

Hydration and mixture design of calcined clay blended cements: Review by the RILEM TC 282-CCL

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Abstract

RILEM TC 282-CCL investigates all the aspects dealing with calcined clay, from clay exploration to the calcination process, hydration reactions and properties of concrete. This white paper focuses on the hydration mechanisms of calcined clay-blended cements, containing both 1:1 and 2:1 calcined clays. The pozzolanic reaction of calcined clay is detailed, and the main reaction products are described. The differences observed depending on the clay type are also discussed, as well as the potential influence of the secondary phases present in calcined clay. The factors controlling and limiting the reaction of calcined clay are investigated, evidencing the role of porosity saturation and refinement of the microstructure. The complete characterisation of the hydration of calcined clay cements is made possible by the determination of the reaction degree of calcined clay. Several methods are compared to estimate the extent of calcined clay reaction. The influence of clinker and limestone mineralogy are also discussed. Finally, guidelines for optimised mixture design of calcined clay blended cements are provided, with special attention to sulphate adjustment and clinker factor.

Keywords: calcined clay cements, hydration, phase assemblage, microstructure, mixture design

1 Introduction

Portland cement is the largest manufactured product on Earth on a mass basis, accountable for about 6-8% of the anthropogenic CO₂ emissions worldwide. An effective strategy to reduce the carbon footprint of the cement industry on a worldwide scale is to reduce the clinker factor of the cements used for general purpose applications [1]. This has accelerated the adoption of blended Portland cements that incorporate supplementary cementitious materials (SCMs) by replacing part of the Portland cement (PC) fraction [2, 3]. Today, blended Portland cements are more common than PC for the production of concrete.

Among commonly used SCMs are fine limestone, granulated blast furnace slag and fly ash [2, 3]. However, fly ash and blast furnace slag are available in combined quantities close to only 15% of the global Portland cement production [1]. The availability of fly ash is expected to decrease as electricity production by combustion of coal is transitioning towards use of cleaner fuels [4]. In the case of blast furnace slag, the production of steel increases more slowly compared to cement; moreover, change of production method and the recycling of steel might have implication in slag availability in the years to come. The scarcity of conventional SCMs limits their ability to further reduce the clinker factor for production of concrete [5]. This has been one of the main drivers for exploration of other SCMs that are widely available globally and have the potential to be used for production of concretes with different performances [6]. In this scenario, calcined clays and limestone play a key role, as they are the only SCMs available in the quantities required for a widespread use and, when combined with limestone, for a significant reduction (30 – 50 wt%) of the clinker content in Portland cement blends [4, 7–10].

Clay particles are made up of stacks of layers, composed of alternating silica tetrahedral and alumina octahedral sheets [11]. The three most abundant clay types are kaolinite, illite and montmorillonite (smectite). Kaolinite (a so called 1:1 clay) has a layer structure of one silica and one alumina layer, while in illite and montmorillonite the layers are composed of two silica layers with one alumina layer in between (2:1 clays) [11]. In the case of kaolinite, two distinct interlayer surfaces coexist, one with aluminate groups and one with silicate groups. A recent review from technical committee [12] provides more detailed information about the mineralogy, physical and chemical characteristics of clays in the context of their utilisation as potential SCMs. Likewise a detailed review on the production of calcined clays, clay mining, and state of the art in clay calcination technology covers the most relevant aspects from the clay deposit to the factory gate [13].

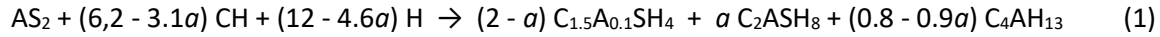
Blended Portland cements incorporating calcined clays, with or without limestone, are technically and economically feasible paths towards a substantial reduction of clinker content [14]. The combination of calcined clay and limestone is sometimes referred to as limestone calcined clay cement (LC³) [8, 9, 15, 16]. The first studies on synergetic effects in this combination of SCMs and Portland cement were given in papers at the 13th International Congress on the Chemistry of Cement (ICCC) in Madrid 2011 [17, 18], including both calcined 1:1 and 2:1 clays. In these materials, there is a synergetic reaction of the alumina in the calcined clay with the limestone to form additional hydration products that further contribute to porosity reduction [3, 10, 19, 20].

In this paper, the main aspects of hydration, properties, characterisation and blend design of cements incorporating calcined clays or calcined clays and limestone are presented, including 1:1 and 2:1 calcined clays. A critical review of the literature regarding the mechanisms of hydration and performance of these systems is provided. Guidelines for optimized mixture design are also presented. Finally, an outlook of pending challenges for future work is presented.

2 Hydration of blended cements incorporating calcined clays

2.1 Reaction mechanism and phase assemblage of blended cements incorporating calcined clay (and limestone)

In general, the principal reactive components of calcined clays are silica and alumina which partly or fully dissolve in an alkaline environment, depending on the type and structure of the calcined clay and on other constituents. Considering metakaolin with the ideal composition, $\text{Al}_2\text{Si}_2\text{O}_7$ (AS_2 in cement oxide notation), as example, some main reactions can be described, depending on the composition of the hydrating system [3]. The pozzolanic properties of metakaolin can most simply be described through its reaction with a saturated portlandite solution, $\text{Ca}(\text{OH})_2$ (CH), which results in the formation of an alumino-substituted C-S-H phase, (illustrative composition $\text{C}_{1.5}\text{A}_{0.1}\text{SH}_4$, i.e., $\text{Al}/\text{Si} = 0,20$), strätlingite (C_2ASH_8), and calcium aluminate hydrate phases of the AFm type, C_4AH_{13} . Assuming these ideal compositions for the hydrate phases, this reaction is described in Eq (1):



These three reaction products can be identified in the solid-state ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR) spectra (Figure 1). The C-(A)-S-H phase is the dominant product, as evidenced by the Q1 and Q2 peaks in the ^{29}Si NMR spectrum.

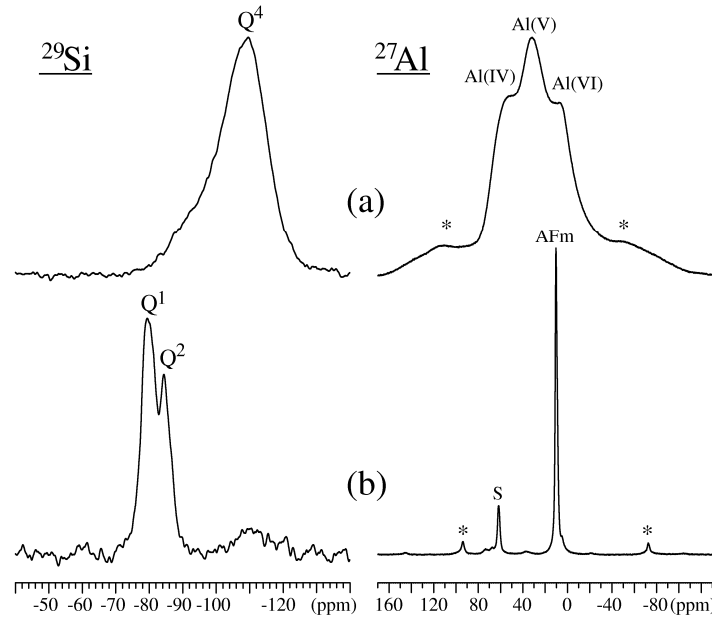
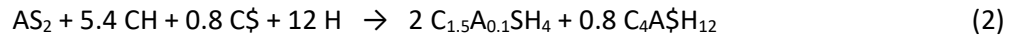
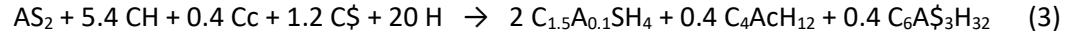


Figure 1: ^{29}Si and ^{27}Al NMR spectra of metakaolin before (a) and after (b) pozzolanic reaction with portlandite in solution for 16 days, illustrating the transformation of a highly disordered material into the hydration products C-(A)-S-H, strätlingite (S) and AFm phases. The ^{27}Al NMR spectrum after pozzolanic reaction includes minor resonances at 73, 67, 36, and 5 ppm originating from four-, five- and six-fold coordinated Al in the C-(A)-S-H phase. Asterisks indicate spinning sidebands, and the spectra are acquired at 7.1 T (^{29}Si) and 14.1 T (^{27}Al).

The hydrate phase assemblage is strongly influenced by the types of anions present in the system. For example, a surplus of portlandite and calcium sulphate (C\$) in a stoichiometric amount will stabilise monosulphate (C₄A\$H₁₂), corresponding to the idealised reaction in Eq (2):



For systems with large fractions of limestone (Cc), the carbonate ions will result in the formation of monocarbonate (C₄ACh₁₂) instead of monosulphate [21, 22], resulting in a stabilisation of ettringite (C₆A\$₃H₃₂), according to the Eq (3):



This phase assemblage is largely responsible for the well-established synergetic effect of limestone and an aluminosilicate-rich SCM in ternary Portland cement-limestone-SCM systems, as reported for fly ashes [23], slags [24], metakaolin [10] and calcined smectite [17] as SCMs. In addition to the retention of ettringite, monocarbonate consumes a large amount of aluminate ions, which contributes to further dissolution of the calcined clay.

The structure and composition of the C-(A)-S-H phase are strongly influenced by the presence of calcined clays and limestone. For these blended systems, the Ca/Si ratio of the C-(A)-S-H phase is found to be significantly lower and the Al/Si ratio somewhat higher than observed for the C-(A)-S-H phases formed by hydration of pure Portland cement [25]. These changes are dependent on the Portland clinker replacement factor and the degree of reaction of calcined clay. For example, the Ca/Si ratio has been found to decrease from 1.8 - 1.9 for the C-(A)-S-H in neat Portland cements to 1.2 - 1.6 in metakaolin blended systems [26–29]. A decalcification of the C-(A)-S-H phase is associated with an increase in the mean chain length of aluminosilicate tetrahedra (MCL) and this parameter is generally found to increase with the age of hydration and the Portland cement replacement level. MCL exhibits typical values of 3 – 5 for the C-(A)-S-H in neat Portland cements [30, 31], whereas it increases to 8 – 11 [25, 29] for blends with metakaolin and 5 – 6 for composite cements with smectitic clays [32, 33].

The amount of Al incorporated in the C-(A)-S-H phase has been found to increase linearly with the substitution level for Portland cement – metakaolin blends incorporating up to 30 wt.% metakaolin [25]. This increase can be ascribed to a higher concentration of aluminium in the pore solution of the hydrating system [20]. ²⁷Al and ²⁹Si NMR studies have shown that the Al_{IV}/Si ratio of the C-(A)-S-H phase is nearly constant with hydration time for Portland cement – metakaolin blends [25], as also found for the C-(A)-S-H phase in hydrated pure Portland cements. Other studies using NMR and energy dispersive X-ray spectroscopy (EDS) have indicated that this ratio increases with hydration time. Similar observations have been reported for blended systems incorporating smectitic clays [32, 33]. The C-(A)-S-H morphology can be both fibrillar and foil-like for binary Portland cement – metakaolin systems [29], whereas transmission electron microscopy (TEM) studies have indicated a fibrillar structure for the C-(A)-S-H phase in ternary systems with calcined kaolinitic clays and limestone [26]. Moreover, Avet et al. [26] have reported that the solid density (~2.8) and bulk density (~1.9) of the C-(A)-S-H phase do not change significantly for calcined clay limestone cements (fixed composition) with clays that contain different kaolinitic contents and curing ages.

