of clinker phases and the composition of calcium - alumino - silicate - hydrate (C-A-S-H) gels forming in two different systems were compared on 90 days hydrated samples analysed using X-Ray diffractometry (XRD) and scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX) respectively. The results show a rapid early strength development in limestone calcined clay cement blend (LC<sup>3</sup>) but a lower clinker hydration in comparison with slag limestone cement blend (SLSC) at later ages. In both the cement blends the formation of hemicarboaluminate (Hc) and monocarboaluminate (Mc) was confirmed at 90 days, but the conversion of Hc to Mc was higher in SLSC. Results further confirmed a lower degree of hydration and higher alumina incorporation in the C-A-S-H gel in the LC<sup>3</sup> comparison to SLSC. The presence of calcium hydroxide was also confirmed in the SLSC blend due to the hydraulic nature of slag that supported the later age conversion of Hc to Mc as not seen in LC<sup>3</sup>.

**Keywords:** LC<sup>3</sup>; Carboaluminate; Slag limestone cement; Hydration

## 1 Introduction

Despite the relatively lower degree of hydration of limestone (LS) (1-3 g/100 g), it is known to significantly influence phase assemblage and sulphate balance [1–5]. LS also reacts with alumina in the presence of calcium hydroxide (CH) as shown in equation 1 [5], and produces carboaluminate phases (hemicarboaluminate - Hc and monocarboaluminate - Mc) [5]. The formation of carboaluminates is favoured thermodynamically to the formation of monosulphate (AFm) [5], thereby preventing the conversion of ettringite (Aft) and helping in pore refinement due to the lower density of carboaluminate phases [1, 2, 6–8]. The conversion of alumina to carboaluminate phases also reduces the availability of alumina ions in the solution, preventing the conversion of ettringite (Aft) to monosulphate (AFm) phase. Even when small quantities of LS are added to the cement, the formation of Hc and Mc as hydration products can be observed because only a minor part of LS gets involved in the reaction and most of unreacted LS particles can be found in the microstructure at later ages [9].



The most efficient way of LS utilisation could be in ternary blended cement with a reactive supplementary cementitious material (SCM) that has high alumina content such as kaolinitic calcined clay (CC) or slag (S). It can support the reaction between calcium carbonate and the alumina in the SCM and help in improving the early hydration and strength even at higher clinker replacement levels [8, 10–12]. Such ternary blended cements are already standardised in several countries. ASTM C595/C595M also defines ternary blended cement containing pozzolana with slag or slag with LS [13]. Limestone calcined clay cement (LC<sup>3</sup>) is another well-known ternary blended cement investigated widely in recent years. Studies have shown that the strength and durability properties of LC<sup>3</sup> are similar or better than OPC even when LS and clay blends (also reported as LC<sup>2</sup>) in 1:2 mix proportion by mass were used for clinker replacement by 45% [14–16].

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While LC<sup>3</sup> is a cement that includes the clinker phases, LC<sup>2</sup> is a blend of LS with CC (and some gypsum).

Other than CC, the addition of slag with 15% LS can also be considered for the production of a ternary blended cement [17]. Similar to LC<sup>3</sup>, slag limestone cement (SLSC) with 55% of clinker replacement is reported to achieve similar strengths as OPC at 28 and higher strengths at 90 days [17]. The utilisation of LS (8-17%) in ternary blended cement can increase the filler effect, resulting in enhanced clinker hydration and faster CH evolution [4, 5, 12, 18]. Other than clay and slag, the blends of fly ash with LS have also been studied individually in some studies [12, 17].

Many studies have tried investigating the mechanical and durability properties of ternary blended cements containing LS and the reactivity properties of blended SCMs containing LS [8, 10–12, 14, 15, 19–21]. The key reason for the interest in ternary blended cements is their having better sustainability credentials in comparison to OPC [10, 22]. However, most available studies have only focused on one individual type of ternary cement containing either clay, slag or fly ash with LS [8, 10, 12, 17, 19]. Very limited studies can be found on the comparison of the effect of the SCM type on the efficiency of LS reactivity. The optimised reaction between LS and alumina from an SCM in a ternary cement can help in further improvement of strength and durability properties. That is why it is essential to optimise the hydration of ternary blended cement containing LS with an alumina rich SCM such as clay, fly ash, slag, etc.

