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# Mechanical activation of muscovite-rich clay: A novel approach for ternary blended cement

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# ABSTRACT

Clay minerals with a 2:1 structure typically exhibit limited pozzolanic activity after calcination, which constrains their use as supplementary cementitious materials. Mechanical activation has emerged as a promising approach to enhance the reactivity of clays, potentially improving the performance of cement containing mixed clays rich in 2:1 clay minerals. This research assesses the properties of ternary blended cement produced with mechanically activated muscovite-rich mixed clay (LMC<sup>2</sup>-MM) in comparison to limestone calcined clay cement containing either calcined muscovite-rich mixed clay (LC<sup>3</sup>-CM) or metakaolin (LC<sup>3</sup>-MK). Results from pozzolanic activity tests (R<sup>3</sup> and modified Chapelle) revealed a significant improvement in the reactivity of muscovite-rich mixed clay via mechanical activation (MM) compared to thermal activation (CM). LMC<sup>2</sup>-MM exhibited similar structure and properties to conventional LC3-MK, and the enhanced reactivity of MM over CM led to improved properties for LMC<sup>2</sup>-MM compared to LC<sup>3</sup>-CM. The hydration of LMC<sup>2</sup>-MM was superior to that of LC<sup>3</sup>-CM, achieving significantly refined porosity at both 3 and 28 days. This study presents a novel approach to ternary blended cement by incorporating mechanically activated mixed clay. It demonstrates that mechanical activation enhances the properties of blended cement, particularly at early ages when using muscovite-rich clays, achieving compressive strength comparable to conventional LC<sup>3</sup> with metakaolin. The mechanical activation of muscoviterich mixed clay presents a promising strategy for using local clay resources in regions where kaolinite-rich clay is scarce

# 1. Introduction

The partial replacement of clinker in ordinary Portland cement (PC) with supplementary cementitious materials (SCMs) is one of the most promising routes for pursuing a more sustainable construction industry [1]. In this context, limestone calcined clay cement (LC<sup>3</sup>) technology has emerged as a suitable alternative to PC and is rapidly growing and being implemented globally [2]. LC<sup>3</sup> is a ternary blended cement containing two SCMs, calcined clay and limestone, which entails a substantial reduction in the clinker factor, typically to 50 wt% of clinker (LC<sup>3</sup>-50), while using worldwide available SCMs that can meet the cement industry's demand [3]. This significant substitution rate in LC<sup>3</sup> is mainly achieved because of the synergistic effect between calcined clay and limestone, which react to form carboaluminate phases, reducing the porosity of the material and increasing its strength [4]. LC<sup>3</sup>-50 can potentially reduce CO<sub>2</sub> emissions by up to 40% compared to PC [5]. Several studies have demonstrated the advantages of using LC<sup>3</sup> over PC.

In this sense,  $LC^3$  is more sustainable, cost-effective, and energy-effective from an environmental perspective and exhibits good mechanical properties and durability comparable to those of PC from a performance point of view [6,7]. These benefits, coupled with the widespread availability of SCMs, make  $LC^3$  a promising alternative to PC.

The LC<sup>3</sup> technology is constantly improving and there is scope for further advancement, for instance, evaluating the substitution of conventional kaolinitic clays by less reactive clays. The kaolinite content in the clay is a critical parameter of calcined clay for its use as an SCM. In this sense, clays containing 40 % kaolinite (typically between 40 % and 60 % by weight) are considered optimal for producing LC<sup>3</sup>, although low-grade kaolinitic clays have also shown potential [8,9]. Calcination of kaolin induces dehydroxylation of kaolinite, resulting in metakaolin (MK), which is mainly formed by an amorphous and highly reactive phase known as metakaolinite. MK is a calcined clay with the highest pozzolanic activity, whereas other calcined clays, particularly those rich

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in 2:1 clay minerals, typically exhibit limited reactivity [10]. Therefore, mixed clays containing significant amounts of 2:1 clay minerals display inferior performance than kaolinite-rich clays as SCMs.

The limited reactivity of 2:1 clay minerals should be addressed because they are predominant in some regions, such as arid and highlatitude regions (illite/mica-rich clays), eastern Australia, central India, and east-central Africa (smectite-rich clays) [11]. Calcined 2:1 clay minerals are typically much less reactive than 1:1 clay minerals because of their crystalline structure. In mica clay minerals, dehydroxylation does not induce the amorphisation of the structure, and the octahedral Al remains trapped between the Si tetrahedra sheets. Furthermore, 2:1 clay minerals generally require a higher calcination temperature to achieve dehydroxylation [12]. Calcined smectitic clays exhibit some degree of reactivity, whereas calcined illitic/muscovitic clays are commonly much less reactive [13]. Therefore, despite their greater abundance than kaolinitic clays in several regions, the limited activity in cement of clays rich in 2:1 clay minerals is a major drawback for countries with a high availability of them.

In this regard, mechanical activation has emerged as an effective method for enhancing the reactivity and pozzolanic activity of clays. The mechanical stresses generated during the highly energetic milling process disrupt the layered structure of the clay minerals and break chemical bonds [14]. Crystalline structure amorphisation coupled with a reduction in particle size improves the reactivity of clays without inducing dehydroxylation [15]. Given the limited reactivity of dehydroxylated 2:1 clay minerals, mechanical activation has emerged as a promising alternative for enhancing the use of mixed clays rich in 2:1 clay minerals, particularly in regions where the availability of kaolinite-rich clays is limited [16]. Furthermore, mechanical activation likely offers a more environmentally friendly approach since industrial milling requires electric power instead of fossil fuels used in thermal activation (calcination) [17], reducing greenhouse gas emissions and pollution associated with energy-intensive combustion processes [18]. Moreover, using renewable energy sources for electric power production would further enhance the sustainability of clay activation processes.

This work aims to assess the effects of incorporating mechanically activated muscovite-rich mixed clay compared to calcined muscoviterich mixed clay on the properties of LC<sup>3</sup> to evaluate the possibility of using 2:1 clays in ternary blended cement. The novelty mainly lies in the evaluation of mechanically activated alternative clays as SCMs to expand the LC<sup>3</sup> technology in regions where kaolinitic-rich clays are not available. To this end, the pozzolanic activity of raw and activated muscovite-rich mixed clays was first analysed and compared with that of metakaolin. Subsequently, ternary blended cement incorporating calcined and mechanically activated muscovite-rich mixed clay was formulated and compared with conventional LC<sup>3</sup> containing metakaolin. A comprehensive analysis was conducted to assess the effects of distinct activated clay on the properties and performance of the cement: the hydration and physicochemical properties of the cements were monitored, the microstructure was assessed using microscopy and porosimetry, and the compressive strength was evaluated.

## 2. Materials and methods

## 2.1. Clay activation and characterisation

#### 2.1.1. Raw clays

A mixed muscovite-rich clay (RM), and a kaolin (RK) were used for ternary blended formulation such as novel and reference SCMs, respectively. Both clays are commercially available and were provided by the company Minerals i Derivats, S.A. (Spain) and activated without prior treatment. Their chemical composition was obtained through Xray fluorescence (XRF) in an Axios device (Malvern Panalytical) on a fused bead prepared at 1100 °C. The mineralogical composition was determined through X-ray powder diffraction (XRD) in a Bragg-Brentano X'Pert PRO MPD alpha1 diffractometer (Malvern Panalytical) operated with a focalising Ge monochromator and five scans from 4 to 100 °20 with a step size of 0.026 ° and a measuring time of 24 min per scan. A semiquantification of the mineral phases was performed through Rietveld refinement with the software TOPAS. Furthermore, the amorphous content ( $W_{amorphous}$ ) was estimated based on the degree of crystallinity method (DOC), which is obtained by measuring the area of the amorphous background and the area of the peaks corresponding to the crystalline phases, according to Eq. 1 and Eq. 2 [19].

$$DOC = \frac{Crystalline Area}{Crystalline Area + Amorphous Area} \cdot 100$$
(1)

$$W_{amorphous} = 100 - DOC \tag{2}$$

The amorphous area was measured by fitting the amorphous background with two broad peaks using the fundamental parameter approach peak phase function in TOPAS, which eliminates the contribution of the instrument. In the 1:1 clay, the amorphous background appeared narrower, while in the 2:1 clay, broader and more asymmetric humps were observed. These differences, which are related to the initial clay structure and composition, were treated accordingly during fitting. This method has an estimated error of less than 2 wt% of amorphous content and is especially useful for samples containing several or unknown amorphous phases [20].

The chemical composition and the mineral phases are compiled in Table 1. RM could be considered a muscovite-rich mixed clay since presented muscovite as the main crystalline phase (~57 %) and significant percentages of kaolinite (16.7 %) and montmorillonite (11.3 %). According to the literature, this kaolinite content is below the threshold of at least 40 wt% of kaolinite, which is considered proper content for the use of clay as SCM in  $LC^3$  formulation [21]. In contrast, RK displayed a high kaolinite content (~82 %) with minor impurities and was selected as a reference SCM.

## 2.1.2. Clay activation

RM was activated through calcination to obtain calcined muscoviterich mixed clay (CM) and through milling to obtain mechanically activated muscovite-rich mixed clay (MM). RK was calcined to obtain metakaolin (MK) for comparison purposes. This section describes the activation methods for each clay type, which are summarised in Table 2.

CM was obtained by thermal activation of RM in a laboratory electric furnace at 900 °C for one hour based on previous tests and literature [16, 22]. The thermal treatment was performed with a heating rate of  $5^{\circ}$ C/min, and the clay was cooled to room temperature inside the furnace. MM was obtained through a highly energetic dry milling process of RM using a planetary ball mill (PM 100, RETSCH) equipped with 500 mL zirconia jars and 10 mm zirconia balls. The milling treatment was carried out at 400 rpm for 90 min under ambient conditions, with no rest intervals. The jar was filled to approximately 20 vol% with a balls-to-sample mass ratio of 20, using approximately 540 g of balls and

## Table 1

Chemical composition (XRF) and mineral phases quantification (through Riet-veld refinement of XRD data) of raw clays.