Although, strätlingite is observed as a product in pure metakaolin-portlandite systems (Figure 1), this phase is not observed in all blended cements incorporating calcined clays. Strätlingite has been identified at late ages, when the degree of hydration is quite high, and mostly in binary Portland cement-metakaolin

blends containing more than 10-15% metakaolin [25, 34, 35]. This reflects that strätlingite and portlandite are thermodynamically incompatible in the ternary $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ phase diagram, implying that strätlingite is theoretically formed when portlandite is consumed [36]. The presence of limestone also suppresses the formation of strätlingite, since a larger fraction of aluminium is bound in the monocarbonate and hemicarbonate AFm phases (Eq. 3), retaining ettringite [36]. However, a recent study on systems incorporating calcined clays and limestone showed that strätlingite is formed in the long-term [28], even in the presence of portlandite. The mutual presence of strätlingite and portlandite has often been reported [27], even at high replacement levels such as 40 % metakaolin [35]. This discrepancy has been attributed to local heterogeneities in the dense microstructure [27] and/or the fact that thermodynamic equilibrium is not reached in the hydrated system. In particular, it has been proposed that the pore solution could become unsaturated towards portlandite when the amount of this phase decreases in the system due to the ongoing pozzolanic reaction [28]. It has been speculated that the formation of strätlingite at late ages may lead to deleterious expansion [37], but this is highly unlikely as expansion by crystallisation pressure requires high degrees of supersaturation which are unlikely to occur. In binary systems (without limestone), thermodynamic modelling (Figure 2) predicts that higher degrees of metakaolin reaction will result in increased formation of strätlingite at the expense of monosulphate, thereby releasing sulphate ions that can form secondary ettringite [27]. In systems incorporating limestone, the formation of strätlingite was not observed to negatively influence porosity reduction and refinement [28]. Thermodynamic modelling also predicts portlandite to be completely depleted when strätlingite forms, corresponding to 10 - 15% reacted metakaolin, but also depending on the clinker degree of hydration.

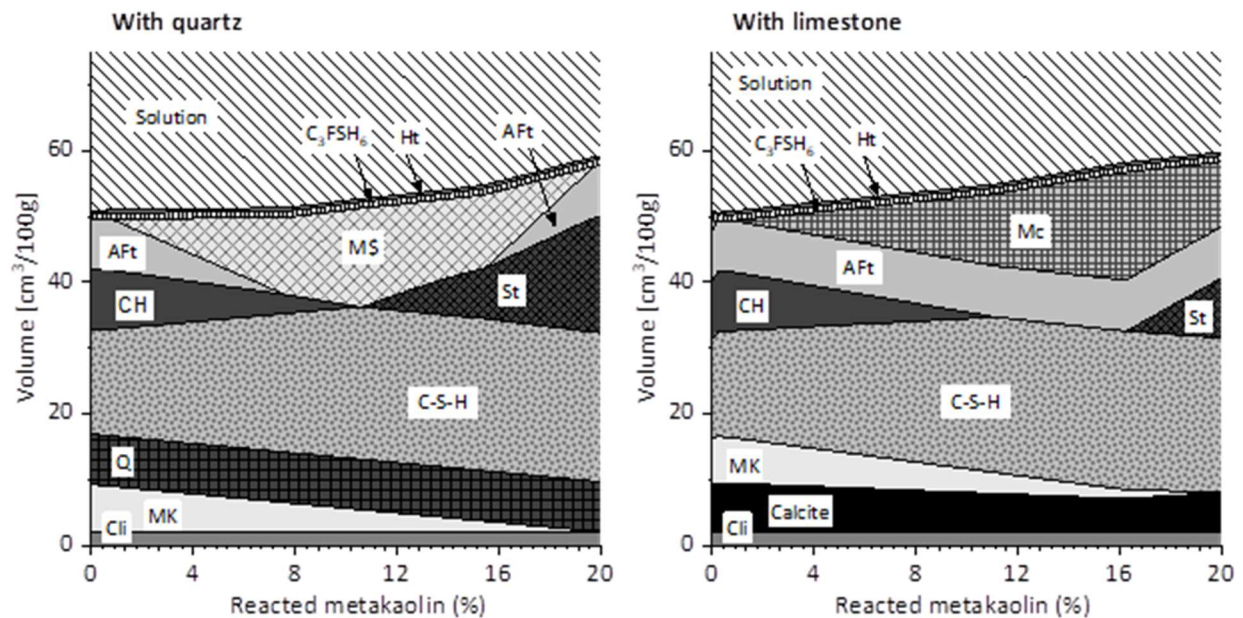


Figure 2: Thermodynamic modelling of 60% cement and 20% metakaolin with left: 20% Quartz and right: 20% Limestone (Adapted from Zajac CCR 2018 [27]). “Cli” refers to unreacted clinker, “MK” to unreacted metakaolin, “Q” to quartz, “AFt” to ettringite, “St” to strätlingite, “MS” to monosulphate, “C₃FSH₆” to hydrogarnet and “Ht” to hydrotalcite.

2.2 Influence of clay type and impurities in clay on reactivity

The reactivity of a clay depends on its structure. Higher dissolution rates of aluminates and silicates are observed for 1:1 clays compared with 2:1 clays [38]. This reactivity difference is explained by the accessibility of aluminate sites in the kaolinite structure whereas aluminate octahedra are trapped between silicate layers in 2:1 clays. Moreover, kaolinite contains more hydroxyl groups compared to 2:1 clays. Reactivity could be favoured by the more important crystallinity loss due to the loss of the hydroxyl groups [39]. Faster strength development of binary blends is observed for calcined kaolinite, compared with calcined illite or calcined montmorillonite, for clays with similar grade [39–41]. A broad study was carried out on about 70 clays and pointed out the key influence of the calcined kaolinite content on the strength development of calcined clay blends [20]. Other parameters such as fineness, specific surface and secondary phases play a minor role in strength development. In this study with 30% of calcined clay (and 15% of limestone), a calcined kaolinite content of 40% in the clay was sufficient to reach similar strength to plain cement from 7 days onwards. Moreover, optimised properties of workability and strength development were obtained for a range of clay kaolinite contents of 40-60%. The use of pure kaolinitic clays worsens rheology while providing a slight increase in compressive strength at late age [8, 9, 15, 16]. Calcined illitic clays are the least reactive type of calcined clay. Calcined montmorillonite reacts slower than kaolinite, but blends can in some cases catch up the strength of calcined 1:1 clay blends at late ages [42].

Clays are most of the time composed of 1:1 or 2:1 minerals mixed with secondary phases. Some of these phases can play a role during the hydration of calcined clay blends:

- (a) Argillites often contain mixed clay minerals, such as mixtures of 1:1 and 2:1 clays, with one clay being dominant as in the kaolinite with secondary illite and Ca-montmorillonite with secondary kaolinite examined in a study by Habert et al. [43]. The degree to which the secondary clays affect reactivity depends on the proportion of the clay minerals present and the calcination process [44].
- (b) Calcite present in raw clay can partially decarbonate during clay calcination. While carbon dioxide is released, the calcium part tends to combine and cover the surface of clay particles, leading to a decrease in the specific surface of calcined clay [45, 46]. The higher the calcination temperature, the higher the influence of calcite on the specific surface of calcined clay. This decrease of specific surface leads to a slight decrease of calcined clay reactivity. To overcome this issue with calcite, it can be recommended to reduce the calcination temperature and to increase the residence time of calcined clay.
- (c) Dolomite decarbonation temperature can cover a range from 500°C to 850°C. Depending on the type of clay and the calcination temperature, a complete decarbonation may occur. This decarbonation of dolomite was recently found to enhance the reactivity of blended cements containing calcined clay. The decomposition of dolomite leads to the formation of some periclase and free lime. These compounds react with aluminosilicate phases but also with other secondary phases such as minerals from the parent rock. The vitreous or poorly-crystalline phases resulting from this reaction are suggested to help the overall reactivity of calcined clay. Significant strength improvement is observed compared to calcined clay without dolomite or containing calcite. This finding opens the path towards a wider range of acceptable range of clay composition [47].
- (d) Quartz is a very common mineral associated with clay. Quartz is often used in research studies as a reference with no reactivity. The separation of quartz, harder to grind, from clay is a fast developing field and could potentially permit to enrich the fraction of clayey minerals, or to

calcine the clay fraction only and the quartz could be then mixed with the calcined clay. However, it may not always be possible to remove quartz from clays, as it may be fine grained and even physically bound to the clay phases [33].

- (e) Iron and aluminium oxides coming from the dehydroxylation of goethite and gibbsite do not play any negative role during hydration. The substitution of calcined gibbsite by quartz in calcined clay leads to a slight decrease of reactivity, explained by the higher specific surface of calcined gibbsite compared with quartz. Calcined gibbsite does not interfere with calcined clay dissolution [48].
- (f) Rutile can come from the raw clay or from the transition of anatase during clay calcination [49]. No influence on calcined clay reactivity has been reported.
- (g) Clays may contain muscovite or mica and other presumably inert crystalline phases such as albite (a feldspar), cristobalite, and hematite [39, 44, 50]. Some of these phases may decompose or structurally rearrange during calcination, depending on the calcination temperature, potentially increasing the perceived reactive clay content [50].
- (h) Sulphides such as pyrite and pyrrhotite can also be present in natural clay deposits. These minerals are known for causing expansion in concrete [51]. However, upon calcination of clay they decompose and oxidise into hematite (iron oxide), which is not an expansive mineral and can be safely used in concrete [52].

2.3 Factors influencing the pozzolanic reaction of calcined clay

The reaction of calcined clay tends to slow down with time. The potential factors that could influence this slowing down were investigated in the study of Briki et al. [53]: portlandite depletion, the presence of aluminium in the pore solution and the lack of capillary pores and/or refined water-saturated pores. The influence of portlandite was assessed by comparing the reaction degree of metakaolin for a reference calcined clay limestone cement, containing calcined kaolinitic clay, and a similar blend with 5% portlandite addition. The reaction degree is shown in Figure 3. Even if higher reaction degree is observed at early age for the system with portlandite addition, the reaction slows down and similar values are obtained at late ages. Thus, the lack of portlandite is not responsible for the slowing down of calcined clay reaction.

The influence of aluminium was investigated by substituting the metakaolin of calcined clay with silica fume, an Al-free SCM. The determination of the reaction degree of silica fume follows a very close trend to metakaolin. A similar slowing down is observed at late ages. This shows that the aluminium present in the pore solution cannot explain the slowing down of calcined clay reaction.

A comparison between sealed-cured and pore solution (simulated) cured samples was also carried out. For pore solution-cured samples, 2 mm-thick slices were cured under pore solution after setting. The objective was to investigate the influence of water saturation of capillaries on the reaction degree of metakaolin. The results indicate that metakaolin reaction degree is significantly increased with higher water saturation in capillary pores. During hydration, a decrease in the reaction rate of metakaolin has been observed after porosity refinement and water consumption of the capillaries takes place in the microstructure [19, 20, 53, 54]. As hydration continues, the internal relative humidity of the material decreases, and pores empty from large-to-small. The Kelvin-Laplace equation can be used to determine the limit (largest) radius of pore that remains saturated for a given internal relative humidity value (r_{lim}) [55, 56]. Using this approach, it has been shown that the lack of (large) saturated pores explains the

slowdown of calcined clay (metakaolin) reaction [53], as hydration can only take place in the smaller pores that remain saturated.

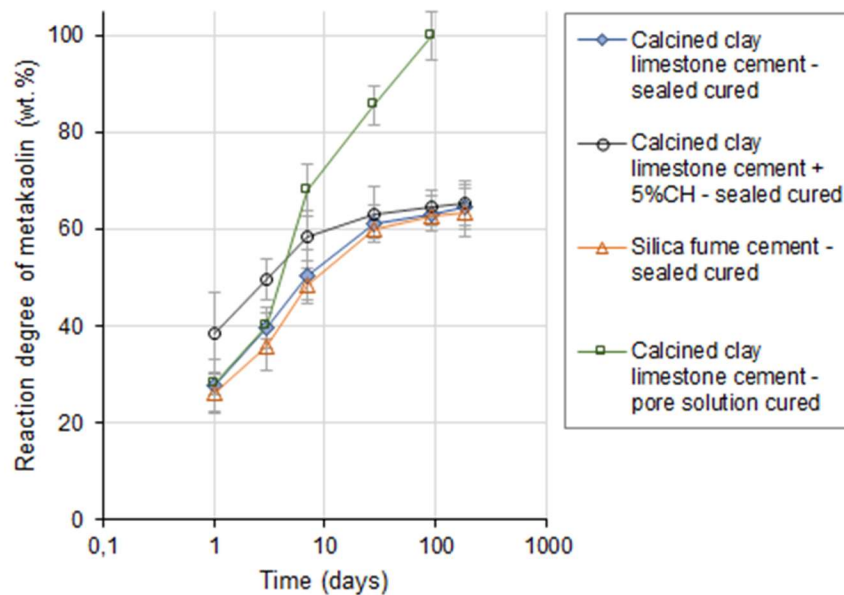


Figure 3. Reaction degree of metakaolin in calcined clay limestone cement pastes. The influence of portlandite addition, a comparison to silica fume cement, and the influence of sealed versus pore solution curing are shown. (Adapted from [53]).