This study focuses on the comparison between the hydration reaction of alumina - carbonate system, with different sources of alumina (CC and slag). For this, a high purity CC and a ground granulated blast-furnace slag (S) were used for the ternary blended cements containing LS. The cement mortar compressive strength, heat of hydration using isothermal calorimeter and hydration behaviour up to 90 days was investigated using X-ray diffraction (XRD), thermo gravimetry (TGA) and scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX).

## 2 Materials and Methods

One high purity CC, one S and one LS were used in this study. The clinker was procured from one of the major cement producers in India and was ground using a lab scale ball mill for the preparation of OPC and blends. The raw materials were characterised for their oxide composition using X-ray fluorescence and for their phase composition using XRD. The physical properties, mainly the loss on ignition and particle size distribution, were analysed using a muffle furnace and laser diffraction. In addition to the physical and chemical properties of the raw materials, their reactivity was measured using the Indian standard lime reactivity test performed in accordance with IS 1727 [20, 23, 24]. The lime reactivity test is standardised in Indian Standard 1727 and specifies the measurement of compressive strength of a CH-SCM mortar cured at 27 °C for first 2 days and then at 50 °C for next 8 days. This compressive strength is considered to be indicative of the reactivity of an SCM with CH [23]. The physical, chemical and the reactivity properties of the raw materials are presented in

Table 1. The physical and chemical properties highlight the key differences between CC and slag, such as the alumina content and fineness. The reactive alumina in clay and slag was calculated using XRF and XRD data [25]. The alumina in crystalline unreactive phases (such as kaolinite, mullite, etc.) was subtracted from the total Al<sub>2</sub>O<sub>3</sub> obtained from the XRF data. The total amorphous alumina in clay was around 35% and in case of slag was around 22%. Despite having a difference in phase composition and fineness, the lime reactivity values were found to be similar [20, 26].

**Table 1.** Chemical compositions and physical properties of SCMs and the OPC used.

Constituents %	CC	S	LS	OPC	
SiO <sub>2</sub>	49.6	32.3	11.1	20.5	
Fe <sub>2</sub> O <sub>3</sub>	1.5	1.93	1.5	4.2	
Al <sub>2</sub> O <sub>3</sub>	46.8	23.16	2.5	4.5	
CaO	0.18	33.9	45.6	64.2	
MgO	---	7.01	1.9	2.1	
SO <sub>3</sub>	0.2	---	---	1.9	
Na <sub>2</sub> O	---	0.3	0.5	0.4	
K <sub>2</sub> O	---	0.6	0.28	0.2	
TiO <sub>2</sub>	0.8	---	---	---	
P <sub>2</sub> O <sub>5</sub>	0.01	0.6	---	---	
Kaolinite	20.1	---	---	---	
Quartz	2.8	0.6	6.3	---	
Mullite	4.9	---	---	---	
Gehlenite	---	2.5	---	---	
Calcium carbonate	---	---	93.6	---	
Amorphous	69.2	96.9	---	---	
C <sub>3</sub> S	---	---	---	46.5	
C <sub>2</sub> S	---	---	---	29.9	
C <sub>3</sub> A	---	---	---	3.6	
C <sub>4</sub> AF	---	---	---	16.1	
Lime reactivity (MPa)	11.34	11.57	0.3	---	
Loss on ignition (wt%)	3.08	0.39 (gain)	35.56	0.96	
Particle size analysis	D <sub>V(10)</sub> (μm)	1.8	3.4	1.7	3.2
	D <sub>V(50)</sub> (μm)	5.8	12.4	11.1	17
	D <sub>V(90)</sub> (μm)	21.9	35.5	56.1	59.6

The clinker was ground in the lab with 3% of mineral gypsum with around 92% purity for producing an OPC that was then mixed with the SCMs for preparing blends. The mineral gypsum used for the study was containing carbonate phase as minor impurity. The OPC was then mixed with the SCMs for preparing blends. The ternary blends as per the mix proportions shown in Table 2 were prepared using a turbo powder mixer with rotations about three axes. The blending process ensured the same fineness of clinker and LS in LC<sup>3</sup> and SLSC. Additional gypsum was added in LC<sup>3</sup> and SLSC for balancing the sulphate content, based on the amount of sulphate required to have clear and separate silicate and aluminate peaks in isothermal calorimetry, as reported in previous studies [8, 27].