Chemical composition (wt%)			Mineral phase quantification (wt%)				
Oxide	RM	RK	Phase	RM	RK		
SiO <sub>2</sub>	51.38	49.85	Muscovite/illite	56.5	5.3		
Al <sub>2</sub> O <sub>3</sub>	30.59	36.31	Kaolinite	16.7	82.0		
K <sub>2</sub> O	6.23	0.69	Montmorillonite	11.3	-		
Fe <sub>2</sub> O <sub>3</sub>	1.46	0.47	Quartz	6.2	5.7		
MgO	1.12	0.11	K-feldspar	4.1	1.6		
CaO	0.48	0.16	Amorphous content	5.1	5.4		
TiO <sub>2</sub>	0.44	0.15					
Na <sub>2</sub> O	0.40	0.03					
$P_2O_5$	0.09	0.08					
LOI	7.81	12.03					

#### Table 2

Summary of clays and activation methods.

Raw/activated clay	Abbreviature	Activation method
Raw muscovite-rich mixed clay	RM	No activation
Calcined mixed clay	CM	Calcination at 900 °C for 1 h
Mechanically activated	MM	Mechanical activation at 400 rpm
mixed clay		for 90 min
Raw kaolin	RK	No activation
Metakaolin	MK	Calcination at 800 °C for 1 h

27 g of RM per batch. These conditions correspond to the optimal milling parameters identified in a previous study by the authors [16].

MK was obtained by calcining RK at 800 °C for one hour in a laboratory electric furnace based on previous tests and literature [23,24]. As for CM, the heating rate was 5 °C/min and the clay was cooled to room temperature inside the furnace.

# 2.1.3. Clay characterisation techniques

Clay-based materials have been evaluated using various characterisation techniques. The techniques and test conditions used are described in this section.

XRF and XRD measurements of activated clays were performed using the same procedure as for the raw clays measurements described in Section 2.1.1. Thermogravimetry (TG) was used to evaluate the mass loss of raw and activated clays, evaluated using an SDT Q600 device (TA Instruments) with a heating rate of 10 °C/min, synthetic air atmosphere (50 mL/min), and measuring up to 1000 °C.

The particle size distribution was assessed using a laser diffraction particle-sizing analyser (LS 13 320, Beckman Coulter). A small amount of clay was dispersed in ethanol and sonicated for 5 min to prevent aggregation, and the particle size was measured using a universal liquid module. The specific surface area (SSA) was measured using the Brunauer-Emmett-Teller (BET) method in a TriStar 3000 V6.04, which is a device employing nitrogen as an inert gas at 77.3 K. Particle morphology was assessed using scanning electron microscopy (SEM) with a JSM-7100F thermal field emission electron microscope (JEOL) operated at an accelerating voltage of 20 kV and a working distance of 10 mm.

### 2.1.4. Activated clays characterisation

The effects of the two activation methods (mechanical and thermal) on muscovite-rich mixed clay should be examined to study the impact of clay type on  $LC^3$  formulation. For this purpose, the characteristics of MM and CM are presented and compared with those of RM, RK, and MK.

Table 3 reveals that thermal and mechanical activation had little effect on the chemical compositions of CM and MM, maintaining the same composition aside from renormalisation in the CM owing to the loss of hydroxyl groups during the calcination process. Thermal activation led to the amorphisation of kaolinite and montmorillonite in the CM, whereas muscovite was still detected in its dehydroxylated form,

with a significant percentage of approximately 41 wt%. In contrast, mechanical activation led to the amorphisation of all clay minerals, resulting in a high amorphous content of approximately 91 wt%. The slight presence of zirconia was derived from sample contamination with the grinding media owing to the highly aggressive milling conditions.

MK is mainly composed of amorphous  $SiO_2$  and  $Al_2O_3$  with approximately 89 wt% of amorphous phase, which corresponds to metakaolinite given the high kaolinite content in RK of approximately 82 wt%, see Table 1. In addition, quartz, K-feldspar, and dehydroxylated muscovite/illite were detected as minor mineral phases. The XRD patterns and TG curves of the raw and activated clays are presented in Supplementary Material.

Fig. 1 shows the particle size distribution and SSA of the raw and activated clays. RM presented a mean particle size (d<sub>50</sub>) of 13 µm and SSA of 10.0 m<sup>2</sup>/g. Thermal activation (CM) had little effect on the particle size, with a d<sub>50</sub> of 13 µm, while the SSA was reduced to 8.4 m<sup>2</sup>/g, maintaining a very similar differential volume curve. Mechanical activation (MM) resulted in a significant decrease in the particle size, detecting a high volume of small particles in the differential volume curve and a mean particle size of 4 µm. However, a reduction in the SSA to 9.0 m<sup>2</sup>/g was also detected, which is attributed to the agglomeration of smaller particles and changes in the pore structure that take place in prolonged milling processes [25]. MK exhibited a mean particle size of 7 µm and a SSA of 9.2 m<sup>2</sup>/g, similar to the values of RK, 7 µm and 10.0 m<sup>2</sup>/g, respectively.

The differences in the clay particle morphology depending on the activation treatment were also assessed using SEM. Fig. 2 presents the SEM micrographs, where RM (Fig. 2a) displays platy particles



Fig. 1. Particle size distribution of RM, CM, MM, RK, and MK.

Table 3

Chemical composition	(XRF) and mineral	phases quantification	(through Rietveld refinement	of XRD data) of activated clays.
· • • • • • •				

Chemical comp	position (wt%)			Mineral phase quantification (wt%)				
Oxide	СМ	MM	МК	Phase	СМ	MM	МК	
SiO <sub>2</sub>	55.33	50.96	56.44	Dehydroxylated muscovite	41.3	-	1.7	
Al <sub>2</sub> O <sub>3</sub>	32.95	30.31	41.12	Quartz	7.8	7.0	8.3	
K <sub>2</sub> O	6.72	6.19	0.79	K-feldspar	2.2	1.6	1.0	
Fe <sub>2</sub> O <sub>3</sub>	1.61	1.48	0.51	Zirconia	-	1.0	-	
MgO	1.20	1.11	0.09	Amorphous content	48.6	90.6	89.0	
CaO	0.52	0.48	0.11					
TiO <sub>2</sub>	0.48	0.44	0.17					
Na <sub>2</sub> O	0.43	0.40	0.03					
$P_2O_5$	0.10	0.09	0.08					
LOI	0.66	8.54	0.67					



Fig. 2. SEM micrographs of (a) RM, (b) CM, (c) MM, (d) RK, and (e) MK.

corresponding primarily to muscovite, the main clay mineral in the sample. The CM (Fig. 2b) exhibited a similar platy morphology, suggesting that the thermal treatment did not significantly alter the morphology of the clay particles. In contrast, MM (Fig. 2c) displayed very small and more rounded particles, indicating significant morphological changes through mechanical activation. As aforementioned, these very small particles tend to agglomerate during mechanical activation because of highly energetic mechanical processes. An agglomerate is displayed in the top-right corner of Fig. 2c. The RK (Fig. 2d) primarily consisted of platy-stacked kaolinite particles. The morphology was maintained after thermal activation in MK (Fig. 2e) but with slightly rounded edges of metakaolinite particles.

## 2.2. Pozzolanic activity measurements

The pozzolanic activity of raw and activated clays was assessed using the modified Chapelle test and the  $R^3$  method. The modified Chapelle test was performed following the procedure described by Šídlová et al. based on the NF P18–513 standard [26]. In this method, 1 g of activated clay and 2 g of CaO were added to a spherical flask with 250 mL of deionised water and agitated for 16 h at 90 °C to measure the consumed CaO. A reflux condenser was used to prevent evaporation. The resultant solution was mixed with 250 mL of sucrose 0.7 M for 15 min (after cooling to room temperature), filtered, and titrated with HCl 0.1 N. The pozzolanic activity, denoted as mg of portlandite (CH) consumed per gram of clay, was calculated through Eq. 3, where V<sub>1</sub> represents the volume of HCl required for blank titration and V<sub>2</sub> is the volume of HCl necessary for the titration of the activated clay solution.

$$CH \ consumption(mg \ CH / gclay) = 2 \cdot \frac{V_1 - V_2}{V_1} \cdot \frac{74}{56} \cdot 1000 \tag{3}$$

The R<sup>3</sup> method, performed according to ASTM C1897–20, involved preparing a solid mixture comprising Ca(OH)<sub>2</sub>, clay, and CaCO<sub>3</sub> while maintaining a mass ratio of 1/3 for clay/Ca(OH)<sub>2</sub> and 2/1 for clay/ CaCO<sub>3</sub>. A potassium solution was prepared by dissolving in 1 L of distilled water 20 g of K<sub>2</sub>SO<sub>4</sub> and 4 g of KOH. The solution was added to the solid blend, maintaining the liquid-to-solid ratio constant (1.2), and the resulting paste was mixed at approximately 1300 rpm with a highshear mixer for 2 min. Subsequently, 15 g was introduced into a plastic ampoule, which was positioned inside an isothermal calorimeter (TAM Air, TA Instruments), and the heat released was measured at a constant temperature of 40 °C for 7 days. The initial 75 min of data were disregarded to ensure signal stabilisation [27,28].

# 2.3. Ternary blended cements

#### 2.3.1. Raw materials preparation and characteristics

In addition to the activated clays previously described, clinker, limestone, and gypsum were used to prepare ternary blended cements. The clinker was treated to refine its particle size, the clays were activated as described in Section 2.1.2, and the limestone and gypsum were used as received. This section presents the clinker treatment and characteristics of the raw materials.

The Spanish company Molins provided the clinker used in this study, which was crushed and milled through a jaw crusher and a ring mill, until obtaining a particle size under 80  $\mu$ m. The characteristics of the particle-size refined clinkers are listed in Table 4. It exhibited a d<sub>50</sub> of 8  $\mu$ m and a BET SSA of 0.8 m<sup>2</sup>/g. The identified crystalline phases included tricalcium silicate (C<sub>3</sub>S), dicalcium silicate (C<sub>2</sub>S), calcium aluminoferrite (C<sub>4</sub>AF), and tricalcium aluminate (C<sub>3</sub>A), whose quantification through Rietveld refinement of the XRD data is also detailed in Table 4. Furthermore, some typical CaO and MgO impurities were detected.

Commercial limestone and gypsum were obtained from LABKEM (Labbox, Spain) and used without prior treatment for the cement preparation. The limestone had a purity higher than 98.5 wt%, a d<sub>50</sub> of 2  $\mu$ m, and a BET SSA of 11.1 m<sup>2</sup>/g, while the gypsum presented a purity higher than 99 wt%, a d<sub>50</sub> of 21  $\mu$ m, and a BET SSA of 0.9 m<sup>2</sup>/g.