In saturated pores, the extent of reaction leads to further porosity reduction. As microstructure refines, a higher degree of supersaturation towards the precipitated phase is required to stabilize the smaller (higher curvature) crystal [55]. The observation of long-term samples shows that precipitation still occurs in small saturated pores, despite the higher degree of supersaturation required for hydrate precipitation [28], reaching critical entry sizes slightly lower than the ones reported at earlier ages (up to 90 days) for similar systems [19, 57]. In addition, slow size reduction of partially emptied pores is observed in the long-term, possibly due to a surface precipitation mechanism taking place in the pore solution film lining the surface of the pores [28]. Thus, the lack of large saturated pores imposes a kinetic (slowdown) limitation to the reaction of metakaolin. The schematic representation of the microstructure of calcined clay blends at late ages is shown in Figure 4, illustrating the difference in water saturation with pore size, and its influence on the progress of hydration reactions and porosity reduction over time.

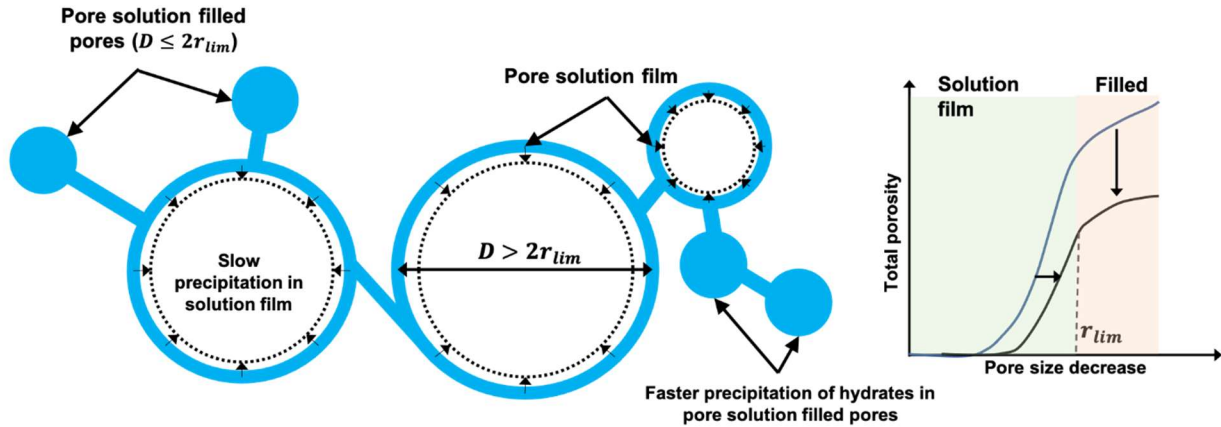


Figure 4: Schematic representation of the proposed mechanisms controlling the kinetics of precipitation at later ages. Adapted from Zunino and Scrivener, CCR 2022 [28].

2.4 Evolution of porosity in calcined clay blends

The microstructure development, including pore structure (pore sizes and its distribution), influences the physical, mechanical and transport properties of cementitious binders. As discussed in previous sections, the clay type and purity play a key role in their chemical reactivity, and the resulting phase assemblage. This section summarises the role of calcined clay on the reduction of porosity in blended Portland cement systems, considering the role of clay type and purity, the influence of calcined clay in combination with limestone, and the pore structure evolution at later curing ages. Furthermore, as different techniques have been applied for porosity assessment in calcined clay cements systems, a comparative analysis of the finding from different techniques is also reported.

At this point, it is convenient to define two terms that are used throughout this section. The pore entry radius is the size of the pore at the point of contact with mercury. Upon intrusion, this value determines the pressure required to intrude. The threshold pore entry radius gives a reference of the minimum pore radius that is geometrically continuous throughout the whole sample (threshold entry size). The critical pore entry radius is the point with the steepest slope in the cumulative intrusion curve. It is mathematically defined by the inflection point of the main intrusion step.

Differences in microstructural development has been observed in hydrated cements containing metakaolin and lower grade calcined kaolinitic clays when using different techniques to determine pore structure, such as mercury intrusion porosimetry (MIP), H^1 NMR, micro-tomography and electrical impedance spectroscopy. A detailed overview of the observation of pore structure features, as a function of the type of technique used for their assessment, is presented in Table 1. A common observation across different techniques is early refinement in the pore structure (e.g. increased fraction of gel pores) with calcined kaolinite clays and metakaolin, showing this refinement between 3 to 7 days of curing. The distribution of different pore fractions was studied by Avet et al. [26] using H^1 NMR. While OPC showed continuous reduction in capillary pore water, the capillary pore water signal in calcined clay systems was found to be limited beyond 3 days and 7 days for systems with 95% and 40% kaolinite content, respectively.

Studies on the impact of metakaolin on pore size and distribution are mostly limited to low Portland cement replacements, in the range of 10-15%. A metakaolin dosage up to 15% was studied in [58], where it was identified that pores reached a threshold radius of ~40 nm by 14 days of curing and remained unchanged at later curing ages. Further analysis of the pore size distribution in those samples showed that the pore fraction < 20 nm increased as the metakaolin content was higher and the pore fraction > 20 nm decreased as metakaolin content was lower, confirming the refinement of pores due to pozzolanic reaction of metakaolin. Frias et al. [59] reported that the pore diameter in metakaolin-blended cements remained unaltered from 14 days until 350 days of curing, because the degree of hydration was limited by depletion of CH in the system. It has also been reported [60] that the pore fraction with sizes of 5 - 0.01 μm reduces consistently and partitioned pore fractions with sizes < 0.01 μm increase consistently with higher degree of metakaolin reaction.

The clay purity and type strongly influence the pore structure of cements produced with them. Cements produced with a low-grade calcined clay, with a kaolinite content of about 50%, showed significant pore refinement as measured by vacuum saturation porosity and conductivity, compared with other with other SCMs (e.g. fly ash) [61]. Cement paste systems with calcined clay with metakaolin contents of 93% and 73% had significantly finer pore structures compared to OPC [62], most notably with calcined clay with lower contents of metakaolin. This is consistent with the results reported by Avet et al. [57] that identified a limiting critical pore entry radius of 3–5 nm, from which the porosity does not get further refined. The higher the calcined kaolinite content, the faster this refinement limit is reached. The identified differences in pore structure were observed as early as 3 days after curing. However, all calcined clays with >50% kaolinite content presented a similar pore structure with a dense microstructure by 28 days [57].

There are a limited number of studies evaluating the pore structure of non-kaolinitic calcined clays-OPC binders. Martirena-Hernandez et al. [63] identified that cement pastes with calcined kaolinite clays had lower capillary porosity than OPC reference samples, while calcined illite or montmorillonite clay-containing cement pastes had higher capillary porosity than OPC. A comparison between cements produced with 25% content of calcined kaolinite or illite clays with similar amorphous content of about 56% was carried out by Cordoba et al. [64]. The study found that kaolinite clay was more effective in refining pore structure than calcined illite shale. This was attributed to the differences in reactivity and reaction products forming in these systems.

The addition of limestone to metakaolin-containing blends influences the pore structure of these materials. For example, a 2 to 1 metakaolin-limestone combination at 45% replacement level of cement produced a refined pore structure compared to cements produced with 45% metakaolin replacement [65]. Studies have shown that the calcined clay-limestone system produced with clays containing 20-60% kaolinite formed a higher amount of monocarbo- and hemicarbo-aluminates than OPC alone [66]. Thus, the low-density carboaluminate phases produced in a higher amount when using a lower grade calcined clay have been shown to benefit from the calcined clay-limestone interaction and refine the porosity. Another study [19] revealed that deposition of these low-density CO_3 -AFm phases occurs along with large pore spaces, as shown in Figure 5. There is a lower tendency to form such low-density hydrate phase at later ages or at lower water to binder ratios. This is due to the fact that significant porosity refinement has already occurred and limits the formation of such crystalline hydrate phase. This is confirmed by the higher amount of CO_3 -AFm phases formed at higher water to binder ratios (w/b). Furthermore, calcined kaolinite clay (with or without limestone) was found refine pore structure in cement mortar (w/b of 0.60-0.75) [67] and in concretes [68, 69] prepared with higher water contents. While CO_3 -AFm phases are known to improve space-filling characteristics, the amount of gypsum is found to control the formation

of additional ettringite/carboaluminate at the expense of each other [70]. This could have a direct effect on the pore structure development in ternary binders containing calcined clay.

Table 1 Summary of calcined clay porosity reduction and pore size evolution captured using different techniques

Method	Salient features of techniques	Salient observations on the performance of calcined clays containing materials	Reference
MIP	Pore size distribution Wide coverage of pore size to cover capillary to gel pores in the capillary region	- Significant refinement of pore structure by 3 - 7 days for metakaolin and lower grade calcined kaolinite clays - Total porosity by MIP is similar due to increase in gel porosity but significant pore refinement was observed - Limited change in critical pore diameter after 7 days for metakaolin and CC with >50% kaolinite content	[58][59][60][71][72]
¹ H NMR	Distribution of pore volume fractions in terms of capillary, gel and interlayer porosity	- Reduction in capillary porosity by 7 days and limited change there was spotted for sample cured in sealed conditions - Signal from capillary porosity continuously reduced in sample cured in moist conditions - Major increase in the fractions of gel pores between initial 10 days could be identified for sample cured in sealed and cured conditions	[26, 53]
Micro tomography	Volumetric analysis of pore structure revealing its pore morphologies such as shape and connectivity.	- Metakaolin containing binder had higher volume of finer pore sizes than neat cement and fly ash cement - Pore connectivity was found to reduce from 90% at 7 days to 9% at 60 days in limestone calcined clay combination were studied using synchrotron micro tomography	[73] [74]
SEM-BSE imaging	Spatial distribution of the phases and porosity can be observed in the microstructure	- Kaolinite clay produce denser microstructure compared to illite and montmorillonite clays - Distribution of carboaluminate phases in calcined clay –limestone systems were categorised based on combined SEM imaging with mapping techniques. - Higher grade kaolinite clays (95%) produce dense microstructure by 3 days. However, 28 days microstructure were similar for calcined clay with 50% and 95% kaolinite content - Calcined clay produces compact microstructure compared to fly ash binder	[63] [19] [66] [69]
Electrical impedance spectroscopy	Non-destructive and continuous assessment of microstructural evolution using electrical response which is a function of porosity, pore connectivity and pore solution conductivity	- 35% metakaolin addition was found to major rise in resistivity by 3 days compared to PC and 35% fly ash binder - Electrical conductivity reduced for calcined clay binder by 3-7 days compared to fly ash reaction which occurred beyond 14 days. - Pore refinement was compliment with higher formation factor and tortuosity values in limestone calcined clay binder using electrical conductivity measurement - Formation factor estimated from electrical response was found to identified pore refinement by 3-7 days and identified the difference in microstructural development of calcined clay and calcined-limestone combinations in long term	[75] [61, 69] [76]
Ultrasound pulse velocity (in-situ)	Increase of stiffness of bulk phases capture the development of physical structure	- In-situ ultrasound was used to confirm the improved hydration behaviour seen in heat evolution for its impact on pore structure using pulse velocity	[19]

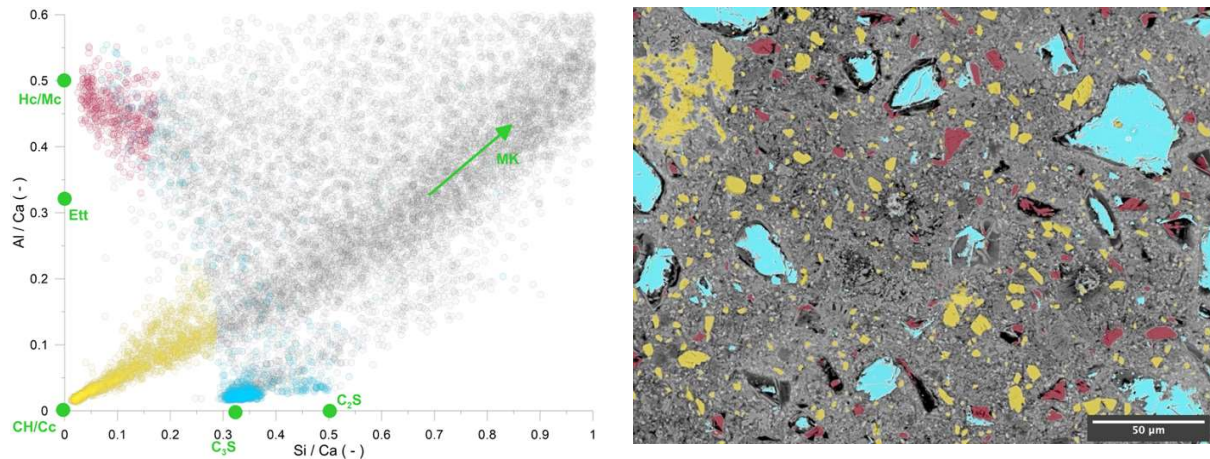


Figure 5. Pore filling due to formation of carboaluminate hydration production in limestone-calcined clay combination as reported in [19]. Note: Portlandite + limestone in yellow, Hc + Mc in red, anhydrous cement grains in cyan.