**Table 2.** Mix composition of the blended cements in weight percent.

Mix ID	Clinker	CC	S	LS	Gypsum
OPC	97	---	---	---	3
LC <sup>3</sup>	50	30	---	15	5
SLSC	50	---	30	15	5

The mixes were tested for cement mortar compressive strength using 7.06 cm cubes at 1, 3, 7, 28 and 90 days. The

mortar cube samples were prepared by using equal quantities of three grades of standard sand and cement mixed in 3:1 proportion and water to binder ratio (w/b) of 0.45. After demoulding, the samples were cured under water at 27 °C.

The heat of hydration of the blends was studied at 27 °C using Calmetrix I-Cal 8000 isothermal calorimeter. This study was performed up to 7 days on paste samples having w/b = 0.45. The preconditioned powder and water was mixed using a vortex mixer, and equal quantities of paste samples were filled in the sample containers used in the test. The paste samples were also cast in the cylindrical centrifuge tubes for measuring the bound water using TGA at 3, 7, 28 and 90 days. For this task, the paste samples were seal-cured and the free water in the samples was removed using solvent exchange before performing TGA. The TGA data was used for analysing the decomposition of hydration phases and for calculating the bound water from 50 °C to 600 °C per dry binder weight.

The phase assemblage and degree of hydration were investigated on the 90 days hydrated samples using Bruker D8 Advance Eco X-ray diffractometer. The XRD scanning was performed on a fresh slice of the hydrated samples, but for the TGA and SEM analysis, free water was removed using the solvent exchange method using isopropanol. The scanning of the samples was performed from 5° 2 $\theta$  to 65° 2 $\theta$ . The XRD data was analysed using TOPAS 4.0 software for quantitative XRD by Rietveld refinement with Rutile as an external standard [19, 28]. The composition of C-A-S-H gel formed in different mixes was studied using SEM-EDX. The hydrated samples were treated for removing free water using solvent exchange for 7 days. The samples were then dried in the vacuum desiccator for another 24 hours. The samples were then impregnated in epoxy before polishing. The polished samples were coated with carbon before carrying out the analysis. The procedure reported in the literature for sample preparation and analysis was followed for SEM-EDX [19].

### 3 Results and discussion

#### 3.1 Cement mortar compressive strength

The cement mortar compressive strength results are plotted in Figure 1. The results show that the LC<sup>3</sup> blend achieved a

higher early strength at the age of 3 days and 7 days in comparison to the SLSC, while similar strengths were seen at 1 day. The compressive strength of LC<sup>3</sup> was comparable to OPC up to 28 days, whereas the SLSC blend gained a lower strength than OPC and LC<sup>3</sup>. While the initial strength development in LC<sup>3</sup> blend was rapid, the strength gain after 7 days was not significant [8, 10, 11]. Such behaviour is reported due to the higher rate of hydration at early ages in LC<sup>3</sup> [28]. In the case of SLSC blend, the strength development was slow at the early ages and continuous gain in strength was observed up to 90 days. The continuous gain in strength in the case of SLSC could be due to the hydraulic nature of slag, which do not require much of CH in in hydration conditions and continuous hydrate slowly [29]. Moreover, the fineness of clay was higher than slag may have helped in the early age strength development in LC<sup>3</sup>, although a slow and continuous gain occurred in the case of SLSC.

#### 3.2 Heat of hydration measured using isothermal calorimeter

The heat flow in mW per gram of clinker is plotted in Figure 2. The two main hydration peaks after the induction period can be noticed in OPC, corresponding to the C<sub>3</sub>S hydration and aluminate hydration. In comparison to OPC, the LC<sup>3</sup> and SLSC blends show higher intensities of both the peaks and a clear separation in between the silicate and aluminate hydration peaks. A stronger aluminate hydration peak occurred due to the additional calcium sulphate in the mix and it appeared earlier in LC<sup>3</sup> than the SLSC. In addition to the acceleration of silicate and aluminate hydration in LC<sup>3</sup> in comparison with SLSC, a third peak corresponding to the carboaluminate formation was noticed at around 34 hours [30]. No such clear peak of carboaluminate was noticed in SLSC sample.

The cumulative heat flow plot shown in Figure 3 indicates the rapid early hydration in the LC<sup>3</sup> and SLSC mixes due to higher heat release in comparison to OPC. The hydration was further investigated using TGA, XRD and SEM-EDX and is presented next.