# 2.3.2. Mix design

The raw materials described in the previous sections were mixed with deionised water and superplasticiser (SP) to prepare ternary blended cements. The mixture proportions, mixing procedures, and curing conditions are listed in Table 5.  $LC^3$ -50 ratios were used for the solid blend, that is 50 wt% of clinker, 30 wt% of clay, 15 wt% of limestone, and 5 wt% of gypsum. For the two calcined clays (MK and CM), the nomenclature used was  $LC^3$ , followed by the type of clay:  $LC^3$ -MK and  $LC^3$ -CM. For MM, which was obtained through mechanical activation instead of calcination, the nomenclature of the ternary blended cement was changed accordingly to  $LMC^2$ , short for Limestone Mechanically activated Clay Cement, followed by the type of clay as in previous samples:  $LMC^2$ -MM.

All the formulations were prepared with 40 wt% of deionised water, expressed to the total solid amount, thus maintaining a water-to-solids

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## Table 4

Clinker chemical composition (XRF), phase quantification (Rietveld refinement of XRD data), particle size distribution, and BET specific surface area.

Chemical c	omposition (wt%)								
<b>CaO</b> 66.19	<b>SiO</b> <sub>2</sub> 21.06	Al <sub>2</sub> O <sub>3</sub> 4.94	<b>Fe<sub>2</sub>O<sub>3</sub></b> 3.67	<b>MgO</b> 1.56	<b>K<sub>2</sub>O</b> 0.91	<b>TiO<sub>2</sub></b> 0.26	<b>Na<sub>2</sub>O</b> 0.18	<b>P</b> <sub>2</sub> <b>O</b> <sub>5</sub> 0.08	<b>LOI</b> 1.11
Phase quan	tification (wt%)								
<b>C<sub>3</sub>S</b> 75.6	<b>C<sub>2</sub>S</b> 10.5	C₄AF 7.5	С <sub>3</sub> А 5.3	<b>CaO</b> 0.6	<b>MgO</b> 0.6				
Particle size	e (µm)								
<b>d</b> <sub>10</sub> 0.8	<b>d</b> <sub>50</sub> 7.6	d <sub>90</sub> 24.8							
BET specifi	c surface area (m <sup>2</sup> /	g)							
0.8									

#### Table 5

Mixture proportions of LC<sup>3</sup> with CM, MM, and MK.

	Clinker (%)	MK (%)	CM (%)	MM (%)	Limestone (%)	Gypsum (%)	Water (%)	W/S	PCE (%)	Spread (mm)
LC <sup>3</sup> -MK	50	30			15	5	40	0.4	2.0	91
LC <sup>3</sup> -CM	50		30		15	5	40	0.4	0.6	177
LMC <sup>2</sup> -MM	50			30	15	5	40	0.4	0.9	102

ratio (w/s) of 0.4. In addition, a polycarboxylate ether (PCE)-based SP from CHRYSO (Spain) was used to maintain similar flow and workability across all formulations. The paste flow was measured using a mini-slump test following the conditions described elsewhere [29].

# 2.3.3. Mixing and curing conditions

The different clays exhibited different water absorption capacities during paste preparation, and adjustments were made to the PCE addition and mixing procedure to achieve consistent workability. First, the solid mixture was homogenised. Subsequently, 80 wt% (for  $LC^3$ -MK and  $LMC^2$ -MM) or 85 wt% (for  $LC^3$ -CM) of the water was added, and the blend was mixed for 2 min at a low velocity (~700 rpm) using a high-shear mixer. For  $LC^3$ -MK and  $LMC^2$ -MM, the remaining water with PCE was added, and the paste was mixed for 2.5 min at a high velocity (~1800 rpm). For  $LC^3$ -CM, the remaining water and PCE were added, and the paste was mixed at a lower velocity (~400 rpm) for 4.5 min.

The paste flow was measured using the mini-slump test following the conditions described elsewhere [29], and comparable spread diameters were obtained for  $LC^3$ -MK and  $LMC^2$ -MM by altering the PCE percentage (see Table 5). However,  $LC^3$ -CM exhibited poor mixability and distinct rheological characteristics after the addition of water and PCE. The mixing of the  $LC^3$ -CM paste was impeded by shear-thickening behaviour, increasing its viscosity at higher mixing speeds (shear velocity). This phenomenon is commonly observed in cements containing calcined muscovitic or montmorillonitic clays as SCM [30,31]. Even with a 2 wt% PCE dosage and a low mixing velocity, the shear-thickening characteristic of the paste led to inadequate workability (low fluidity). However, after mixing, the samples exhibited high fluidity when no shear stress was applied, making it impossible to maintain a spread similar to the other two pastes throughout the mini-slump test, as shown in Table 5.

The lower PCE requirement for LMC<sup>2</sup>-MM may be attributed to two factors: the presence of weakly bonded water and hydroxyls and the different particle morphologies compared to calcined clay. When clay minerals are mechanically activated, weakly bonded water and hydroxyl groups detach from the structure [32]. These may be released during the mixing process, decreasing water or superplasticiser demand. Additionally, recent studies have demonstrated that the platelet structure of calcined clay causes an increase in the water (or SP) demand, unlike the rounded particle morphology of MM, which can reduce the SP requirement in clay-containing blended cement [33]. Considering the significant advantages associated with this approach, further research is needed to validate the reduced PCE demand. The variations in the rheological properties of the paste should be studied in future research. In particular, measuring the adsorption curves of the superplasticiser onto the different activated clays surfaces could help clarify the mechanisms behind the observed differences in PCE demand.

After mixing, the paste of each formulation was poured into 20 mm cubic moulds and vibrated to release enclosed air. After moulding, the samples were cured in sealed plastic bags with water for the first 24 h to maintain a humid atmosphere. Subsequently, specimens were unmoulded and placed in a climatic chamber, at 95 % relative humidity and 20  $^{\circ}$ C, until testing.

## 2.4. Cement characterisation techniques

The hydration of the cement reactions was monitored by isothermal calorimetry at 20 °C for 7 days using TAM Air (TA Instruments). The paste was prepared following the proportions in Table 5 in a high-shear mixer using the same mixing procedure described in Section 2.3.3. Subsequently, 10 g of the paste was poured into a plastic ampoule and placed in a calorimeter. A reference plastic ampoule with water was prepared to avoid noise from external temperature deviations.

The physicochemical properties of the samples were analysed after 3 and 28 days. A representative sample was crushed and sieved to a particle size < 1 mm. Subsequently, the crushed cement was submerged in isopropanol for 15 min to stop the curing process, and then vacuum-filtered by washing with isopropanol and diethyl ether. The filtered sample was dried in a ventilated oven at 40 °C for 8 min [34]. The crushed samples were ground in an agate mortar.

The ground samples were analysed using XRD to assess the evolution of the crystalline phases with increasing curing time. The measurements were performed under the conditions stated for the XRD characterisation of the raw materials in Section 2.1.1. Phase quantification was performed through Rietveld refinement using TOPAS in the 7–70  $2\theta^{\circ}$ , estimating the amorphous content through the DOC method with Eq. 1 and Eq. 2, as described in Section 2.1.1: The amorphous area was fitted with two broad peaks using the TOPAS peak phase function.

The measurements of <sup>27</sup>Al MAS NMR (magic angle spinning nuclear magnetic resonance) were performed at room temperature using a Bruker AXS AVANCEIII HD 600 spectrometer with a 4 mm double-resonance CPMAS probe at a spinning rate of 13 kHz. A magnetic field of 14.1 T, corresponding to a <sup>27</sup>Al resonance frequency of 156.37 MHz,

was utilised. The <sup>27</sup>Al chemical shifts were referenced to Al(NO<sub>3</sub>)<sub>3</sub>. The spectra were recorded with a 0.7- $\mu$ s 90° pulse and 1-s delay with <sup>1</sup>H decoupling (<sup>27</sup>Al Hpdec with cw decoupling sequence for Al) and summing up 2000 scans.

The thermal evaluation was performed through thermogravimetry with an SDT Q600 device from TA Instruments, in a 30–1000 °C temperature range, with 50 mL/min of synthetic air flow and a heating rate of 10 °C/min.

The microstructure was examined at 3 and 28 days on a transverse cut of the cement. Hydration was paused using the solvent exchange method by submerging the cut sample in isopropanol for six days and renewing the solvent regularly [35]. The samples were then dried in a silica gel desiccator for 24 h. The analysis was performed using a scanning electron microscope (SEM, Quanta 200, FEI) equipped with an energy-dispersive X-ray spectrometer (EDS). Micrographs were obtained using backscattered electrons at a working distance of 10 mm and an accelerating voltage of 20 kV.

The porosity was evaluated by mercury intrusion porosimetry (MIP) using a Quantachrome POREMASTER-60 GT. The crushed cement samples were intruded at a  $140^{\circ}$  contact angle with a pressure of 7–240 MPa (minimum pore diameter of 6 nm).

The compressive strength was determined using an Incotecnic MULTI-R1 featuring a 20 kN load cell. The testing was performed according to the EN 196–1 standard, employing a loading rate of 240 kg/s across six 20-mm cubic samples for each cement formulation.

## 3. Results and discussion

#### 3.1. Pozzolanic activity

Understanding the pozzolanic activity of SCMs is critical to assess their role in cementitious environments, particularly focusing on their interactions with CH. Fig. 3 shows the pozzolanic activity of the clays used in the LC<sup>3</sup> formulation (CM, MM, and MK) alongside the raw clays (RM and RK), to evaluate the efficacy of the activation processes. Two tests are presented to validate the pozzolanic activity of the clays: the R<sup>3</sup> test and the modified Chapelle test. RM and RK exhibited notably poor pozzolanic activity in both the modified Chapelle and R<sup>3</sup> tests, which is an expected behaviour of clays attributable to their robust crystalline structure [36]. Conversely, the MK exhibited remarkably high pozzolanic activity in both tests. The amorphous nature and high Al and Si availability of metakaolinite favour the reaction with CH, mainly forming AFm phases and C-(A)-S-H gel [37].