The effect of metakaolin-limestone (or dolomite) ratio on pore structure was reported in [77]. Up to 25% addition of limestone or dolomite did not induce any increase in porosity or critical pore size in a cement containing 60% OPC and 15-30% metakaolin [77]. The effect of metakaolin – limestone ratio on pore structure development was studied by Tang et al. [78], and the results showed that about 10% metakaolin is sufficient to avoid dilution of hydrates caused by about 30% limestone addition. It has also been observed that in comparison to the quartz-calcined clay combination, the limestone-calcined clay combination produced a lower critical pore size [79]. On the contrary, the effect of curing temperature on the pore structure of calcined clay in combination with limestone has shown to increase pore volume and threshold pore diameter in [80]. While the addition of limestone was found to reduce threshold pore diameter at 5 °C, the threshold pore sizes increased at 20 °C and 38 °C, as shown in Figure 6. The change in porosity and threshold pore sizes were limited up to 10 % carbonate addition, and dilution effects were clearly visible at 20% limestone addition.

In summary, significant pore refinement produced by calcined kaolinitic clay has been confirmed by numerous studies using multiple techniques. Kaolinite clays positively influence pore refinement at early ages (typically 3-7 days) in both binary system and ternary formulations containing limestone additions when the kaolinite content of the clay are above 40%. Studies on other alternative clays are limited and not exhaustive compared to kaolinitic clays.

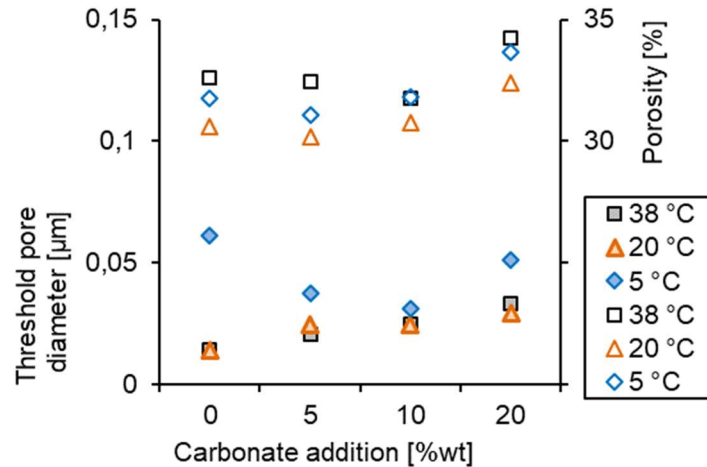


Figure 6. Threshold pore diameters of OPC-metakaolin systems with the addition of limestone at different curing temperature at 90 days (Adapted from [80]).

3 Methods for determining the reaction degree of calcined clay

Calcined clays used for industrial applications often refer to materials not only containing clay minerals, but secondary phases such as quartz, iron, aluminium, titanium oxides, calcite, and others. During hydration, clay minerals are the dominant reactive phases. The determination of the reaction degree of the clay minerals is essential to better understand their contribution to the performance of calcined clay-blended cements. A wide range of methods have been used to determine the reaction degree of supplementary cementitious materials (SCMs). Some of these methods can be applied to calcined clay, and the main characteristics of each method are summarised in Table 2.

1. Isothermal calorimetry permits quantification of the heat release during hydration. The difference in heat between a blended cement with calcined clay and a reference system with quartz could provide an indication of the extent of calcined clay reaction [81]. However, the hydration degree of clinker can be influenced by the calcined clay reaction, even at early ages [20]. Thus, this heat release comparison is not straightforward and is biased by the difference in clinker hydration. The type of hydration product formed can also vary, leading to variation in the heat release. Moreover, the determination of the reaction degree requires the specific heat of hydration of the reactive phases in the calcined clay, which not generally known.
2. Selective dissolution [72] assumes the preferential dissolution of all hydrates and anhydrous phases except calcined clay. The mass residue after dissolution is compared with the initial sample mass, and the ratio gives an indication of the extent of reaction of calcined clay. This technique has been applied to metakaolin-cement paste [72]. The main disadvantage of this method is that an incomplete dissolution of hydration products and anhydrous phases can be observed, leading to poor accuracy [81].
3. Image analysis using a scanning electron microscopy in backscattered electron mode (SEM-BSE) consists of isolating SCM unreacted grains in the microstructure thanks to their brightness and chemical composition when combined with energy-dispersive spectroscopy analysis (EDS) [81, 82]. This method is not suitable for the assessment of calcined clay reaction because of the

fineness of calcined clay particles. Future improvement of the resolution of scanning electron microscopy might make this quantification possible, but this is currently not the case, even using high-resolution SEM.

4. ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) permits accurately quantification of the reaction degree of calcined clay [25, 36, 38]. The quantification is not influenced by the clinker phases nor by hydration products. The main issue concerning NMR is the presence of paramagnetic iron ions (Fe^{3+}). These ions can come from the clinker and from the calcined clay, since iron oxide is often found as secondary phase in the clay. The accuracy of NMR results is directly impacted by the amount of Fe^{3+} , which leads to a decrease of magnetisation.
5. Mass balance allows estimation of the whole phase assemblage from the consumption of anhydrous phases [83]. The amount of reacted clinker phases and sulphate source are quantified by X-ray diffraction combined with Rietveld analysis. These values are converted into oxides, and these oxides are redistributed into a sequence of expected hydration products, as described in Figure 6. SEM-EDS is used to quantify the aluminium incorporation and the Si/Ca of C-A-S-H. The reactive phase in calcined clay is the free variable. An increase in metakaolin degree of reaction leads to an increase of reacted Al_2O_3 and SiO_2 , which influences the phase assemblage formation [54]. The chemistry of the reactive compound in the clay can be adjusted depending on the composition of the clay. Thus, mass balance can be used for blends containing 2:1 clays. The main drawback of this method is that reliable inputs from XRD-Rietveld and SEM-EDS are required to get relevant information.
6. Thermodynamic modelling is also suitable for determining the reaction degree of calcined clay, using the same inputs as the mass balance approach. The main difference between mass balance and thermodynamic modelling is that a thermodynamic database is used for predicting the hydration products formed in the latter. Special attention must be paid to the C-A-S-H composition used such that it considers aluminium incorporation and accurate Ca/Si. The Al incorporation may have to be implemented manually in the modelling software.
7. XRD combined with the partially or not known crystalline structure (PONKCS) method is another way of estimating the reaction degree of calcined clay. The PONKCS method permits quantification of amorphous humps in XRD patterns [84]. The hump for calcined clay is calibrated from a sample tested with a known quantity of unreacted calcined clay, and this hump is then fitted on the hydrated sample diffractogram [85]. The amorphous peaks of metakaolin or calcined illite or montmorillonite do not overlap with C-A-S-H. The main advantages of this method are that XRD is widely available and the measurement is quick. However, the analysis of the results requires highly skilled technical staff, and the pertinence of the results significantly decreases with the grade of calcined clay [54] and decreasing replacement levels.

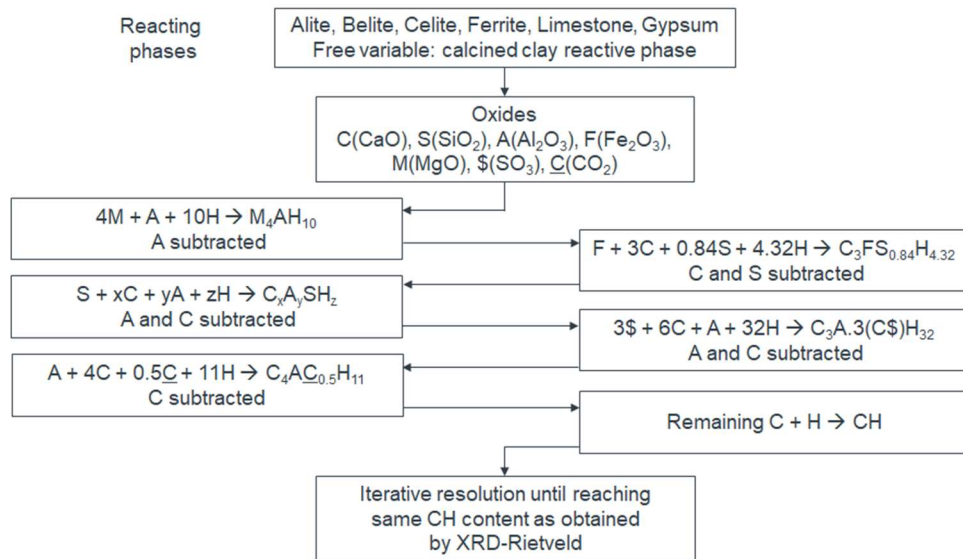


Fig. 6 Mass balance procedure, adapted from [54].

Table 2. Comparative summary of the methods for determining the reaction degree of calcined clay.

Method	Rating	Advantages	Drawbacks	Equipment	References
Isothermal calorimetry	Not recommended	Simple experiment	Isolation of calcined clay reaction not straightforward	Isothermal calorimeter	Not on calcined clay
Selective dissolution	Not recommended		Deviations due to remaining undissolved phases	Vacuum filter	[72]
Image analysis	Not possible		Too high fineness of calcined clay particles	SEM	Not on calcined clay
²⁷ Al and ²⁹ Si NMR	Recommended	Direct quantification	Issue with paramagnetic iron	NMR	[25, 36, 86]
Mass balance	Recommended but reliable inputs needed	Full assessment of hydration	Indirect method	XRD + SEM	[27, 54, 87–89]
Thermodynamic modelling	Recommended but reliable inputs needed	Full assessment of hydration	Indirect method	XRD	[36, 54, 72]
PONKCS	Possible	Equipment widely available	Low accuracy Complex for mixed clay	XRD	[35, 54, 90]

Figure 7 summarises published data on the amount of reacted metakaolin using different methods in binary and ternary blends containing calcined kaolinitic clays. All data have been collected on 28-day samples for experiments carried out at 20°C. A large scatter is observed. Overall, it seems that above 20% of metakaolin in the blend composition, full reaction is not reached and metakaolin is in excess. The scatter of the data can be explained by several factors: the influence of cement type, clay characteristics, and curing conditions [88], but also by the method used to determine the reaction degree of metakaolin. Much less data is available on 2:1 clays, even if most of the methods could be applied to such clays. Solid state NMR was successfully used [32, 33], demonstrating that lower reaction degree is reached for 2:1 clays compared with 1:1 clays.