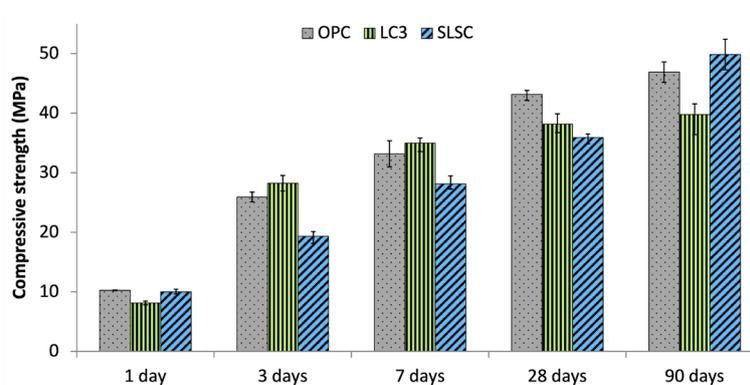


Figure 1. Cement mortar compressive strength plot for OPC, LC<sup>3</sup> and SLSC.

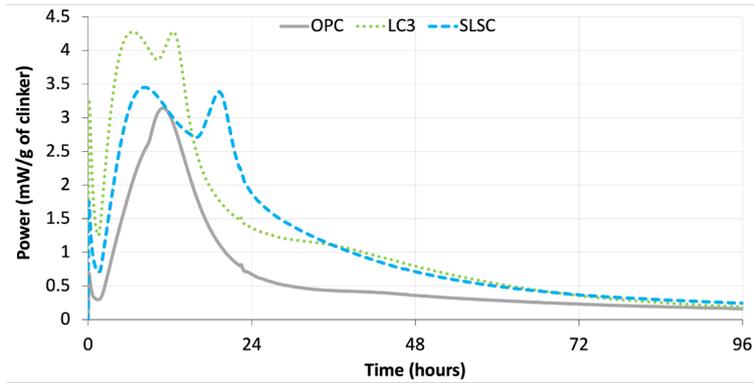


Figure 2. Heat flow plot for OPC, LC<sup>3</sup> and SLSC.

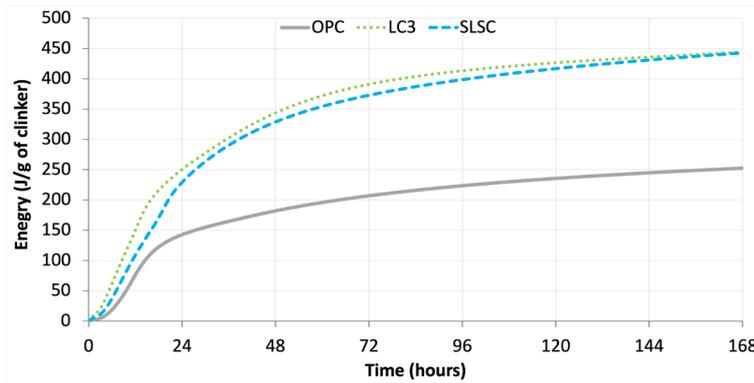


Figure 3. Cement mortar compressive strength plot for OPC, LC<sup>3</sup> and SLSC.

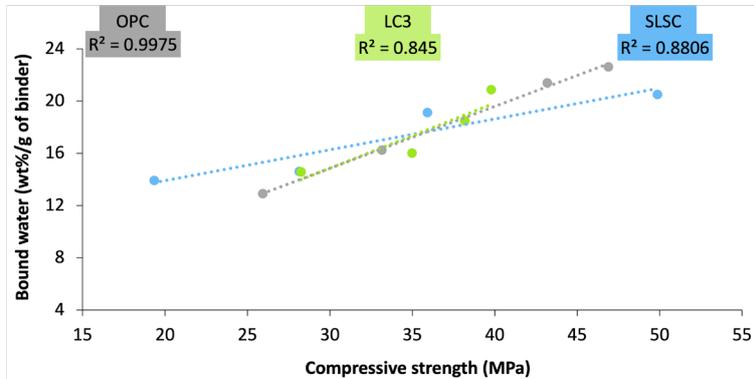


Figure 4. Comparison of the hydrated cement bound water with the cement mortar compressive strength.