The pozzolanic activity of the muscovite-rich mixed clay increased through thermal and mechanical activation. The increase in pozzolanic activity in the modified Chapelle and the R<sup>3</sup> test is relatively modest. The CM exhibited a CH consumption of 554 mg Ca(OH)<sub>2</sub>/g CM, categorising it as a poor SCM, which was significantly lower than the proposed 700 mg of fixed CH [38]. With a 7-day heat release of 324 J/g CM, CM may be considered a less reactive pozzolanic material because it is slightly lower than the 370 J/g SCM threshold proposed by Suraneni

et al. [39]. According to the classification of calcined clays suggested by Londono-Zuluaga et al., CM can be considered moderately reactive clay [40] The significant difference from MK, which was identified as an excellent pozzolanic material in both tests, was remarkable. This confirms that thermal activation is an ineffective method for obtaining reactive SCM from mixed clays rich in muscovite. The reactivity of CM can be mainly attributed to the percentage of reactive clay minerals, such as kaolinite and montmorillonite, which can be thermally activated. In contrast, muscovite (the main clay mineral) was dehydroxylated but not amorphised as can be seen in Table 3, and remained unreactive [16].

MM exhibited substantially higher pozzolanic activity than CM. This material can be considered a good SCM for CH fixation (1219 mg Ca (OH)<sub>2</sub>/g MM), which is nearly comparable to that of MK (1423 mg Ca (OH)<sub>2</sub>/g MK). MM released 558 J/g of heat at seven days and can be regarded as a highly reactive clay [40]. The difference with MK was more pronounced in the  $R^3$  test than in the modified Chapelle test because the small particle size of MM likely accelerated the pozzolanic reactions, and some heat release was not accounted for due to the initial signal stabilisation in the isothermal calorimeter as reported elsewhere [41].

Overall, MM showed higher pozzolanic activity compared to CM, emphasising that mechanical activation is a superior activation method for mixed clays rich in 2:1 clay minerals such as muscovite. In previous studies, it was demonstrated that less energetic mechanical treatments led to lower pozzolanic activity despite the highly reduced particle size [16]. Therefore, the high pozzolanic activity of MM is mainly due to its high amorphous content and higher availability of silica and alumina, rather than a reduction in particle size.

To validate the results, Table 6 presents the cumulative heat release at 7 days for various clays measured using the  $R^3$  test, including values from this study and relevant literature. MM displays a heat release of 558 J/g, which is comparable to that of a mechanically activated kaolinitic clay (584 J/g), indicating good pozzolanic activity. Mechanically activated montmorillonitic clays also show favourable heat release (~400 J/g), highlighting that mechanical activation can significantly enhance reactivity across a range of clay minerals, including 2:1 swelling and non-swelling clay minerals (montmorillonite and muscovite) as well as 1:1 clay minerals (kaolinite).

In contrast, CM in this study shows a heat release of 324 J/g, similar to values reported for clays with low kaolinite content or partially reactive phases, confirming its limited pozzolanic performance. These findings confirm that not only the clay mineralogy but also the activation method plays a key role in determining pozzolanic performance, with mechanical activation being particularly effective for muscovitic and montmorillonitic clays, which typically show lower reactivity under thermal activation.

# 3.2. Cement characterisation

The isothermal calorimetry results of the  $LC^3$  pastes in terms of heat flow and cumulative heat are shown in Fig. 4. Cement hydration



Fig. 3. Pozzolanic activity of RM, CM, MM, RK, and MK measured with modified Chapelle test and R<sup>3</sup> test.

#### Table 6

Compilation of pozzolanic activity of clays measured through the R<sup>3</sup> test.

Raw clay	Clay minerals in raw clay	Activation method	<b>R<sup>3</sup> test</b> 7-day heat release (J/g activated clay)	Reference
Mixed muscovitic clay	57 % muscovite; 17 % kaolinite; 11 % montmorillonite	Thermal	324	a
		Mechanical	558	b
Kaolinitic clay	82 % kaolinite; 5 % muscovite/illite	Thermal	969	_c
		Mechanical	584	[41]
Ca-montmorillonitic clay	78 % montmorillonite	Thermal	359	[42]
		Mechanical	~400*	[42]
Na-montmorillonitic clay	61 % montmorillonite	Thermal	503	[42]
		Mechanical	~400*	[42]
Medium-kaolinitic clay	42 % kaolinite; 15 % muscovite	Thermal	388	[9]
Low-kaolinitic clay	18 % kaolinite; 27 % muscovite	Thermal	216	[9]
Kaolinitic clay	90 % kaolinite; 3 % mica	Thermal	758	[24]
Natural clay	60 % kaolinite	Thermal	699	[24]
Kaolinitic clay	93 % kaolinite	Thermal	917	[43]
Kaolinitic clay	71 % kaolinite; 13 % illite	Thermal	538	[43]
Smectitic clay	54 % smectite; 7 % kaolinite; 4 % illite	Thermal	380	[43]
Illitic clay	67 % illite; 7 % kaolinite; 5 % muscovite	Thermal	237	[43]
Common clay	38 % smectite-illite; 20 % kaolinite; 6 % muscovite	Thermal	258	[43]

values estimated from figures in referenced publication.

<sup>a</sup> CM;

<sup>b</sup> MM;

<sup>c</sup> MK from this work.



Fig. 4. Heat flow and cumulative heat of LC<sup>3</sup>-MK, LC<sup>3</sup>-CM, and LMC<sup>2</sup>-MM pastes focused in (a) 0-7 days range, and (b) 0-30 h range.

typically presents five periods: pre-induction, induction, acceleration, deceleration, and steady state [44]. Three heat flow peaks (I-III) were observed during the acceleration and deceleration periods. (I) is the silicate peak associated with C3S dissolution and C-S-H and CH

formation, (II) is the aluminate peak related to the reaction of aluminates and secondary ettringite precipitation, and (III) is the AFm peak associated with the formation of hemicarboaluminate (Hc), and monocarboaluminate (Mc) phases [45]. The onset of the aluminate peak corresponds to sulphate depletion in the system [46]. LMC<sup>2</sup>-MM displayed accelerated hydration (earlier peaks I, II, and III) due to the incorporation of mechanically activated clay, which accelerates the reactions in the cementitious system [47].

The maximum of the carboaluminate peak was detected at approximately one day of hydration for LMC<sup>2</sup>-MM, whereas the AFm peak was delayed to approximately three days in LC<sup>3</sup>-MK and to 4–6 days in LC<sup>3</sup>-CM, the latter exhibiting a broad and low shape. Faster Hc formation should imply higher early strength, which would be beneficial for the material, as one of the main drawbacks of binders with significant clinker replacement is a lower early age strength [48].

Fig. 4b shows the heat flow curves from 0 to 30 h, focusing on peaks (I) and (II). Acceleration of the hydration of LMC<sup>2</sup>-MM was readily noticeable in this region. The faster reaction of LMC<sup>2</sup>-MM was first detected at the silicate peak, with the onset and maximum observed at approximately 1.4 and 6.5 h, respectively. In contrast, LC<sup>3</sup>-MK presented an onset at 1.7 h and a maximum at 7 h, and LC<sup>3</sup>-CM at 2.4 and 8.9 h, respectively. Therefore, faster hydration of C<sub>3</sub>S could be expected in LMC<sup>2</sup>-MM owing to the presence of mechanically activated clay with a very small particle size, which could act as nucleation points for C-S-H [49]. The gap increased in the aluminate peak. The onset of  $LMC^2$ -MM was detected at 11.3 h, earlier than in LC3-MK (12.6 h) and LC3-CM (14.2 h), indicating that sulfate was also consumed faster in this system. The shape of the aluminate peak was also affected because the delayed aluminate peaks are typically broader and less intense than the earlier aluminate peaks [50]. The time difference increased at the maximum of the aluminate peak, monitored at 14 h, 15.4 h, and 17.5 h in LMC<sup>2</sup>-MM, LC<sup>3</sup>-MK, and LC<sup>3</sup>-CM, respectively.

The faster hydration in LC<sup>3</sup> particularly in the aluminate peaks is usually linked to an increase in the SSA [51]. However, the three activated clays from this work presented similar SSA, 9.0  $m^2/g$ , 9.2  $m^2/g$ , and 8.4  $m^2/g$  for MM, MK, and CM, respectively. Therefore, the significantly smaller particle size of MM, described in Section 2.1.4, likely plays a key role in the kinetics of the reaction of the blended cement rather than increased SSA.

The introduction of clay with very low kaolinite content (< 25 wt%) in LC<sup>3</sup> still leads to carboaluminate precipitation [52]. Therefore, the presence of kaolinite and montmorillonite in the CM (approximately 28 wt% in RC before calcination) probably allowed the formation of carboaluminates in  $LC^3$ -CM. The delay of  $LC^3$ -CM compared to that of  $LC^3$ -MK could be due to the variation in clay characteristics and to the higher PCE content, which has been reported to delay clinker reactions at high percentages [53].

Overall, MM influences the kinetics of hydration of the ternary blended cement through two factors. First, it accelerates the early hydration of clinker phases due to the very fine particle size which likely acts as nucleation points for hydrates to precipitate and grow. On the other hand, MM also reacts faster through pozzolanic reactions to produce carboaluminates.

X-ray powder diffractograms of ternary blended cement formulated with MK, CM, and MM at 3 and 28 days in the 5–50  $2\theta^{\circ}$  region are shown in Fig. 5. The typical reflections corresponding to hydrated and unreacted anhydrous phases were detected at 3 and 28 days for the three ternary blended cements, together with a halo corresponding to the amorphous phase. The most notable difference was the presence of dehydroxylated muscovite at 3 and 28 days in LC<sup>3</sup>-CM, confirming the low reactivity of this crystalline phase. At 3 days, the reflections corresponding to CH were significantly less intense in LMC<sup>2</sup>-MM, suggesting faster pozzolanic activity. Accordingly, the Hc reflections were also more intense in this sample. At 28 days, the reflections of portlandite were lower than those at 3 days in all samples because of pozzolanic reactions with clay. The CH reflection intensity was still higher in LC<sup>3</sup>-CM at 28 days because of the lower pozzolanic activity of CM. On the other hand, the intensity of the Hc peaks in all LC<sup>3</sup> samples was very similar, while a higher intensity of the Mc reflection was detected in LC<sup>3</sup>-CM. The formation of the carboaluminate phases in LC<sup>3</sup>-CM should be driven by the aluminium of the metakaolinite present in the CM or clinker aluminate phases because the dehydroxylated muscovite reflections were unaltered with increasing hydration time. In dehydroxylated muscovite, Al is constrained between silica tetrahedral layers, restricting its reactivity [54]. A reduction of the intensities of clinker phases compared to the diffractograms at 3 days could be observed especially in LC<sup>3</sup> with CM and MK. At 28 days, the intensities of the clinker phases ( $C_3S$  and  $C_4AF$ ) appeared to be lower in  $LC^3$ -CM, indicating that, given the lower and later reactions of aluminates from

CM, the clinker phases may react to a higher extent [50].