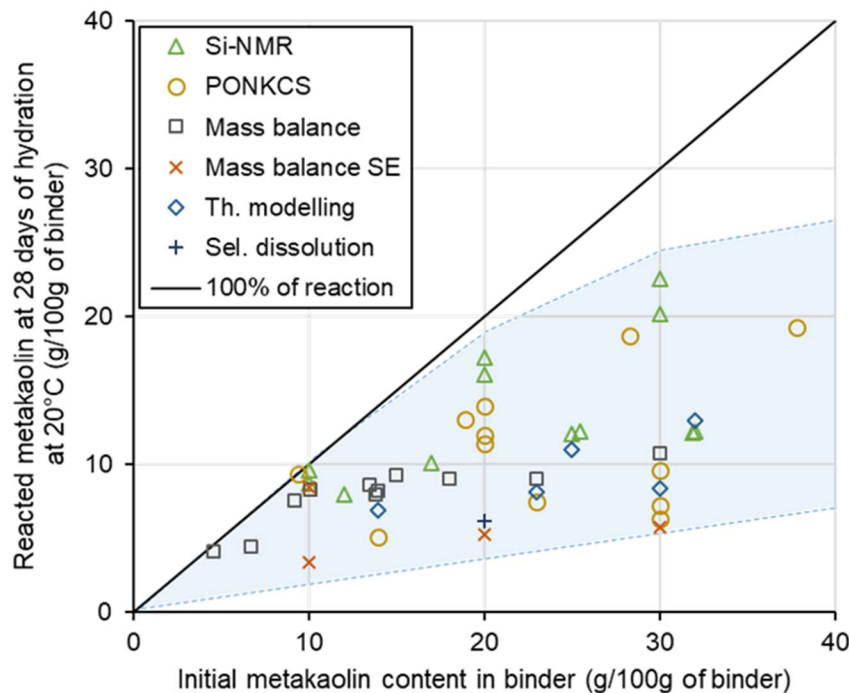


Figure 7. Range of measured reacted metakaolin in blended paste at 28 days of hydration at 20°C, compared with the initial metakaolin content of the blends. The solid line indicates full reaction of metakaolin. Collected data are based on Si-NMR [25, 36, 86], PONKCS [35, 54, 90], mass balance [27, 54, 87–89], mass balance single-equation (SE) approach [91, 92], thermodynamic modelling [36, 54] and selective dissolution [72].

Even using the recommended methods, the investigation of the reaction degree of calcined clay on mixed clays composed of 1:1 and 2:1 clays is challenging:

- First, the distinction of different minerals in calcined clay is not possible when using a mass balance method. Only one stoichiometry is considered for the reactive compound in clay, even if several clay minerals are identified.
- Thermodynamic modelling could be potentially used if metakaolin and the other calcined clay minerals are defined in the thermodynamic database.

- For solid state NMR and PONKCS methods, calcined clay minerals should interfere with each other. The humps of the calcined clay minerals must be isolated to ensure accurate fitting. Moreover, the amount of the secondary clay mineral can be relatively low. For example, if a clay contains 50% kaolinite, 30% quartz and 20% illite, for a substitution of 30% of cement by calcined clay, the initial amount of activated illite in cement would be only 6 g per 100 g of binder. The quantification of the reaction degree of calcined clay is less accurate since the signal-to-noise ratio decreases with the grade of the clay phase.

4 Impact of cementitious components on reactivity

4.1 Interaction of clinker phases and calcined clay hydration

The type of clinker influences the performance of calcined clay blended cements. Obviously, a highly-reactive PC blended with calcined clay should provide higher strength than a less-reactive PC mixed with calcined clay. This is the reason why relative strength, i.e., the strength of the blend normalised by the strength of the plain cement, is often used to assess the influence of cement physical and chemical properties on the strength development of calcined clay cements. Cyr et al. [93] tested the performance cement with calcined kaolinitic clay, using eleven different plain cements for preparing the blends. From this study, the authors could not observe a clear correlation between the total calcium silicate content in the cement and the relative strength values. This is not very surprising considering the complex, simultaneous reactions occurring during the hydration of cements. However, cements with higher C_3A contents appear to enhance the reactivity of calcined clay [93]. Overall, some correlations have been observed between the C_3A , C_4AF , SO_3 contents and the strength development in calcined clay blended systems [93].

Calcined clay particles also influence clinker hydration through physical effects [2, 23, 94–96]. These physical effects lead to the enhancement of the hydration of clinker compared to plain cement [97–99]. The physical influence has three contributions:

- The surface of calcined clay particles provides nucleation sites for heterogeneous nucleation of hydration products.
- Calcined clay particles react slower than the most reactive clinker phases. Clinker substitution by calcined clay leads to an increase of the water to cement ratio for a constant water to binder ratio. Thus, more space is available for hydrates to grow in calcined blended cements.
- The presence of particles finer than clinker leads to a decrease of the inter-particle distance. The shearing of particles during mixing is increased by this closer distribution [100].

Calcined clay may also negatively influence the hydration of clinker. In some specific cases, especially with high-grade metakaolin, it has been observed that calcined clay leads to a slowing down of clinker hydration, even alite, as early as 3 days of hydration [20]. This slowing down can occur earlier than calcined clay reaction. The reasons for this slowing down are likely to be similar to the ones explained in section 2b for calcined clay reaction. The growth of hydrates only occurs in saturated pores or on the walls of partially-saturated pores; and the kinetics of the growth is limited by the increase of the supersaturation

with respect to hydration products required to overcome the increase of curvature of the pore with the refinement of porosity.

4.2 Influence of alkali content of clinker

Alkalis influence the reaction kinetics of alite [101], with a consequent effect on early-age strength. In cements with similar phase compositions, the dissolution of metakaolin is seen to be enhanced in the cements with higher alkali content [102], which suggests that using a clinker with higher alkali content would be beneficial for producing calcined clay-blended cements. Replacing a large proportion of Portland cement by calcined clays and limestone reduces the total alkali content, which may affect the hydration reactions as the reactivity of the SCM is dependent on the pH of the system which gets affected by the partial replacement of clinker [93].

As shown in Figure 8, an increase of the total alkali content can lead to an increase in the early age strength [7, 103]. In this case, the alkali content was adjusted by addition of KOH to the mixing water. However, for $\text{Na}_2\text{O}_{\text{EQ}}$ contents beyond about 1% by mass of binder, it has been observed that the strength at later ages reduces significantly [87]. The mechanism leading to the decrease in long term strength with high contents of alkalis is still a matter of debate and an interesting subject to be addressed in future studies. The presence of alkalis leads to a decrease in internal relative humidity in the material [56]. Recent work suggests that this might be responsible for the slowdown in clinker hydration and consequently, lower strength at later ages in systems incorporating higher amounts of alkalis [104]. It is important to note here that the alkali contents of cement systems, in a majority of the studies, were increased by dissolving the respective alkali salt in the mixing water which modifies the initial pH of the water. The effect of dissolved alkalis (from the mixing water) on the hydration mechanisms, therefore, need not necessarily be similar as that of the soluble alkalis present in the clinker. Therefore, the methodology presently used to ascertain the effect of alkalis on cement hydration may not be realistic representation of the actual hydration process.

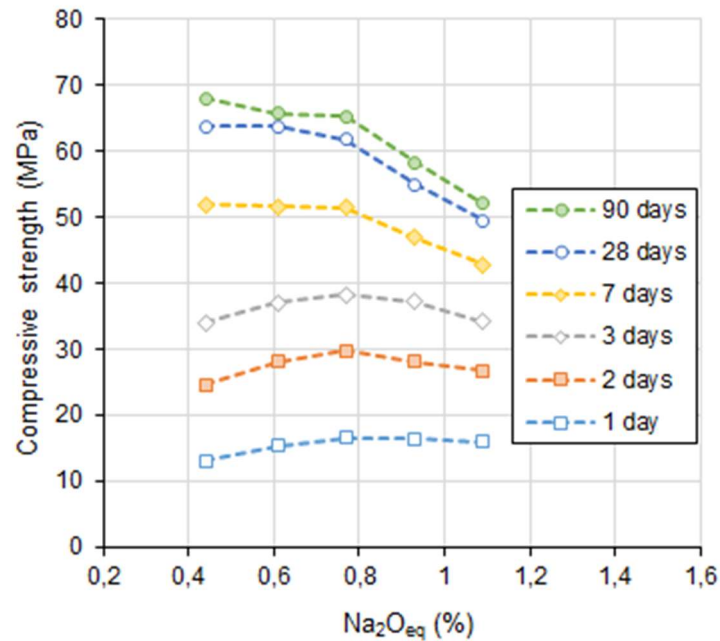


Figure 8: Compressive strength of calcined clay cements having limestone addition with different levels of alkali content adjustment (adapted from [105]). The lowest level refers to a mix design without alkali addition, i.e. alkalis only come from the clinker.

4.3 Impurities in limestone in calcined clay limestone systems

The advantages of calcined clay cements containing limestone additions have been well documented. In many limestone mines, dolomite ($\text{CaMg}(\text{CO}_3)_2$) is present as a minor impurity along with the major phase calcite (one of the polymorphs of CaCO_3). Such dolomitic limestones are generally not suitable for clinker production due to the potential unsoundness issues in the cement. Dolomite decomposes in the rotary kiln to form periclase, and the long-term hydration of periclase produces brucite resulting in an increase in solid volume, which leads to cracking. Therefore, a significant amount of limestone resources remains unutilised due to the presence of dolomite. Since dolomitic limestones are expected to be mixed directly (by inter-grinding or inter-mixing) with clinker and calcined clay, addition of these limestones to the calcined clay cements system offers a potential avenue for their utilisation and helps in conserving the valuable limestone reserves. Studies using pure dolomite indicate that the synergetic reactions present in the Portland cement – calcined clay-limestone system also exist in the Portland cement – calcined clay – dolomite system [79, 80]. Similar phase assemblages i.e., the formation of the carboaluminate phases and stabilisation of ettringite have also been observed in the presence of dolomite and limestone, as shown in Figure 8. In addition to these common phases, the Mg-bearing hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 3(\text{H}_2\text{O})$) phase also precipitates in the dolomite system [27]. The reaction rate of dolomite appears to be slower than the reaction rate of limestone, with the availability of portlandite being an important factor that limits the dolomite reactivity [77, 79]. Formation of strätlingite, a low density AFm phase, is observed in systems where the reactivity of dolomite is limited [27, 106]. Strätlingite formation is advantageous due to its space filling nature, but the exact reaction mechanisms behind its formation in the Portland cement – calcined clay – dolomite system needs to be further investigated. The slower reaction of limestone,

however, does not appear to have any impact on the strength development process. The reaction of limestone, however, does not appear to be similarly constrained by the portlandite content. Hence, it is expected that limestone will preferentially react over dolomite in the calcined clay cement systems that utilise dolomitic limestones as the carbonate source. It is important to note that only a small part of the limestone (<5% relative to the binder content) reacts in the calcined-clay cement system to form carboaluminate phases, with the remaining limestone acting as an inert filler [10]. Therefore, it is also possible to utilise other carbonate sources such as marble dust (which is a combination of minerals like calcium carbonate, magnesium carbonate, quartz, and dolomite) or quartz-rich limestone (where quartz is the secondary mineral) for producing calcined clay cements [27, 106]. It is expected that these secondary minerals will remain as unreactive fillers and help in achieving a densified microstructure in these systems.

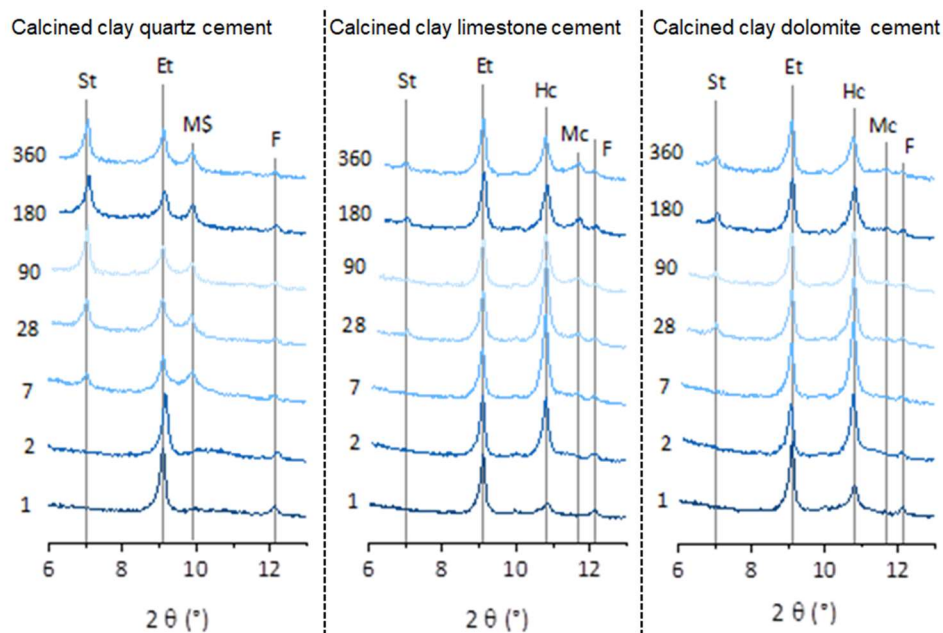


Figure 8. XRD-patterns for the ternary blends containing calcined clay with quartz, limestone and dolomite. The main peaks of ferrite (F), ettringite (Et), monosulphate (MS), possibly a sulphate and carbonate containing hydroxy-AFm(Hc-MS) and stratlingite (St) are indicated (Adapted from [27]).