### 3.3 TGA

The bound water calculated from 50 °C to 600 °C and the cement mortar compressive strength were compared and are shown in Figure 4. The results show a good correlation with the cement mortar compressive strength confirming the rapid early strength development in LC<sup>3</sup> and later age strength development in SLSC. The bound water in the 90 days hydrated samples of LC<sup>3</sup>, SLSC and OPC were 20.5%, 20.8% and 22.6%, indicating a lower degree of hydration of clinker phases in LC<sup>3</sup> in comparison with SLSC. As expected, the bound water was highest in the OPC sample especially at later ages due to the higher quantity of CH available in the system. The differential TG (DTG) plot shown in Figure 5 confirms the presence of CH in the 3 days hydrated LC<sup>3</sup> mix and absence of

CH in the 7, 28 and 90 days hydrated samples. But the presence of CH was confirmed at all the testing ages in SLSC. The rapid hydration in the LC<sup>3</sup> mix was once again observed in the DTG plot due to a stronger decomposition peak of C-S-H, AFt/AFm and carboaluminates phases (50 °C to 200 °C) in comparison to SLSC. A rapid CH consumption due to the pozzolanic reaction and carboaluminate formation was also observed [8, 10, 19]. But the presence of carboaluminates only increased slightly at the later ages. Although in the case of SLSC, clearly the decomposition of C-A-S-H, AFt/AFm and carboaluminate phases was less in comparison to LC<sup>3</sup>, the later age formation of carboaluminates can be seen in the results.

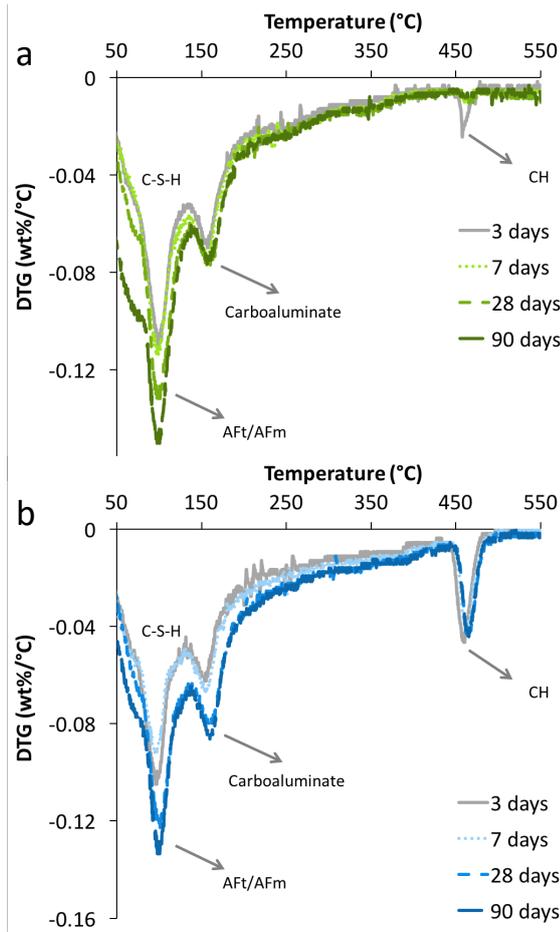


Figure 5. (a) DTG plot for hydrated LC<sup>3</sup> samples at different ages and (b) DTG plot for hydrated SLSC samples at different ages.

### 3.4 Hydration products and degree of hydration measured using XRD

The evolution of hydration products in the 90 days hydrated samples and the degree of hydration of clinker phases were

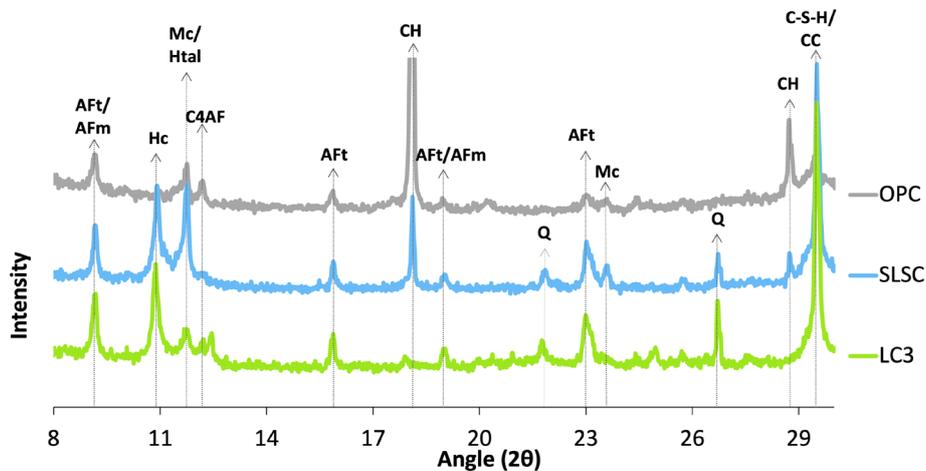


Figure 6. Evolution of hydration products observed using XRD on the 90 day hydrated samples of OPC, LC<sup>3</sup> and SLSC.