The results of the Rietveld refinement are presented in Fig. 6 to better evaluate the changes in the cement composition at 3 and 28 days of curing. The samples showed some differences, especially at three days. The faster hydration of LMC<sup>2</sup>-MM led to a higher amorphous content (approximately 37 wt%) compared to LC<sup>3</sup>-MK and LC<sup>3</sup>-CM (29 and 24 wt%, respectively) and a lower amount of portlandite. Furthermore, the amount of carboaluminates at 3 days in LMC<sup>2</sup>-MM was nearly identical to that determined on 28 days, 5.9 and 5.1 wt%, respectively. In contrast, LC<sup>3</sup>-MK displayed 2.6 wt% carboaluminates after 3 days and 6.4 wt% at 28 days, and LC<sup>3</sup>-CM displayed only 0.2 wt% at 3 days and 5.3 wt% at 28 days. This delay could have resulted from the high PCE content and lower reactivity of the CM [55]. These values agree with the carboaluminate peak in the calorimetry study (peak III in Fig. 4a), where LC<sup>3</sup>-MK was only around halfway through the formation of carboaluminates at 3 days, whereas for LC<sup>3</sup>-CM, the reaction had barely started. Overall, given the fast reaction of MM, the variations in the crystalline phases and amorphous fraction over curing time were less pronounced in LMC<sup>2</sup>-MM than in the other samples.

The results also confirmed that all samples displayed a higher degree of hydration at 28 days, with a lower content of CH and clinker-related phases, leading to the formation of C-(A)-S-H, as revealed by the increase in amorphous content. The formation of carboaluminates was promoted with increasing curing time, as indicated by the diminishing calcite (Cc) percentage and the increase in Hc and Mc content. At 28 days, the samples  $LC^3$ -MK and  $LMC^2$ -MM displayed very similar amorphous contents, suggesting a similar degree of hydration. In contrast,  $LC^3$ -CM displayed a lower amorphous content despite the lower content of clinker phases. In all formulations, the ettringite content was similar at 3 and 28 days, likely because the formation of hemi- and monocarboaluminate prevents the transition of ettringite to monosulphate [56]. Notably, the amount of dehydroxylated muscovite (D.Mus) was similar at 3 and 28 days for  $LC^3$ -CM. These findings suggest that the reactivity of the CM is lower than that of the MM.

The amount of carboaluminates at 28 days was barely higher in  $LMC^2$ -MM than in  $LC^3$ -CM. This suggests that a significant part of the Al from MM, which exhibits higher Al availability than CM, may be



Fig. 5. X-ray powder diffractograms of LC<sup>3</sup>-MK, LC<sup>3</sup>-CM, and LMC<sup>2</sup>-MM at (a) 3 and (b) 28 days.  $1 = \text{Ettringite}; 2 = \text{Hemicarboaluminate}; 3 = \text{Monocarboaluminate}; 4 = C_4\text{AF}; 5 = \text{Portlandite}; 6 = \text{Quartz}; 7 = \text{Calcite}; 8 = C_3\text{S}; 9 = C_2\text{S}; + = C_3\text{A}; * = \text{Dehydroxylated muscovite}.$ 



Fig. 6. Phase quantification through Rietveld refinement of  $LC^3$  samples at 3 and 28 days.  $C_3S$  = tricalcium silicate;  $C_2S$  = dicalcium silicate;  $C_4AF$  = tetracalcium aluminoferrite;  $C_3A$  = tricalcium aluminate; Cc = calcite; D.Mus = dehydroxylated muscovite; Ett = ettringite; Hc = hemicarboaluminate; Mc = monocarboaluminate.

incorporated into C-S-H to form C-A-S-H in LMC<sup>2</sup>-MM. The hydration of the clinker significantly increased in  $LC^3$ -MK and  $LC^3$ -CM from 3 to 28 days, primarily owing to the C<sub>3</sub>S reaction, whereas LMC<sup>2</sup>-MM displayed less clinker reaction. Notably, the addition of CM resulted in an enhanced reaction of clinker phases at 28 days compared with ternary blended cement incorporating MM and MK.

Fig. 7 displays <sup>27</sup>Al MAS NMR spectra of activated clays and the corresponding ternary blended cements at 28 curing days for comparison. The ranges of  $Al^{IV}$ ,  $Al^{V}$ , and  $Al^{VI}$  were obtained from Walkley and Provis [57]. In the cements, two sharp peaks corresponding to ettringite and carboaluminates were detected in the  $Al^{VI}$  region (20–0 ppm) [58]. The broad peaks detected in the  $Al^{VI}$  and  $Al^{IV}$  regions were attributed to the overlap of unreacted aluminium from the activated clays and the Al



Fig. 7. <sup>27</sup>Al MAS NMR of LC<sup>3</sup> and activated clay samples.

incorporated in C-(A)-S-H. The incorporation of Al from metakaolinite to form C-A-S-H gel in  $LC^3$  was demonstrated elsewhere [59], and this could be detected mainly by the change in the spectral shape and the diminishing of the prominent  $Al^V$  peak to increase the  $Al^{IV}$  peak.

 $LC^3$ -CM presented a spectrum similar to that of CM in the Al<sup>IV</sup> region, showing the same peaks (dashed lines). Therefore, Al<sup>IV</sup> from CM could be assigned mostly to dehydroxylated muscovite, with the appearance of a small hump at approximately 75 ppm, probably due to some Al substitution in C-(A)-S-H. Therefore, the minor variation in the CM-related peaks confirms the low reactivity of dehydroxylated muscovite in  $LC^3$ . The small peak of Al<sup>V</sup> observed in CM seemed to decrease because it was not detected in  $LC^3$ -CM. This decrease was likely due to the reaction of the metakaolinite in the CM with limestone to form mainly carboaluminates or the incorporation of Al into C-(A)-S-H. In this sample, the amount of Al from dehydroxylated muscovite incorporated into C-S-H should be marginal because Al is entrapped between the silica tetrahedral layers in the dehydroxylated muscovite [54]. Therefore, the reacting aluminium should have originated from the dehydroxylated montmorillonite and metakaolinite.

In contrast, Al from MM appeared to react to a greater extent because the shape of the  $LMC^2$ -MM spectrum was significantly different from that of MM. Here, the Al<sup>IV</sup> from the amorphous phase derived from mechanically activated muscovite changed, resulting in a spectrum similar to that of  $LC^3$ -MK in the Al<sup>IV</sup> region. This could indicate the incorporation of Al to form C-A-S-H gel, aside from the reaction with limestone to precipitate the carboaluminates previously observed in the XRD, owing to the amorphous nature of the material and the very fine particle size. In the Al<sup>VI</sup> region, Hc/Mc and ettringite peaks were detected, obtaining a spectrum very similar to that of  $LC^3$ -CM, which could be due to the similar content of these hydrated phases in the cement. However, the Al content in C-(A)-S-H in the cements should be further analysed using complementary techniques to verify the effect of different Al availabilities in CM, MM, and MK.

Fig. 8 shows the thermogravimetric analyses of the  $LC^3$  samples after 3 and 28 days. Four main decomposition steps (I-IV) were detected: (I) is related to the mass loss of water from C-(A)-S-H and ettringite, (II) to the elimination of water from Hc and Mc, (III) to the decomposition of



Fig. 8. Mass loss (TG) and derivative mass loss (DTG) of LC<sup>3</sup>-MK, LC<sup>3</sup>-CM, and LMC<sup>2</sup>-MM at (a) 3 and (b) 28 days.

calcium hydroxide, and (IV) to the release of CO<sub>2</sub> from calcium carbonate and carboaluminates [60,61]. The last peak can be split into two decompositions: a first mass loss at around 600 °C related to carboaluminate phases and carbonated C-S-H or portlandite, and a second decomposition at higher temperature due to unreacted calcite [62]. The TG curve of LMC<sup>2</sup>-MM suggested a higher degree of hydration at 3 days, showing a higher mass loss up to 500 °C related to C-(A)-S-H water elimination, lower CH content, and a lower peak of CaCO<sub>3</sub>. LC<sup>3</sup>-CM exhibited the lowest mass loss at temperatures up to 500 °C, suggesting a lower degree of hydration. In the 120–150 °C region corresponding to the DTG peak (II), LC<sup>3</sup>-MK displayed a hump related to some Hc or Mc presence, while LMC<sup>2</sup>-MM showed a more intense DTG peak, indicating a higher carboaluminate content. LC<sup>3</sup>-CM exhibited the lowest peak, suggesting that it had the lowest Hc/Mc content.

After 28 days, the cements displayed a higher mass loss and lower

calcium hydroxide content than at 3 days, indicating a higher bound water content and increased pozzolanic reactions of the activated clays.  $LMC^2$ -MM and  $LC^3$ -MK displayed very similar CH contents, while  $LC^3$ -CM still displayed a slightly higher portlandite DTG peak, which indicates a lower pozzolanic activity of CM compared to MK and MM. However, the intensity of the DTG peak related to the water loss from the carboaluminates was similar for the three samples.  $LMC^2$ -MM displayed a similar degree of hydration at 3 and 28 days, which could be due to a small-sized porosity in the sample, which may limit the formation of hydrated phases. The thermogravimetry results are in accordance with previous results, where faster hydration of  $LMC^2$ -MM and lower pozzolanic activity of  $LC^3$ -CM were detected.

Fig. 9 shows the backscattered electron SEM micrographs of the  $LC^3$  samples after 3 and 28 days of curing. The distinct phases were identified using EDS mapping, where the most abundant elements in the



Fig. 9. SEM micrographs of (a, d, g, j) LC<sup>3</sup>-MK, (b, e, h, k) LC<sup>3</sup>-CM, and (c, f, i, l) LMC<sup>2</sup>-MM at 3 and 28 days of curing, including a mapping image for each sample coloured with red for Si, pink for Al, green for Ca, and light blue for Fe.

cement are coloured in the micrograph: Ca (green), Si (red), Al (pink), and Fe (light blue). The faceted light-green particles corresponded mainly to the unreacted clinker  $C_3S/C_2S$  and the light-blue particles to  $C_4AF$ . The irregularly shaped green zones correspond to the portlandite. The pink particles correspond to the activated clay particles, and the red particles correspond to quartz from the activated clay.