5 Blend design optimisation – Guidelines for making blends of cement and calcined clay

5.1 Sulphate adjustment

In blended cements, the sulphate content per unit binder is lower due to the partial replacement of PC by SCMs. The incorporation of calcined clays in cements leads, in some cases, to undersulphation of the system. This can be observed by heat release curves where the aluminate peak occurs before the silicate one. In these cases, the silicate peak appears suppressed compared to a properly sulphated system, negatively influencing early-age strength [107, 108]. The balance of the system can be restored by the incorporation of additional sulphate (gypsum or other sulphate salt) to retard the aluminate reaction [57,

105, 109]. The distinction between the silicate and the aluminate peaks become visible by isothermal calorimetry.

For a given cementitious system (PC or blended cements), the sulphate balance can be associated with two main controlling factors established by Zunino and Scrivener [108]:

- Adsorption of sulphate on hydration products, mainly C-A-S-H. Sulphate is adsorbed on C-A-S-H during the acceleration period. Thus, an increased amount of C-A-S-H formed due to the enhanced reaction of alite (filler effect), which leads to an earlier depletion of solid gypsum and consequently, an earlier aluminate peak [97, 98, 105, 108]. Some studies suggest that other surfaces can contribute to the sulphate adsorption process. A recent study [110] reported the faster occurrence of the C_3A hydration peak in C_3A -gypsum-calcined clay systems. Due to the lack of calcium silicate phases in this system, this cannot be attributed to sulphate uptake from C-S-H, or reaction of calcined clays (due to the lack of portlandite).
- The formation of ettringite before gypsum depletion (i.e., before the aluminate peak). The amount of ettringite formed depends on the reaction rate of C_3A and the solubility of the sulphate source [108]. Although the reaction of calcined clays is much slower, the alumina dissolved in the first hours of hydration is not negligible. Skocek et al. [35] report hydration of ~3-8 (g/100g binder) of metakaolin depending on the replacement level after 6 hours. However, recent studies suggest that the contribution of alumina from SCMs to sulphate balance is second order compared to the effect on alite hydration and C-S-H precipitation rate. Particularly, the contribution does not seem to be related to the alumina content of the SCM.

The requirement of additional gypsum in calcined clay cements is mainly linked to the acceleration of alite hydration (filler effect) introduced in the system by the addition of the calcined clays and other SCMs, which increases the precipitation rate of C-A-S-H [97].

It is important to note that gypsum (or any other sulphate salts added to control setting) may also react with the reactive alumina from the calcined clay to form additional ettringite as soon as the alumina from metakaolin dissolves [19, 111, 112]. This effect is particularly observed in over-sulphated systems, where the amount of sulphate added stoichiometrically surpasses the alumina availability from C_3A . The source of calcium for this reaction has been shown to correspond to portlandite and a decrease in carboaluminates is observed [19]. The consumption of the portlandite would be at the expense of pozzolanic reaction (C-A-S-H precipitation and carboaluminate formation) of calcined clays.

Guideline: the incorporation of activated clay in a cement must lead to an adjustment of the sulphate-source to optimise hydration and early strength. The dilution of sulphate by the incorporation of calcined clay should be partially compensated. The optimum of gypsum content can be defined either by isothermal calorimetry, with the separation between the silicate peak and the aluminate peak, or on a strength basis.

5.2 Clinker factor

The clinker replacement level in calcined clay cement can influence the engineering properties of the resulting concrete [113]. The need for sustainability pushes reduction of the clinker factor further, and some studies have also tried producing calcined clay-based (clay and limestone) cement with 50-80 % clinker replacement, resulting in compressive strength between 30 - 65 MPa for water to binder ratios varying between 0.3 to 0.5 [114, 115].

Such a high clinker replacement level can help improve the sustainability by reducing the embodied CO₂ [115]. The phase assemblage does not significantly vary with different clinker replacement levels. Still, their quantities, especially for carboaluminates, can vary [19, 116]. The conversion of Hc to Mc occurs later [117]. The formation of C₂ASH₈ at higher replacement levels is also reported [91]. The appearance of C₂ASH₈ can be observed at lower clinker replacement levels when a high purity clay is used [91]. The increased Al concentration in the pore solution leads to more Al ion uptake by C-A-S-H [116].

Overall, a limitation of using calcined clay in cements comes from the slower reactivity of calcined clay compared with clinker. As a consequence, early-age strength of calcined clay cements tends to be lower than PC and it also decreases with the decrease of the clinker content. This is observed up to 3 or 7 days (and sometimes up to 28 days) depending on the mix design considered and the clinker-calcined clay used. Even if highly-reactive finely-ground metakaolin can contribute to strength at 2 days, most of calcined clay, and more generally SCMs, does not significantly influence early-age strength [118]. The reactivity at early is more related to clinker content and reactivity.

The optimal clinker content has to be put in perspective with the desired application of calcined clay cements. The clinker factor and the calcined clay cement formulation have to fit the strength values required in standards, or by the market. The need for early-age strength for masonry is much lower than for the precast industry. This means that depending on the application, the clinker substitution level can vary significantly.

Guideline: the optimum of clinker replacement corresponds to a compromise between sufficient strength for a given application, especially at early age, sufficient workability, and the maximum ecological and/or economic benefits. The required strength at early age does not mainly depend on calcined clay type, but also on the clinker replacement level and clinker reactivity.

6 Final remarks and perspectives

6.1 Main findings

The hydration of blended cement with calcined clays follows a similar pattern to Portland cement in terms of hydration, space filling and mechanical properties development. The differences are mainly associated with the reactions taking place and proportions of hydrates precipitated as a consequence of these reactions. Portlandite is consumed by the pozzolanic reaction of calcined clay. The composition of C-(A)-S-H changes, incorporating Al in its structure and with a lower Ca/Si compared with the C-S-H observed in plain cement. In presence of limestone, a higher amount of carboaluminate hydrates is obtained thanks to the alumina provided by calcined clay.

Among the different clay types, kaolinitic clays show the highest potential. Calcined kaolinitic clays are much more reactive than calcined illite or smectite. Calcined illitic clays are the least reactive. For kaolinitic clays, pure clays are not necessary to get satisfactory properties.

The extent of calcined clay reaction is not limited by the lack of portlandite availability or the presence of aluminium in the pore solution. The reaction of calcined clay slows down because of the lack of (large) solution-saturated pores. The precipitation of hydrates continues in these places but much more slowly in the fine saturated pores where higher supersaturation is required to stabilise the higher curvature of the smaller crystal. The precipitation may also keep occurring in the pore solution film lining the surface of the pores.

The reaction of calcined clay can be monitored using various methods. Solid state NMR and POKCS are the most direct methods. Solid state NMR is the most precise method for clays (and cements) with low iron content. Mass balance and thermodynamic modelling are both suitable but the results depend on reliable inputs from XRD-Rietveld (and SEM-EDS for C-A-S-H composition for mass balance). Other methods are not recommended due to their lack of precision.

Smaller size of critical pore entry size or pore threshold size is often reported for calcined clay blended cements. The refined microstructure is related to the formation of hydrates (C-A-S-H, AFm phases) and the space filling capacity of these phases. It has been experimentally demonstrated that the precipitation of all these hydration products contributes favourably to strength development and durability.

The properties of calcined clay cements, and especially strength development, also depends on the type of cement used. Overall, a highly-reactive clinker or cement, relatively rich in alkali can provide higher strength.

6.2 Identification of research gaps

The following potential areas of research could be further investigated:

- One of the main limitations for further reducing the clinker content in calcined clay cements is the slower strength development. It is possible to reach similar strength to plain cement at 28 days of hydration, sometimes at 7 days, depending on the clay type, the cement type, the substitution level, etc. However, equivalent strength level at 2 days is very challenging. Most of cements produced must reach minimum strength values at 2 days to be ranked in well-defined performance class, and even earlier for some applications. The acceleration of early strength development is of high interest.
 - o Optimized grinding strategies can allow strength gain at early age. Clinker is mainly responsible for early strength. Co-grinding is likely to overgrind “soft” calcined clay particles whereas “hard” clinker remains in the coarse fraction. A better control of the particle size of each compound is possible by separate grinding.
 - o A possibility could come from the development of specific admixtures (accelerators/activators).
 - o The enhancement of clinker reactivity could also allow to offset the decrease in early age strength at low clinker factor.

- Ways of enhancing the dissolution of calcined clay at early age could also permit to partially compensate the decrease of the clinker content.
- The development of other binder types containing calcined clays has started, much less intensively than for Portland cements. Still, calcined clay offers a very promising potential for their use in calcium sulphoaluminate cements (CSAs) or calcium aluminate cements (CACs).
- There is little data available on the properties of ternary blends containing clinker, calcined clay and slags or fly ashes or natural pozzolans. Such situation might appear complicated from an industrial point of view. However, this area might be of interest especially in case of limited access or supply of these SCMs.

7 Acknowledgements

F. Zunino and K. Scrivener acknowledge the financial support provided by the Swiss Agency of Development and Cooperation (SDC), grant 81026665. Participation of T. Hanein was funded by UKRI through a Future Leaders Fellowship (MR/V023829/1) and through the Circular Economy Centre for Mineral-based Construction Materials (EP/V011820/1).

8 Credit statement

	FZ	FA	YD	TH	MBH	MJ	AP	SK	SJ	JS
Introduction	X									x
Section 2.1	X								x	x
Section 2.2	X	X				X				
Section 2.3	X	X			X					
Section 2.4	X		X							
Section 3		X								X
Section 4.1		X						x		
Section 4.2	X			X				x		
Section 4.3							X			
Section 5.1	X							x		
Section 5.2	X	X						x	x	
Conclusion	X	X								
Review	X	X		X		X			x	

9 References

1. IEA, CSI (2018) Technology Roadmap: Low-Carbon transition in the Cement Industry
2. Lothenbach B, Scrivener K, Hooton RD (2011) Supplementary cementitious materials. *Cement and Concrete Research* 41:1244–1256. <https://doi.org/10.1016/j.cemconres.2010.12.001>
3. Skibsted J, Snellings R (2019) Reactivity of supplementary cementitious materials (SCMs) in cement blends. *Cement and Concrete Research* 124:105799. <https://doi.org/10.1016/j.cemconres.2019.105799>
4. Scrivener KL, John V, Gartner EM (2016) Eco-efficient cements: potential, economically viable solutions for a low-CO₂, cement-based materials industry. United Nations Environmental Programme (UNEP)
5. IEA Cement Technology Roadmap: Carbon Emissions Reductions up to 2050. OECD Publishing, Paris
6. Juenger MCG, Snellings R, Bernal SA (2019) Supplementary cementitious materials: New sources, characterization, and performance insights. *Cement and Concrete Research* 122:257–273. <https://doi.org/10.1016/j.cemconres.2019.05.008>
7. Zunino F (2020) Limestone calcined clay cements (LC3): raw material processing, sulfate balance and hydration kinetics. EPFL Thesis 8173
8. Scrivener K, Martirena F, Bishnoi S, Maity S (2017) Calcined clay limestone cements (LC3). *Cement and Concrete Research* 1–8. <https://doi.org/10.1016/j.cemconres.2017.08.017>
9. Zunino F, Martirena F, Scrivener K (2021) Limestone calcined clay cements (LC3). *ACI Materials Journal* 118:49–60. <https://doi.org/10.14359/51730422>
10. Antoni M, Rossen J, Martirena F, Scrivener K (2012) Cement substitution by a combination of metakaolin and limestone. *Cement and Concrete Research* 42:1579–1589. <https://doi.org/10.1016/j.cemconres.2012.09.006>
11. Gruner JW (1932) The Crystal Structure of Kaolinite. *Zeitschrift für Kristallographie - Crystalline Materials* 83:75–88
12. Alujas Diaz A, Almenares-Reyes R, Hanein T, et al (Submitted.) Properties and occurrence of clay resources for use as supplementary cementitious materials. *Materials and Structures*
13. Theodore Hanein, Karl-Christian Thienel, Franco Zunino, Alastair T., Marsh, Matthias Maier, Bin, Wang, Mariana Canut, Maria C.G. Juenger, Mohsen Ben Haha, François Avet, Anuj Parashar, Layth A., Al-Jaberi, Roger S. Almenares Reyes, Adrián Alujas Diaz, Karen L. Scrivener, Susan A. Bernal, John L., Provis, Tongbo Sui, Shashank Bishnoi, and Fernando Martirena Hernández (2021) Clay Calcination Technology: State-of-the-Art Review by the RILEM TC 282-CCL. *Materials and Structures* Accepted, in press:

14. Dhandapani Y, Santhanam M, Kaladharan G, Ramanathan S (2021) Towards ternary binders involving limestone additions — A review. *Cement and Concrete Research* 143:106396. <https://doi.org/10.1016/j.cemconres.2021.106396>
15. Scrivener K, Avet F, Maraghechi H, et al (2019) Impacting factors and properties of limestone calcined clay cements (LC³). *Green Materials* 7:3–14. <https://doi.org/10.1680/jgrma.18.00029>
16. Scrivener KL (2014) Options for the future of cement. 11
17. Steenberg M, Herfort D, Skibsted J, Damtoft JS (2011) Composite cement based on Portland cement clinker, limestone and calcined clay. Madrid, p 97
18. Antoni M (2011) Investigation of cement substitution by combined addition of calcined clays and limestone. École Polytechnique Fédérale de Lausanne
19. Zunino F, Scrivener K (2021) The reaction between metakaolin and limestone and its effect in porosity refinement and mechanical properties. *Cement and Concrete Research* 140:106307. <https://doi.org/10.1016/j.cemconres.2020.106307>
20. Avet F, Scrivener K (2018) Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3). *Cement and Concrete Research* 107:124–135. <https://doi.org/10.1016/j.cemconres.2018.02.016>
21. Kuzel HJ, Pöllmann H (1991) Hydration of C3A in the presence of Ca(OH)₂, CaSO₄·2H₂O and CaCO₃. *Cement and Concrete Research* 21:885–895. [https://doi.org/10.1016/0008-8846\(91\)90183-I](https://doi.org/10.1016/0008-8846(91)90183-I)
22. Damidot D, Lothenbach B, Herfort D, Glasser FP (2011) Thermodynamics and cement science. *Cement and Concrete Research* 41:679–695. <https://doi.org/10.1016/j.cemconres.2011.03.018>
23. De Weerd K, Kjellsen KO, Sellevold E, Justnes H (2011) Synergy between fly ash and limestone powder in ternary cements. *Cement and Concrete Composites* 33:30–38. <https://doi.org/10.1016/j.cemconcomp.2010.09.006>
24. Adu-Amankwah S, Zajac M, Stabler C, et al (2017) Influence of limestone on the hydration of ternary slag cements. *Cement and Concrete Research* 100:96–109. <https://doi.org/10.1016/j.cemconres.2017.05.013>
25. Dai Z, Tran TT, Skibsted J (2014) Aluminum Incorporation in the C-S-H Phase of White Portland Cement-Metakaolin Blends Studied by ²⁷Al and ²⁹Si MAS NMR Spectroscopy. *J Am Ceram Soc* 97:2662–2671. <https://doi.org/10.1111/jace.13006>
26. Avet F, Boehm-Courjault E, Scrivener K (2019) Investigation of C-A-S-H composition, morphology and density in Limestone Calcined Clay Cement (LC3). *Cement and Concrete Research* 115:70–79. <https://doi.org/10.1016/j.cemconres.2018.10.011>
27. Zajac M, Durdzinski P, Stabler C, et al (2018) Influence of calcium and magnesium carbonates on hydration kinetics, hydrate assemblage and microstructural development of metakaolin containing

- composite cements. *Cement and Concrete Research* 106:91–102.
<https://doi.org/10.1016/j.cemconres.2018.01.008>
28. Zunino F, Scrivener K (2022) Microstructural developments of limestone calcined clay cement (LC3) pastes after long-term (3 years) hydration. *Cement and Concrete Research* 153:106693.
<https://doi.org/10.1016/j.cemconres.2021.106693>
 29. Love CA, Richardson IG, Brough AR (2007) Composition and structure of C–S–H in white Portland cement–20% metakaolin pastes hydrated at 25 °C. *Cement and Concrete Research* 37:109–117.
<https://doi.org/10.1016/j.cemconres.2006.11.012>
 30. Skibsted J, Andersen MD (2013) The Effect of Alkali Ions on the Incorporation of Aluminum in the Calcium Silicate Hydrate (C-S-H) Phase Resulting from Portland Cement Hydration Studied by ²⁹Si MAS NMR. *J Am Ceram Soc* 96:651–656. <https://doi.org/10.1111/jace.12024>
 31. Sevelsted TF, Herfort D, Skibsted J (2013) ¹³C chemical shift anisotropies for carbonate ions in cement minerals and the use of ¹³C, ²⁷Al and ²⁹Si MAS NMR in studies of Portland cement including limestone additions. *Cement and Concrete Research* 52:100–111.
<https://doi.org/10.1016/j.cemconres.2013.05.010>
 32. Garg N, Skibsted J (2014) Thermal Activation of a Pure Montmorillonite Clay and Its Reactivity in Cementitious Systems. *J Phys Chem C* 118:11464–11477. <https://doi.org/10.1021/jp502529d>
 33. Garg N, Skibsted J (2016) Pozzolanic reactivity of a calcined interstratified illite/smectite (70/30) clay. *Cement and Concrete Research* 79:101–111.
<https://doi.org/10.1016/j.cemconres.2015.08.006>
 34. Ambroise J, Maximilien S, Pera J (1994) Properties of Metakaolin blended cements. *Advanced Cement Based Materials* 1:161–168. [https://doi.org/10.1016/1065-7355\(94\)90007-8](https://doi.org/10.1016/1065-7355(94)90007-8)
 35. Skocek J, Zajac M, Stabler C, Ben Haha M (2017) Predictive modelling of hydration and mechanical performance of low Ca composite cements: Possibilities and limitations from industrial perspective. *Cement and Concrete Research* 100:68–83.
<https://doi.org/10.1016/j.cemconres.2017.05.020>
 36. Kunther W, Dai Z, Skibsted J (2016) Thermodynamic modeling of hydrated white Portland cement–metakaolin–limestone blends utilizing hydration kinetics from ²⁹Si MAS NMR spectroscopy. *Cement and Concrete Research* 86:29–41. <https://doi.org/10.1016/j.cemconres.2016.04.012>
 37. Wolf JJ, Jansen D, Goetz-Neunhoeffler F, Neubauer J (2021) Relating phase transitions to pore size distributions and mechanical mortar properties in CSA-OPC-C\$ based systems – The potential impact of delayed straetlingite formation. *Cement and Concrete Research* 147:106496.
<https://doi.org/10.1016/j.cemconres.2021.106496>
 38. Garg N, Skibsted J (2019) Dissolution kinetics of calcined kaolinite and montmorillonite in alkaline conditions: Evidence for reactive Al(V) sites. *J Am Ceram Soc* 102:7720–7734.
<https://doi.org/10.1111/jace.16663>

39. Fernandez R, Martirena F, Scrivener KL (2011) The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. *Cement and Concrete Research* 41:113–122. <https://doi.org/10.1016/j.cemconres.2010.09.013>
40. Hollanders S, Adriaens R, Skibsted J, et al (2016) Pozzolanic reactivity of pure calcined clays. *Applied Clay Science* 132–133:552–560. <https://doi.org/10.1016/j.clay.2016.08.003>
41. Schulze SE, Rickert J (2019) Suitability of natural calcined clays as supplementary cementitious material. *Cement and Concrete Composites* 95:92–97. <https://doi.org/10.1016/j.cemconcomp.2018.07.006>
42. Ferreira S, Canut MMC, Lund J, Herfort D (2019) Influence of fineness of raw clay and calcination temperature on the performance of calcined clay-limestone blended cements. *Applied Clay Science* 169:81–90. <https://doi.org/10.1016/j.clay.2018.12.021>
43. Habert G, Choupay N, Montel JM, et al (2008) Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity. *Cement and Concrete Research* 38:963–975. <https://doi.org/10.1016/j.cemconres.2008.02.005>
44. Taylor-Lange SC, Lamon EL, Riding KA, Juenger MCG (2015) Calcined kaolinite–bentonite clay blends as supplementary cementitious materials. *Applied Clay Science* 108:84–93. <https://doi.org/10.1016/j.clay.2015.01.025>
45. Zunino F, Boehm-Courjault E, Scrivener K (2020) The impact of calcite impurities in clays containing kaolinite on their reactivity in cement after calcination. *Mater Struct* 53:44. <https://doi.org/10.1617/s11527-020-01478-9>
46. Zunino F, Scrivener KL (2017) Morphological characterization of calcite-contaminated calcined clays using high resolution scanning electron microscopy (HR-SEM). In: Euroseminar on Microscopy Applied to Building Materials. Les Diablerets
47. Bullerjahn F, Zajac M, Pekarkova J, Nied D (2020) Novel SCM produced by the co-calcination of aluminosilicates with dolomite. *Cement and Concrete Research* 134:106083. <https://doi.org/10.1016/j.cemconres.2020.106083>
48. Zunino F, Scrivener KL (2020) The Effect of Calcite and Gibbsite Impurities in Calcined Clay on Its Reactivity. In: Bishnoi S (ed) *Calcined Clays for Sustainable Concrete*. Springer Singapore, Singapore, pp 357–362
49. Czanderna AW, Rao CNR, Honig JM (1958) The anatase-rutile transition. Part 1.—Kinetics of the transformation of pure anatase. *Trans Faraday Soc* 54:1069–1073. <https://doi.org/10.1039/TF9585401069>
50. Msinjili NS, Gluth GJG, Sturm P, et al (2019) Comparison of calcined illitic clays (brick clays) and low-grade kaolinitic clays as supplementary cementitious materials. *Mater Struct* 52:94. <https://doi.org/10.1617/s11527-019-1393-2>

51. Schmidt T, Leemann A, Gallucci E, Scrivener K (2011) Physical and microstructural aspects of iron sulfide degradation in concrete. *Cement and Concrete Research* 41:263–269. <https://doi.org/10.1016/j.cemconres.2010.11.011>
52. Zunino F, Scrivener K (2022) Oxidation of pyrite (FeS₂) and troilite (FeS) impurities in kaolinitic clays after calcination. *Mater Struct* 55:9. <https://doi.org/10.1617/s11527-021-01858-9>
53. Briki Y, Avet F, Zajac M, et al (2021) Understanding of the factors slowing down metakaolin reaction in limestone calcined clay cement (LC3) at late ages. *Cement and Concrete Research* 146:106477. <https://doi.org/10.1016/j.cemconres.2021.106477>
54. Avet F, Li X, Scrivener K (2018) Determination of the amount of reacted metakaolin in calcined clay blends. *Cement and Concrete Research* 106:40–48. <https://doi.org/10.1016/j.cemconres.2018.01.009>
55. Zajac M, Skocek J, Lothenbach B, Mohsen BH (2020) Late hydration kinetics: Indications from thermodynamic analysis of pore solution data. *Cement and Concrete Research* 129:105975. <https://doi.org/10.1016/j.cemconres.2020.105975>
56. Lura P, Jensen OM, van Breugel K (2003) Autogenous shrinkage in high-performance cement paste: An evaluation of basic mechanisms. *Cement and Concrete Research* 33:223–232. [https://doi.org/10.1016/S0008-8846\(02\)00890-6](https://doi.org/10.1016/S0008-8846(02)00890-6)
57. Avet F, Scrivener K (2018) Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3). *Cement and Concrete Research* 107:124–135. <https://doi.org/10.1016/j.cemconres.2018.02.016>
58. Khatib JM, Wild S (1996) Pore size distribution of metakaolin paste. *Cement and Concrete Research* 26:1545–1553. [https://doi.org/10.1016/0008-8846\(96\)00147-0](https://doi.org/10.1016/0008-8846(96)00147-0)
59. Frías M, Cabrera J (2000) Pore size distribution and degree of hydration of metakaolin ± cement pastes. *Cement and Concrete Research* 30:561–569. [https://doi.org/10.1016/S0008-8846\(00\)00203-9](https://doi.org/10.1016/S0008-8846(00)00203-9)
60. Ilić B, Radonjanin V, Malešev M, et al (2017) Study on the addition effect of metakaolin and mechanically activated kaolin on cement strength and microstructure under different curing conditions. *Construction and Building Materials* 133:243–252. <https://doi.org/10.1016/j.conbuildmat.2016.12.068>
61. Dhandapani Y, Santhanam M (2017) Assessment of pore structure evolution in the limestone calcined clay cementitious system and its implications for performance. *Cement and Concrete Composites* 84:36–47. <https://doi.org/10.1016/j.cemconcomp.2017.08.012>
62. Tironi A, Castellano CC, Bonavetti VL, et al (2014) Kaolinitic calcined clays - Portland cement system: Hydration and properties. *Construction and Building Materials* 64:215–221. <https://doi.org/10.1016/j.conbuildmat.2014.04.065>