analysed using XRD. The X-ray diffractograms plotted in Figure 6 confirm the formation of carboaluminate phases (Hc and Mc) and the AFt phase can be seen to be stable even at 90 days in both LC<sup>3</sup> and SLSC mixes. It is interesting to note that the conversion of Hc to Mc phase is visible in SLSC mix but in LC<sup>3</sup> mix only a minor part of Hc gets converted into Mc by 90 days. Also, the absence of CH in LC<sup>3</sup> was again confirmed in the XRD results.

The degrees of hydration of four main clinker phases (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF) were measured with quantitative XRD analysis using the external standard method [19, 28] and the results with respect to the clinker composition are plotted in Figure 7. A degree of hydration for C<sub>3</sub>S and C<sub>3</sub>A was close to 100% in all the 3 samples but a lower hydration of C<sub>2</sub>S was observed in LC<sup>3</sup> in comparison with OPC and SLSC. The overall degree of hydration of four main clinker phases was found to be 80% in the case of OPC, 70% in the case of LC<sup>3</sup> and 75% in the case of SLSC. The formation of C-A-S-H is reported next to further compare the hydration in LC<sup>3</sup> and SLSC.

### 3.5 SEM-EDX

SEM-EDX analysis was carried out to investigate the C-A-S-H produced in different cement systems and to compare them with OPC. The inner and outer products have a non-directional and fibrillary/foil-like morphology, respectively and the morphology appears to be similar in all three systems. A total of 150 data points were collected over 5 frames at 5000 X. The examples of one of the frames for LC<sup>3</sup> (left) and SLSC (right) shown in Figure 8 highlights that the maximum data points collected within the boundary of the hydrated clinker grains which is mainly surrounded by inner and outer hydration product. [31].

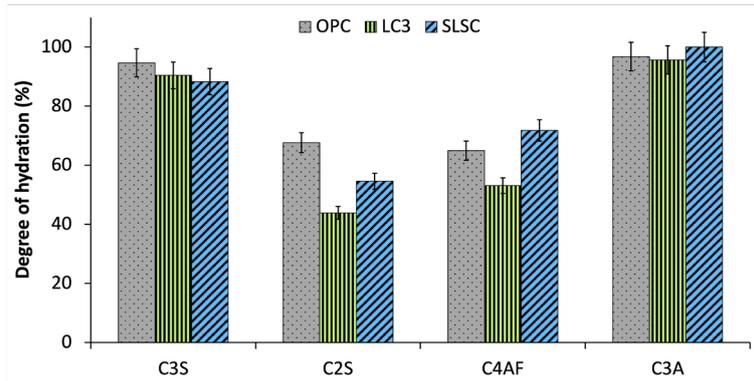


Figure 7. Degree of hydration of clinker phases in the 90 hydrated samples of LC<sup>3</sup>, SLSC and OPC.