 $LC^3$ -MK displayed a denser microstructure at 28 days as the pozzolanic reactions occurred and the hydration degree increased, yielding carboaluminates and more C-(A)-S-H gel.  $LC^3$ -CM contained acicular particles embedded in the cement matrix, corresponding to dehydroxylated muscovite. The presence of particles with this morphology was probably the main reason for the decrease in paste fluidity during the mixing process [63]. The low hydration of the  $LC^3$ -CM sample at 3 days led to a poor compactness matrix, while the greater reaction of the clinker phases at 28 days led to a denser microstructure, similar to that of  $LC^3$ -MK.

In contrast, the LMC<sup>2</sup>-MM micrographs were very similar at 3 and 28 days, showing a microstructure of a dense cement matrix with embedded clay and unreacted clinker particles. By comparing the different samples, LMC<sup>2</sup>-MM seemed denser than cement containing CM at all ages. At 3 days of curing, this could be mainly due to the higher degree of hydration observed in the previous techniques. Both the acicular shape of CM particles and their low reactivity can adversely affect the compactness of the material.



Fig. 10. Porosimetry of  $LC^3$ -MK,  $LC^3$ -CM, and  $LMC^2$ -MM at 3 and 28 curing days expressed as (a) cumulative pore volume and (b) differential pore size distribution.

Fig. 10 shows the porosity and pore size distribution of the LC<sup>3</sup> samples measured by MIP at 3 and 28 days as solid and dashed lines, respectively. For the samples LC<sup>3</sup>-MK and LC<sup>3</sup>-CM, the total porosity was significantly reduced at 28 days owing to the precipitation of hydrated products and pozzolanic reactions with portlandite. The total porosity decreased from 30 % to 22 % in  $LC^3$ -MK, and from 31 % to 27 % in  $LC^3$ -CM. In contrast, LMC<sup>2</sup>-MM presented virtually the same total porosities of 24.5 % and 24.1 % at 3 and 28 days, respectively, given the faster hydration and pozzolanic activity of the mechanically activated clay. The pore distribution of the samples was mainly bimodal, with two welldefined peaks in the differential pore size distribution. The porosity was refined with curing time, increasing the volume of pores in the first peak of the differential curve, and corresponding to smaller pore diameters. Given the pore size distribution, most porosities could be considered small capillary pores (10–100 nm) and gel pores (<10 nm), with a few remaining air pores (several  $\mu$ m) [64].

 $LC^3$ -CM and  $LC^3$ -MK displayed similar pore size distributions. This could be owing to the lack of portlandite in the highly substituted binders, which limits the reactions with metakaolinite in MK, which displays a much higher pozzolanic activity than CM [65].

Remarkably, LMC<sup>2</sup>-MM exhibited porosity with a smaller pore size at 3 and 28 days than LC<sup>3</sup>-CM and LC<sup>3</sup>-MK. The rounded shape and smaller size of MM particles could improve the compactness of the paste could than with platelet-like particles, such as MK, or acicular particles, such as CM. At 3 days, the pore size of LMC<sup>2</sup>-MM was already small, and the precipitation of new hydrates or growth of existing hydrates from 3 to 28 days probably caused further refinement in the porosity, leading to a virtually monomodal pore size distribution. The rapid porosity refinement in LMC<sup>2</sup>-MM could be the cause of the limited increase in hydration from 3 to 28 days despite the high reactivity of MM, since a very small pore size likely slows down the growth of hydrated phases and the precipitation of new hydrated phases [66]. This could also be the reason why the heat release isothermal calorimetry curve of LMC<sup>2</sup>-MM slowed by 7 days (see Fig. 4). The faster precipitation of carboaluminates should also play a key role in pore refinement because they precipitate in the remaining pores after hydration of the clinker phases [21].

Fig. 11 shows the compressive strengths of  $LC^3$ -MK,  $LC^3$ -CM, and  $LMC^2$ -MM, which is closely related to the physicochemical properties described in previous analyses.  $LMC^2$ -MM displayed a high compressive strength of approximately 42 MPa at 3 days, indicating that the faster hydration of this sample due to the addition of MM contributed to a



Fig. 11. Compressive strength of  $\rm LC^3\text{-}MK,\ \rm LC^3\text{-}CM,$  and  $\rm LMC^2\text{-}MM$  at 3 and 28 days.

faster strength gain.  $LC^3$ -MK presented a slightly lower compressive strength (35 MPa), whereas  $LC^3$ -CM exhibited the lowest compressive strength of approximately 22 MPa, almost half that of  $LMC^2$ -MM. These differences confirmed that mechanically activated clay, although slightly less reactive than MK (Fig. 3), improved strength at an early age. This is consistent with previous results (Fig. 4), which showed that the hydration kinetics accelerate with MM incorporation. This effect is likely due to enhanced hydrates' nucleation, facilitated by MM's very fine particle size and its faster pozzolanic reaction. As one of the main drawbacks of highly-substituted blended cements is their low hydration rate at early ages, using mechanically activated clay could be beneficial for increasing their mechanical performance for up to three days [67].

The LC<sup>3</sup>-MK compressive strength at 28 days reached the values of LMC<sup>2</sup>-MM with very similar values, 58 and 54 MPa, respectively, within the standard deviation boundaries. Because LMC<sup>2</sup>-MM presented accelerated hydration, the increase in compressive strength from 3 to 28 days was less pronounced for LMC<sup>2</sup>-MM than for LC<sup>3</sup>-MK and LC<sup>3</sup>-CM owing to later pozzolanic reactions. For LC<sup>3</sup>-CM, the increase in strength should be due to the reaction of clinker phases, amorphous meta-kaolinite, and dehydroxylated montmorillonite, as previous results demonstrated scant reactivity of crystalline dehydroxylated muscovite over time in cementitious environments.

Despite presenting a reasonable compressive strength at 28 days (approximately 41 MPa),  $LC^3$ -CM compressive strength remained significantly lower than that of  $LMC^2$ -MM, confirming the superior effectiveness of mechanical activation in obtaining suitable SCM from muscovite-rich mixed clays. The gap between  $LMC^2$ -MM and  $LC^3$ -CM would be even more significant if the CM contained less reactive clay minerals (i.e. kaolinite and montmorillonite). In such a scenario, clay would probably act only as a filler, leading to a dilution effect of the cementitious phases and lowering the mechanical properties of the  $LC^3$ .

## 4. Conclusions

In this study, the use of mechanically activated muscovite-rich mixed clay (MM) for producing ternary blended cement was first investigated. The aim was to broaden the range of suitable clay sources for the formulation of limestone calcined clay cement ( $\text{LC}^3$ ), enabling the use of 2:1 clays to achieve properties and performances comparable to those of  $\text{LC}^3$  produced with calcined kaolin (MK). To achieve this, a comprehensive analysis comparing  $\text{LC}^3$  formulated with metakaolin ( $\text{LC}^3$ -MK), calcined muscovite-rich mixed clay ( $\text{LC}^3$ -CM), and mechanically activated muscovite-rich mixed clay ( $\text{LMC}^2$ -MM) was conducted. The microstructure, physicochemical properties, porosity, and compressive strength of the materials were assessed, and the following key findings were obtained:

- The addition of MM to LC<sup>3</sup> accelerated the hydration of the system at three days, leading to a faster reaction of MM with limestone, and expedited the consumption of portlandite compared to CM and MK, which are crucial for the formation of carboaluminate phases.
- CM displayed lower reactivity than MM at all curing ages because of the high content of dehydroxylated muscovite, which exhibited practically no pozzolanic activity owing to its high crystallinity. However, the contents of clay minerals in the raw clay that become reactive after calcination, that is, kaolinite and montmorillonite (~28 wt%), reacted to form carboaluminates, mitigating the loss of properties to some extent.
- The faster reaction kinetics observed in MM compared to MK and CM through isothermal calorimetry translated into reduced pore size and a denser cement matrix. LMC<sup>2</sup>-MM displayed significantly lower pore size at 3 days than LC<sup>3</sup>-MK and LC<sup>3</sup>-CM, likely due to space filling by clay particles and hydrates precipitation in the pores.
- The compressive strength of LMC<sup>2</sup>-MM at 3 days was very slightly higher than that of LC<sup>3</sup>-MK, and at 28 days, it was similar to that of

LC<sup>3</sup>-MK. Compared to LC<sup>3</sup>-CM, the compressive strength of LMC<sup>2</sup>-MM was significantly higher at all curing ages.

In summary, these findings confirm the potential of the mechanical activation of 2:1 clays to enhance their performance in the  $LC^3$  formulation. Furthermore, the increase in early age strength observed in LMC<sup>2</sup>-MM is beneficial because it counters the typical reduction in properties associated with the significant addition of supplementary cementitious material (SCM) at early ages. The promising results of this investigation open doors for utilising other clays, facilitating the production of  $LC^3$  in countries with limited access to kaolinite-rich clays and offering an alternative to calcination which avoids fuel usage and potentially reduces the carbon footprint of the clay activation process.

In future work, the work should be tested on a larger production scale to ensure the viability of mechanical activation as an industrial process and assess the environmental impact of mechanical activation compared to that of thermal activation in terms of energy consumption and  $CO_2$  footprint. The better workability of  $LMC^2$ -MM with a lower superplasticiser content suggests a promising way to mitigate the high water demand typically associated with  $LC^3$ , potentially reducing superplasticiser usage or even the water-to-cement ratio. Therefore, a rheological study should be performed, because different particle sizes and morphologies have been found to affect the workability and flowability of pastes. Additionally, the C-(A)-S-H composition and morphology should be evaluated to assess the role of Al from MM compared to that from MK or CM in the composition and properties of C-(A)-S-H.

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# CRediT authorship contribution statement

Jofre Mañosa: Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation. Alex Maldonado-Alameda: Writing – review & editing, Visualization, Supervision. Josep Maria Chimenos: Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.conbuildmat.2025.142182.

## Data Availability

Data will be made available on request.

#### References

- [1] G. Habert, S.A. Miller, V.M. John, J.L. Provis, A. Favier, A. Horvath, K.L. Scrivener, Environmental impacts and decarbonization strategies in the cement and concrete industries, Nat. Rev. Earth Environ. 1 (2020) 559–573, https://doi.org/10.1038/ s43017-020-0093-3.
- [2] J. Mañosa, A. Calderón, R. Salgado-Pizarro, A. Maldonado-Alameda, J. M. Chimenos, Research evolution of limestone calcined clay cement (LC<sup>3</sup>), a promising low-carbon binder – a comprehensive overview, Heliyon 10 (2024) e25117, https://doi.org/10.1016/j.heliyon.2024.e25117.
- [3] K. Scrivener, F. Martirena, S. Bishnoi, S. Maity, Calcined clay limestone cements (LC<sup>3</sup>), Cem. Concr. Res 114 (2018) 49–56, https://doi.org/10.1016/j. cemconres.2017.08.017.
- [4] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cem. Concr. Res 42 (2012) 1579–1589, https://doi.org/10.1016/j.cemconres.2012.09.006.
- [5] J. Sun, F. Zunino, K. Scrivener, Hydration and phase assemblage of limestone calcined clay cements (LC<sup>3</sup>) with clinker content below 50, Cem. Concr. Res 177 (2024) 107417, https://doi.org/10.1016/j.cemconres.2023.107417.
- [6] B. Kanagaraj, N. Anand, R. Samuvel Raj, E. Lubloy, Techno-socio-economic aspects of Portland cement, Geopolymer, and Limestone Calcined Clay Cement (LC<sup>3</sup>) composite systems: a-State-of-Art-Review, Constr. Build. Mater. 398 (2023), https://doi.org/10.1016/j.conbuildmat.2023.132484.
- [7] S. Barbhuiya, J. Nepal, B.B. Das, Properties, compatibility, environmental benefits and future directions of limestone calcined clay cement (LC3) concrete: a review, J. Build. Eng. 79 (2023), https://doi.org/10.1016/j.jobe.2023.107794.
- [8] N. Blouch, K. Rashid, I. Zafar, M. Ltifi, M. Ju, Prioritization of low-grade kaolinite and mixed clays for performance evaluation of limestone calcined clay cement (LC<sup>3</sup>): Multi-criteria assessment, Appl. Clay Sci. 243 (2023), https://doi.org/ 10.1016/j.clay.2023.107080.
- [9] K. Ram, M. Flegar, M. Serdar, K. Scrivener, Influence of low- to medium-kaolinite clay on the durability of limestone calcined clay cement (LC3) concrete, Materials 16 (2022) 374, https://doi.org/10.3390/ma16010374.
- [10] Y. Cao, Y. Wang, Z. Zhang, Y. Ma, H. Wang, Recent progress of utilization of activated kaolinitic clay in cementitious construction materials, Compos B Eng. 211 (2021) 108636, https://doi.org/10.1016/j.compositesb.2021.108636.
- [11] A. Ito, R. Wagai, Global distribution of clay-size minerals on land surface for biogeochemical and climatological studies, Sci. Data 4 (2017), https://doi.org/ 10.1038/sdata.2017.103.
- [12] A. Alujas Diaz, R.S. Almenares Reyes, T. Hanein, E.F. Irassar, M. Juenger, F. Kanavaris, M. Maier, A.T. Marsh, T. Sui, K.C. Thienel, L. Valentini, B. Wang, F. Zunino, R. Snellings, Properties and occurrence of clay resources for use as supplementary cementitious materials: a paper of RILEM TC 282-CCL, Mater. Struct. /Mater. Et. Constr. 55 (2022), https://doi.org/10.1617/s11527-022-01972-2
- [13] S. Hollanders, R. Adriaens, J. Skibsted, Ö. Cizer, J. Elsen, Pozzolanic reactivity of pure calcined clays, Appl. Clay Sci. 132133 (2016) 552–560, https://doi.org/ 10.1016/j.clay.2016.08.003.
- [14] I. Tole, F. Delogu, E. Qoku, K. Habermehl-Cwirzen, A. Cwirzen, Enhancement of the pozzolanic activity of natural clays by mechanochemical activation, Constr. Build. Mater. 352 (2022), https://doi.org/10.1016/j.conbuildmat.2022.128739.
- [15] V.A. Baki, X. Ke, A. Heath, J. Calabria-Holley, C. Terzi, M. Sirin, The impact of mechanochemical activation on the physicochemical properties and pozzolanic reactivity of kaolinite, muscovite and montmorillonite, Cem. Concr. Res 162 (2022) 106962, https://doi.org/10.1016/j.cemconres.2022.106962.
- [16] J. Mañosa, A. Alvarez-Coscojuela, J. Marco-Gibert, A. Maldonado-Alameda, J. M. Chimenos, Enhancing reactivity in muscovitic clays: Mechanical activation as a sustainable alternative to thermal activation for cement production, Appl. Clay Sci. 250 (2024) 107266, https://doi.org/10.1016/j.clay.2024.107266.
- [17] T. Hanein, K.C. Thienel, F. Zunino, A.T.M. Marsh, M. Maier, B. Wang, M. Canut, M. C.G. Juenger, M. Ben Haha, F. Avet, A. Parashar, L.A. Al-Jaberi, R.S. Almenares-Reyes, A. Alujas-Diaz, K.L. Scrivener, S.A. Bernal, J.L. Provis, T. Sui, S. Bishnoi, F. Martirena-Hernández, Clay calcination technology: state-of-the-art review by the RILEM TC 282-CCL, Mater. Struct. /Mater. Et. Constr. 55 (2022), https://doi.org/10.1617/s11527-021-01807-6.
- [18] M. Fitos, E.G. Badogiannis, S.G. Tsivilis, M. Perraki, Pozzolanic activity of thermally and mechanically treated kaolins of hydrothermal origin, Appl. Clay Sci. 116117 (2015) 182–192, https://doi.org/10.1016/j.clay.2015.08.028.

- [19] A.R.D. Costa, S.R.C. Matos, G. Camarini, J.P. Gonçalves, Hydration of sustainable ternary cements containing phosphogypsum, Sustain. Mater. Technol. 28 (2021), https://doi.org/10.1016/j.susmat.2021.e00280.
- [20] I.C. Madsen, N.V.Y. Scarlett, A. Kern, Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction, Z. Fur Krist. 226 (2011) 944–955, https://doi.org/10.1524/zkri.2011.1437.
- [21] F. Zunino, K. Scrivener, The reaction between metakaolin and limestone and its effect in porosity refinement and mechanical properties, Cem. Concr. Res 140 (2021) 106307, https://doi.org/10.1016/j.cemconres.2020.106307.
- [22] N. Garg, J. Skibsted, Pozzolanic reactivity of a calcined interstratified illite/ smectite (70/30) clay, Cem. Concr. Res 79 (2016) 101–111, https://doi.org/ 10.1016/j.cemconres.2015.08.006.
- [23] F. Scrivener, H. Avet, F. Maraghechi, J. Zunino, W. Ston, A. Hanpongpun, Favier, Impacting factors and properties of limestone calcined clay cements (LC<sup>3</sup>, Green. Mater. 7 (2018) 3–14, https://doi.org/10.1680/jgrma.18.00029.
- [24] F. Zunino, K. Scrivener, Reactivity of kaolinitic clays calcined in the 650 °C-1050 °C temperature range: Towards a robust assessment of overcalcination, Cem. Concr. Compos 146 (2024) 105380, https://doi.org/10.1016/j. cemconcomp.2023.105380.
- [25] I. Tole, K. Habermehl-Cwirzen, A. Cwirzen, Mechanochemical activation of natural clay minerals: an alternative to produce sustainable cementitious binders – review, Miner. Pet. 113 (2019) 449–462, https://doi.org/10.1007/s00710-019-00666-y.
- [26] M. Šídlová, R. Šulc, F. Škvára, K. Puľcová, P. Formáček, R. Snop, Pozzolanic activity of stockpile ash: Comparison of test methods, Case Stud. Constr. Mater. 19 (2023), https://doi.org/10.1016/j.cscm.2023.e02396.
- [27] ASTM International, C 1897-20 "Standard Test Methods for Measuring the Reactivity of Supplementary Cementitious Materials by Isothermal Calorimetry and, Bound Water Meas." West Conshohocken PA (2020), https://doi.org/ 10.1520/C1897-20.2.
- [28] F. Avet, R. Snellings, A. Alujas Diaz, M. Ben Haha, K. Scrivener, Development of a new rapid, relevant and reliable (R<sup>3</sup>) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays, Cem. Concr. Res 85 (2016) 1–11, https://doi. org/10.1016/j.cemconres.2016.02.015.
- [29] Z. Tan, S.A. Bernal, J.L. Provis, Reproducible mini-slump test procedure for measuring the yield stress of cementitious pastes, Mater. Struct. /Mater. Et. Constr. 50 (2017) 1–12, https://doi.org/10.1617/s11527-017-1103-x.
- [30] R. Sposito, N. Beuntner, K.C. Thienel, Characteristics of components in calcined clays and their influence on the efficiency of superplasticizers, Cem. Concr. Compos 110 (2020), https://doi.org/10.1016/j.cemconcomp.2020.103594.
- [31] L. Lei, J. Plank, Synthesis and properties of a vinyl ether-based polycarboxylate superplasticizer for concrete possessing clay tolerance, Ind. Eng. Chem. Res 53 (2014) 1048–1055, https://doi.org/10.1021/ie4035913.
- [32] J. Mañosa, J.Calvo-de la Rosa, A. Silvello, A. Maldonado-Alameda, J.M. Chimenos, Kaolinite structural modifications induced by mechanical activation, Appl. Clay Sci. 238 (2023), https://doi.org/10.1016/j.clay.2023.106918.
- [33] P. Hou, T.R. Muzenda, Q. Li, H. Chen, S. Kawashima, T. Sui, H. Yong, N. Xie, X. Cheng, Mechanisms dominating thixotropy in limestone calcined clay cement (LC3), Cem. Concr. Res 140 (2021) 106316, https://doi.org/10.1016/j. cemconres.2020.106316.
- [34] R. Snellings, J. Chwast, Ö. Cizer, N. De Belie, Y. Dhandapani, P. Durdzinski, J. Elsen, J. Haufe, D. Hooton, C. Patapy, M. Santhanam, K. Scrivener, D. Snoeck, L. Steger, S. Tongbo, A. Vollpracht, F. Winnefeld, B. Lothenbach, RILEM TC-238 SCM recommendation on hydration stoppage by solvent exchange for the study of hydrate assemblages, Mater. Struct. /Mater. Et. Constr. 51 (2018), https://doi.org/ 10.1617/s11527-018-1298-5.
- [35] J. Zhang, G.W. Scherer, Comparison of methods for arresting hydration of cement, Cem. Concr. Res 41 (2011) 1024–1036, https://doi.org/10.1016/j. cemconres 2011 06 003
- [36] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, Appl. Clay Sci. (2001) 73–80, https://doi.org/10.1016/S0169-1317(01)00040-0.
- [37] K. Weise, N. Ukrainczyk, E. Koenders, Pozzolanic Reactions of Metakaolin with Calcium Hydroxide: Review on Hydrate Phase Formations and Effect of Alkali Hydroxides, Carbonates and Sulfates, Mater. Des. 231 (2023), https://doi.org/ 10.1016/j.matdes.2023.112062.
- [38] M. Siline, B. Mehsas, Effect of increasing the Blaine fineness of Metakaolin on its chemical reactivity, J. Build. Eng. 56 (2022), https://doi.org/10.1016/j. iobe.2022.104778.
- [39] P. Suraneni, A. Hajibabaee, S. Ramanathan, Y. Wang, J. Weiss, New insights from reactivity testing of supplementary cementitious materials, Cem. Concr. Compos 103 (2019) 331–338, https://doi.org/10.1016/j.cemconcomp.2019.05.017.
- [40] D. Londono-Zuluaga, A. Gholizadeh-Vayghan, F. Winnefeld, F. Avet, M. Ben Haha, S.A. Bernal, Ö. Cizer, M. Cyr, S. Dolenec, P. Durdzinski, J. Haufe, D. Hooton, S. Kamali-Bernard, X. Li, A.T.M. Marsh, M. Marroccoli, M. Mrak, Y. Muy, C. Patapy, M. Pedersen, S. Sabio, S. Schulze, R. Snellings, A. Telesca, A. Vollpracht, G. Ye, S. Zhang, K.L. Scrivener, Report of RILEM TC 267-TRM phase 3: validation of the R<sup>3</sup> reactivity test across a wide range of materials, Mater. Struct. /Mater. Et. Constr. 55 (2022), https://doi.org/10.1617/s11527-022-01947-3.
- [41] J. Mañosa, S. Huete-Hernández, A. Alvarez-Coscojuela, A. Maldonado-Alameda, J. M. Chimenos, Comparative study of limestone calcined clay cement produced with mechanically activated kaolin and calcined kaolin, J. Build. Eng. 97 (2024) 110748, https://doi.org/10.1016/j.jobe.2024.110748.
- [42] A.T.M. Marsh, S. Krishnan, S.A. Bernal, Structural features of thermally or mechano-chemically treated montmorillonite clays as precursors for alkaliactivated cements production, Cem. Concr. Res 181 (2024) 107546, https://doi. org/10.1016/j.cemconres.2024.107546.