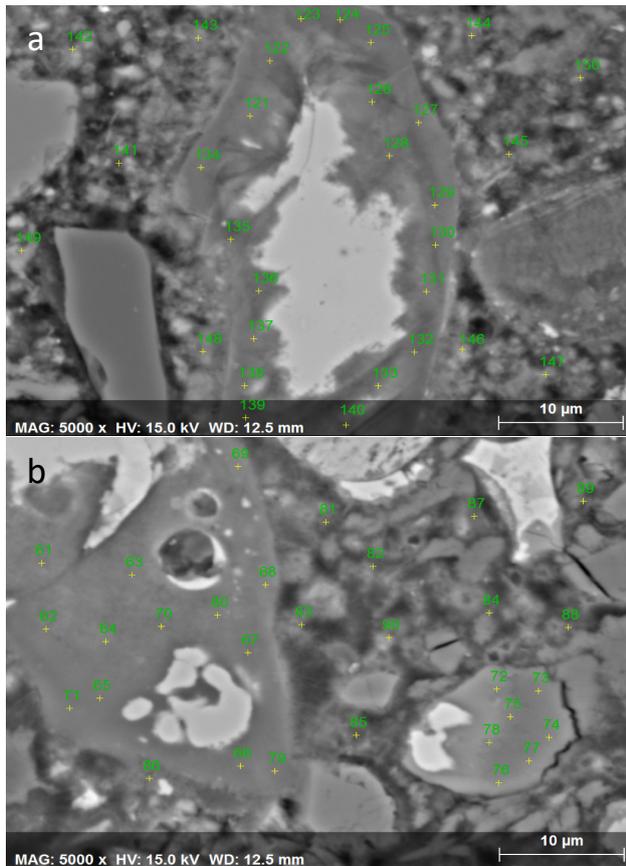


Figure 8. (a) BSE images of the 90 hydrated samples of LC<sup>3</sup>, and (b) SLSC.

The total Al<sub>2</sub>O<sub>3</sub> content as per the oxide composition presented in Table 1 in CC and slag are different, and the proportion of reactive alumina in each of the SCMs is seen to influence the Al/Ca ratio in the product. The SEM-EDX analysis in Figure 9 shows that with the replacement of OPC with SCMs, a reduction in calcium to silica ratio (Ca/Si) can be noticed. While the Ca/Si is similar in LC<sup>3</sup> and SLSC, the amount of alumina (Al) incorporated in C-A-S-H is higher in LC<sup>3</sup> due to the higher Al content in the clay as compared to the slag [19, 28, 30, 32]. A higher spread in the composition of the C-A-S-H was observed in the blended systems compared to the OPC. While the high fineness of the calcined clay particles and intermixing of hydration products may influence the EDX measurements, the higher spread and higher alumina content in the C-A-S-H in LC<sup>3</sup> is well-established [19, 28, 30, 33].

#### 4 Discussion

The cement mortar compressive strength results show a rapid strength gain in the case of LC<sup>3</sup> and a slower strength gain in the case of the SLSC blend. Despite the same clinker fineness in both the blends, the isothermal calorimetry results confirmed that the peak corresponding to the silicate hydration was influenced by the type of SCM used in the cement. The type of SCM can influence the hydration of clinker from the early ages as the aluminate ions from an SCM can start to dissolve even at a lower pH in comparison to silicate ions [34]. The higher slope of the acceleration peak in LC<sup>3</sup> and the occurrence of the silicate peak that appeared around 6 hours was even earlier than OPC (observed at about 8 hours).

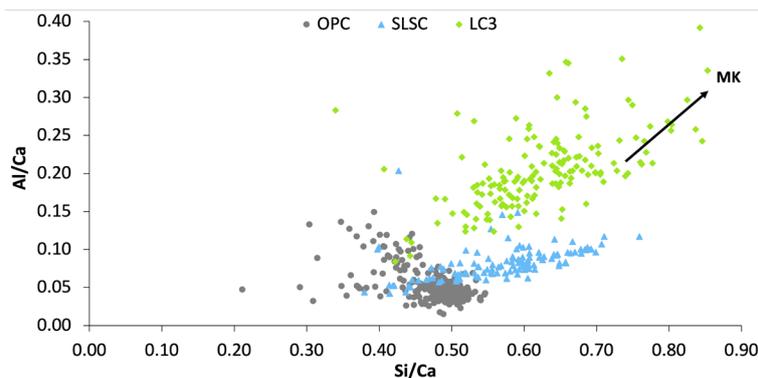


Figure 9. Comparison of Al/Ca and Si/Ca ratios in C-A-S-H gel at the age of 90 days for OPC, LC<sup>3</sup> and SLSC.

The acceleration of clinker hydration can further be confirmed from the aluminate hydration peaks occurred at different times for LC<sup>3</sup> and SLSC. Due to lower reactive alumina in slag, the aluminate hydration peak appeared at around 19 hours which was observed at around 13 hours for LC<sup>3</sup> with the same amount of sulphate content in both the mixes. Moreover, a clear carboaluminate formation peak was seen in the LC<sup>3</sup> mix. Though the cumulative heat for LC<sup>3</sup> and SLSC was found similar, the reason for lower early strength was not clear in SLSC. The formation of carboaluminate phases was observed to be much later in SLSC. Despite the accelerated early age hydration in LC<sup>3</sup>, the bound water measured using TGA data was slightly lower than OPC. But, even with a higher bound water content in OPC, the strength of OPC was similar to that of LC<sup>3</sup> at early ages (upto 7 days) and similar to SLSC at 90 days. This indicates that the higher bound water in OPC was mainly due to the presence of CH, which was significantly reduced in LC<sup>3</sup>. Higher bound water may not necessarily mean higher strength as the amount of bound water mainly depends on the type of hydration products and the mechanical efficiency of the hydration products depends on many factors [35]. The DTG and XRD results indicate that the formation of carboaluminate at an early age could be the reasons for the rapid early strength in LC<sup>3</sup>. In the later age of hydration, a significantly higher formation of carboaluminates is seen in the case of SLSC compared to LC<sup>3</sup>. Minor amounts of Aft is also observed in the OPC specimen. This may be due to the presence of minor amounts of calcite in the paste, either due to carbonation or as an impurity in the gypsum. From the XRD results, it appears that the lack of CH in the LC<sup>3</sup> system reduces this conversion as shown in equation 1 (a) and (b). Therefore, the calcium available in slag seems to support the transformation of Hc to Mc. The higher pozzolanic reactivity of calcined clay and the hydraulic nature of slag are the reason for such behaviour. This phenomenon also supports the later age strength development in SLSC. A refinement of the pores due to the rapid reaction of the clay has also been reported to be the cause of the lower degree of hydration in LC<sup>3</sup> [33, 36].

Although the higher reactivity of calcined clay is well known, the impact of such high reactive SCM was seen to act as a barrier in the later age strength development and hydration. As the higher reactivity of clay consumed CH at a rapid rate, the maximum potential of the carbonate reaction could not be reached in LC<sup>3</sup>. It was seen that a lower reactivity SCMs such as impure kaolinite clay or slag can help in the later age improvement of hydration and strength. Irrespective of the type of SCM, the C-A-S-H in LC<sup>3</sup> and SLSC had a higher alumina content as compared to OPC. The scatter in the C-A-S-H composition, is seen to be higher in the higher reactive alumina systems, showing a non-uniform Al uptake in C-A-S-H or a greater inter-mixing of the aluminates with the product. The incorporation of more Al in C-A-S-H can also increase the polymerisation of the product and reduce the hydration of clinker [32]. Another reason for lower clinker hydration in LC<sup>3</sup> could be reduction of the pH of the pore solution. It is also reported that the incorporation of Al in C-S-H gel increases alkali binding. This could lead to a reduction in

the pH of pore solution [32, 37], slowing down the hydration of clinker phases.

Several studies have suggested that the physical presence of the high surface-area SCM increases the clinker hydration [38]. But based on the results obtained in this study, it is expected that the change in the pore-solution concentrations due to the presence of the rapidly dissolving calcined clay particles not only influences the early-hydration, but also the long-term hydration. In the long-term, the dissolution of clinker phases is prevented due to the higher concentration of alumina. It is also confirmed by results in the literature, where it has been shown that there is a dramatic increase in the alumina content in C-A-S-H with the addition of more pure calcined clays, even at early ages [33, 39]. Also, the formation of hydroxy-AFm and carboaluminate phases will be thermodynamically preferred due to the higher enthalpy of these reactions [5]. Such a preferential reaction of the calcium in the solution may suppress the dissolution of silicates in the clinker grains, leading to the formation of a silica-rich and calcium depleted zone around the grains. This layer may act as an impediment to further dissolution or hydration of clinker particles. Such a layer has been reported to form when carbonation of pastes with sufficient clinker grains occurs [19].

## 5 Conclusions

The key findings from this study are listed below:

- Like LC<sup>3</sup>, a reaction of the alumina in slag is seen with the carbonate in LS. The phase assemblage of SLS system is similar to the LC<sup>2</sup> system.
- While the faster reaction of the calcined clay and LS increases the rate of strength development, a higher long-term strength is seen in the slag system.
- The higher availability of calcium in the slag system influences the phase assemblage in the long-term, especially the conversion of the carboaluminate phases.
- The higher alumina content in the calcined clay system, compared to the slag system appears to reduce its long-term hydration and strength development. The cause for this needs to be investigated further.

## Acknowledgements

The sponsorship of the Swiss Agency for Development and Cooperation is acknowledged for this work.

The RILEM PhD grant awarded during the 74<sup>th</sup> RILEM Week at the University of Sheffield is acknowledged for providing the support to submit this manuscript.

## Authorship statement (CRediT)

Anuj Parashar: Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review and editing, Visualization.

Shashank Bishnoi: Supervision, Conceptualization, Validation, Resources, Writing – review and editing, Project administration, Funding acquisition.

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