- [43] M. Panzer, S. Scherb, N. Beuntner, K.C. Thienel, An approach to estimate the strength contribution of calcined clays in blended cements, Constr. Build. Mater. 447 (2024) 137800, https://doi.org/10.1016/j.conbuildmat.2024.137800.
- [44] X. Pang, L. Sun, F. Sun, G. Zhang, S. Guo, Y. Bu, Cement hydration kinetics study in the temperature range from 15 °C to 95 °C, Cem. Concr. Res 148 (2021), https:// doi.org/10.1016/j.cemconres.2021.106552.
- [45] P.R. de Matos, J.S. Andrade Neto, R.D. Sakata, C.E.M. Campos, A.P. Kirchheim, E. D. Rodríguez, Effect of superplasticizer addition time and metakaolin source on the early-age hydration of limestone calcined clay cement (LC<sup>3</sup>), Mater. Struct. /Mater. Et. Constr. 55 (2022), https://doi.org/10.1617/s11527-022-02049-w.
- [46] O. Canbek, C. Szeto, N.R. Washburn, K.E. Kurtis, A quantitative approach to determining sulfate balance for LC<sup>3</sup>, CEMENT 12 (2023) 100063, https://doi.org/ 10.1016/j.cement.2023.100063.
- [47] J. Mañosa, M. Torres-Carrasco, J.C. Córdoba, A. Maldonado-Alameda, J. M. Chimenos, In-situ characterisation of early hydration of low-carbon cements containing thermally and mechanically activated kaolin, Constr. Build. Mater. 457 (2024) 139469, https://doi.org/10.1016/j.conbuildmat.2024.139469.
- [48] F. Boscaro, M. Palacios, R.J. Flatt, Formulation of low clinker blended cements and concrete with enhanced fresh and hardened properties, Cem. Concr. Res 150 (2021) 106605, https://doi.org/10.1016/j.cemconres.2021.106605.
- [49] E. Berodier, K. Scrivener, Understanding the filler effect on the nucleation and growth of C-S-H, J. Am. Ceram. Soc. 97 (2014) 3764–3773, https://doi.org/ 10.1111/jace.13177.
- [50] R. Hay, L. Li, K. Celik, Shrinkage, hydration, and strength development of limestone calcined clay cement (LC<sup>3</sup>) with different sulfation levels, Cem. Concr. Compos 127 (2022), https://doi.org/10.1016/j.cemconcomp.2021.104403.
- [51] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC<sup>3</sup>), Cem. Concr. Res 107 (2018) 124–135, https://doi.org/10.1016/j.cemconres.2018.02.016.
- [52] A.H. Ahmed, S. Nune, M. Liebscher, T. Köberle, A. Willomitzer, I. Noack, M. Butler, V. Mechtcherine, Exploring the role of dilutive effects on microstructural development and hydration kinetics of limestone calcined clay cement (LC<sup>3</sup>) made of low-grade raw materials, J. Clean. Prod. 428 (2023), https://doi.org/10.1016/j. jclepro.2023.139438.
- [53] L. Valentini, M. Favero, M.C. Dalconi, V. Russo, G. Ferrari, G. Artioli, Kinetic Model of Calcium-Silicate Hydrate Nucleation and Growth in the Presence of PCE Superplasticizers, Cryst. Growth Des. 16 (2016) 646–654, https://doi.org/ 10.1021/acs.cgd.5b01127.
- [54] R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite, Cem. Concr. Res 41 (2011) 113–122, https://doi.org/10.1016/j. cemconres.2010.09.013.

- [55] R. Hay, K. Celik, Performance enhancement and characterization of limestone calcined clay cement (LC<sup>3</sup>) produced with low-reactivity kaolinitic clay, Constr. Build. Mater. 392 (2023), https://doi.org/10.1016/j.conbuildmat.2023.131831.
- [56] K. De Weerdt, M.Ben Haha, G. Le Saout, K.O. Kjellsen, H. Justnes, B. Lothenbach, Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash, Cem. Concr. Res 41 (2011) 279–291, https://doi.org/10.1016/j. cemconres.2010.11.014.
- [57] B. Walkley, J.L. Provis, Solid-state nuclear magnetic resonance spectroscopy of cements, Mater. Today Adv. 1 (2019), https://doi.org/10.1016/j. mtadv.2019.100007.
- [58] Z. Dai, T.T. Tran, J. Skibsted, Aluminum incorporation in the C-S-H phase of white portland cement-metakaolin blends studied by <sup>27</sup>Al and <sup>29</sup>Si MAS NMR spectroscopy, J. Am. Ceram. Soc. 97 (2014) 2662–2671, https://doi.org/10.1111/ jace.13006.
- [59] F. Avet, E. Boehm-Courjault, K. Scrivener, Investigation of C-A-S-H composition, morphology and density in Limestone Calcined Clay Cement (LC<sup>3</sup>), Cem. Concr. Res 115 (2019) 70–79, https://doi.org/10.1016/j.cemconres.2018.10.011.
- [60] R.S. Lin, S. Oh, W. Du, X.Y. Wang, Strengthening the performance of limestonecalcined clay cement (LC<sup>3</sup>) using nano silica, Constr. Build. Mater. 340 (2022) 127723, https://doi.org/10.1016/j.conbuildmat.2022.127723.
- [61] A. Zolfagharnasab, A.A. Ramezanianpour, F. Bahman-Zadeh, Investigating the potential of low-grade calcined clays to produce durable LC<sup>3</sup> binders against chloride ions attack, Constr. Build. Mater. 303 (2021) 124541, https://doi.org/ 10.1016/j.conbuildmat.2021.124541.
- [62] K. Scrivener, R. Snellings, B. Lothenbach, A practical guide to microstructural analysis of cementitious materials, CRC Press, 2016.
- [63] C. Zhang, M. Wang, R. Liu, X. Li, Y. Liu, P. Jiang, J. Yan, Z. Zhu, M. Chen, Rheological properties of cement-based slurry and evaluation of rheological model: Influence of particle size and shape, Constr. Build. Mater. 406 (2023), https://doi. org/10.1016/j.conbuildmat.2023.133498.
- [64] Y. Song, J. Zhou, Z. Bian, G. Dai, Pore structure characterization of hardened cement paste by multiple methods, Adv. Mater. Sci. Eng. 2019 (2019), https://doi. org/10.1155/2019/3726953.
- [65] K. Weise, N. Ukrainczyk, A. Duncan, E. Koenders, Enhanced metakaolin reactivity in blended cement with additional calcium hydroxide, Materials 15 (2022), https://doi.org/10.3390/ma15010367.
- [66] Y. Briki, F. Avet, M. Zajac, P. Bowen, M.Ben Haha, K. Scrivener, Understanding of the factors slowing down metakaolin reaction in limestone calcined clay cement (LC<sup>3</sup>) at late ages, Cem. Concr. Res 146 (2021), https://doi.org/10.1016/j. cemconres.2021.106477.
- [67] A. Cuesta, A. Morales-Cantero, A.G. De la Torre, M.A.G. Aranda, Recent advances in C-S-H nucleation seeding for improving cement performances, Materials 16 (2023), https://doi.org/10.3390/ma16041462.