63. Fernandez R, Martirena F, Scrivener KL (2011) The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. *Cement and Concrete Research* 41:113–122. <https://doi.org/10.1016/j.cemconres.2010.09.013>
64. Cordoba GP, Zito S V., Sposito R, et al (2020) Concretes with Calcined Clay and Calcined Shale : Workability , Mechanical , and Transport Properties. *Journal of Materials in Civil Engineering* 32:1–11. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0003296](https://doi.org/10.1061/(ASCE)MT.1943-5533.0003296)
65. Antoni M, Rossen J, Martirena F, Scrivener K (2012) Cement substitution by a combination of metakaolin and limestone. *Cement and Concrete Research* 42:1579–1589
66. Avet F, Scrivener K (2018) Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC 3). *Cement and Concrete Research* 107:124–135
67. Paiva H, Velosa A, Cachim P, Ferreira VM (2012) Effect of metakaolin dispersion on the fresh and hardened state properties of concrete. *Cement and Concrete Research* 42:607–612. <https://doi.org/10.1016/j.cemconres.2012.01.005>
68. Dhandapani Y, Sakthivel T, Santhanam M, et al (2018) Mechanical properties and durability performance of concretes with Limestone Calcined Clay Cement (LC3). *Cement and Concrete Research* 107:136–151. <https://doi.org/10.1016/j.cemconres.2018.02.005>
69. Dhandapani Y, Santhanam M (2020) Investigation on the microstructure-related characteristics to elucidate performance of composite cement with limestone-calcined clay combination. *Cement and Concrete Research* 129:105959. <https://doi.org/10.1016/j.cemconres.2019.105959>
70. Krishnan S, Emmanuel AC, Bishnoi S (2019) Hydration and phase assemblage of ternary cements with calcined clay and limestone. *Construction and Building Materials* 222:64–72. <https://doi.org/10.1016/j.conbuildmat.2019.06.123>
71. Badogiannis E, Tsivilis S (2009) Exploitation of poor Greek kaolins: Durability of metakaolin concrete. *Cement and Concrete Composites* 31:128–133. <https://doi.org/10.1016/j.cemconcomp.2008.11.001>
72. Poon CS, Lam L, Kou SC, et al (2001) Rate of pozzolanic reaction of metakaolin in high-performance cement pastes. *Cement and Concrete Research* 31:1301–1306. [https://doi.org/10.1016/S0008-8846\(01\)00581-6](https://doi.org/10.1016/S0008-8846(01)00581-6)
73. Rattanasak U, Kendall K (2005) Pore structure of cement/pozzolan composites by X-ray microtomography. *Cement and Concrete Research* 35:637–640. <https://doi.org/10.1016/j.cemconres.2004.04.022>
74. Bernal IMR, Shirani S, Cuesta A, et al (2021) Phase and microstructure evolutions in LC3 binders by multi-technique approach including synchrotron microtomography. *Construction and Building Materials* 300:124054. <https://doi.org/10.1016/j.conbuildmat.2021.124054>
75. Cruz JM, Fita IC, Soriano L, et al (2013) The use of electrical impedance spectroscopy for monitoring the hydration products of Portland cement mortars with high percentage of pozzolans. *Cement and Concrete Research* 50:51–61. <https://doi.org/10.1016/j.cemconres.2013.03.019>

76. Dhandapani Y (2020) Composite cements with limestone additions: Microstructure and Transport properties. IIT Madras
77. Machner A, Zajac M, Ben Haha M, et al (2018) Limitations of the hydrotalcite formation in Portland composite cement pastes containing dolomite and metakaolin. *Cement and Concrete Research* 105:1–17. <https://doi.org/10.1016/j.cemconres.2017.11.007>
78. Tang J, Wei S, Li W, et al (2019) Synergistic effect of metakaolin and limestone on the hydration properties of Portland cement. *Construction and Building Materials* 223:177–184. <https://doi.org/10.1016/j.conbuildmat.2019.06.059>
79. Krishnan S, Bishnoi S (2018) Understanding the hydration of dolomite in cementitious systems with reactive aluminosilicates such as calcined clay. *Cement and Concrete Research* 108:116–128. <https://doi.org/10.1016/j.cemconres.2018.03.010>
80. Machner A, Zajac M, Ben Haha M, et al (2017) Portland metakaolin cement containing dolomite or limestone – Similarities and differences in phase assemblage and compressive strength. *Construction and Building Materials* 157:214–225. <https://doi.org/10.1016/j.conbuildmat.2017.09.056>
81. Kocaba V, Gallucci E, Scrivener KL (2012) Methods for determination of degree of reaction of slag in blended cement pastes. *Cement and Concrete Research* 42:511–525. <https://doi.org/10.1016/j.cemconres.2011.11.010>
82. Durdzinski PT, Dunant CF, Haha MB, Scrivener KL (2015) A new quantification method based on SEM-EDS to assess fly ash composition and study the reaction of its individual components in hydrating cement paste. *Cement and Concrete Research* 73:111–122. <https://doi.org/10.1016/j.cemconres.2015.02.008>
83. Durdziński PT, Ben Haha M, Zajac M, Scrivener KL (2017) Phase assemblage of composite cements. *Cement and Concrete Research* 99:172–182. <https://doi.org/10.1016/j.cemconres.2017.05.009>
84. Scarlett NVY, Madsen IC (2006) Quantification of phases with partial or no known crystal structures. *Powder Diffraction* 21:278–284. <https://doi.org/10.1154/1.2362855>
85. Snellings R, Bazzoni A, Scrivener K (2014) The existence of amorphous phase in Portland cements: Physical factors affecting Rietveld quantitative phase analysis. *Cement and Concrete Research* 59:139–146. <https://doi.org/10.1016/j.cemconres.2014.03.002>
86. Shi Z, Geiker MR, De Weerd K, et al (2017) Role of calcium on chloride binding in hydrated Portland cement–metakaolin–limestone blends. *Cement and Concrete Research* 95:205–216. <https://doi.org/10.1016/j.cemconres.2017.02.003>
87. Hanpongpan W (2019) Investigation of the use of Limestone Calcined Clay Cement (LC3) applied to Thailand. École Polytechnique Fédérale de Lausanne
88. Briki Y (2021) Maximizing the use of supplementary cementitious materials (SCMs) in blended cements. EPFL Thesis

89. Ston J (2019) Basic creep and autogenous shrinkage of Limestone Calcined Clay Cement (LC3). EPFL Thesis
90. Snellings R, Salze A, Scrivener KL (2014) Use of X-ray diffraction to quantify amorphous supplementary cementitious materials in anhydrous and hydrated blended cements. *Cement and Concrete Research* 64:89–98. <https://doi.org/10.1016/j.cemconres.2014.06.011>
91. Antoni M, Rossen J, Martirena F, Scrivener K (2012) Cement substitution by a combination of metakaolin and limestone. *Cement and Concrete Research* 42:1579–1589. <https://doi.org/10.1016/j.cemconres.2012.09.006>
92. Souri A, Kazemi-Kamyab H, Snellings R, et al (2015) Pozzolanic activity of mechanochemically and thermally activated kaolins in cement. *Cement and Concrete Research* 77:47–59. <https://doi.org/10.1016/j.cemconres.2015.04.017>
93. Cyr M, Trinh M, Husson B, Casaux-Ginestet G (2014) Effect of cement type on metakaolin efficiency. *Cement and Concrete Research* 64:63–72. <https://doi.org/10.1016/j.cemconres.2014.06.007>
94. Zunino F, Lopez M (2016) Decoupling the physical and chemical effects of supplementary cementitious materials on strength and permeability: A multi-level approach. *Cement and Concrete Composites* 65:19–28. <https://doi.org/10.1016/j.cemconcomp.2015.10.003>
95. Zunino F, Lopez M (2017) A methodology for assessing the chemical and physical potential of industrially sourced rice husk ash on strength development and early-age hydration of cement paste. *Construction and Building Materials* 149:869–881. <https://doi.org/10.1016/j.conbuildmat.2017.05.187>
96. De la Varga I, Castro J, Bentz DP, et al (2018) Evaluating the hydration of high volume fly ash mixtures using chemically inert fillers. *Construction and Building Materials* 161:221–228. <https://doi.org/10.1016/j.conbuildmat.2017.11.132>
97. Zunino F, Scrivener KL (2019) The influence of the filler effect in the sulfate requirement of blended cements. *Cement and Concrete Research* 126:. <https://doi.org/10.1016/j.cemconres.2019.105918>
98. Bentz DP, Ferraris CF, Jones SZ, et al (2017) Limestone and silica powder replacements for cement: Early-age performance. *Cement and Concrete Composites* 78:43–56. <https://doi.org/10.1016/j.cemconcomp.2017.01.001>
99. Gutteridge WA, Dalziel JA FILLER CEMENT: THE EFFECT OF THE SECONDARY COMPONENT ON THE HYDRATION OF PORTLAND CEMENT Part I. A Fine Non-hydraulic Filler. 5
100. Berodier E, Scrivener K (2014) Understanding the filler effect on the nucleation and growth of C-S-H. *Journal of the American Ceramic Society* 97:3764–3773. <https://doi.org/10.1111/jace.13177>
101. Mota B, Matschei T, Scrivener K (2015) The influence of sodium salts and gypsum on alite hydration. *Cement and Concrete Research* 75:53–65. <https://doi.org/10.1016/j.cemconres.2015.04.015>

102. Lagier F, Kurtis KE (2007) Influence of Portland cement composition on early age reactions with metakaolin. *Cement and Concrete Research* 37:1411–1417.
<https://doi.org/10.1016/j.cemconres.2007.07.002>
103. Zunino F, Martirena F, Scrivener K (2020) Limestone calcined clay cements (LC3). *ACI Materials Journal* In press.:
104. Zhang M, Zunino F, Yang L, et al (2022) The influence of pore desaturation on the strength evolution of cement with alkali additions. *Cement and Concrete Research*
105. Zunino F (2020) Limestone calcined clay cements (LC3): raw material processing, sulfate balance and hydration kinetics. EPFL Thesis 8173
106. Krishnan S, Kanaujia SK, Mithia S, Bishnoi S (2018) Hydration kinetics and mechanisms of carbonates from stone wastes in ternary blends with calcined clay. *Construction and Building Materials* 164:265–274. <https://doi.org/10.1016/j.conbuildmat.2017.12.240>
107. Quennoz A, Scrivener KL (2013) Interactions between alite and C3A-gypsum hydrations in model cements. *Cement and Concrete Research* 44:46–54.
<https://doi.org/10.1016/j.cemconres.2012.10.018>
108. Zunino F, Scrivener K (2020) Factors influencing the sulfate balance in pure phase C3S/C3A systems. *Cement and Concrete Research* 133:. <https://doi.org/10.1016/j.cemconres.2020.106085>
109. Antoni M, Rossen J, Martirena F, Scrivener K (2012) Cement substitution by a combination of metakaolin and limestone. *Cement and Concrete Research* 42:1579–1589.
<https://doi.org/10.1016/j.cemconres.2012.09.006>
110. Maier M, Scherb S, Neißer-Deiters A, et al (2021) Hydration of cubic tricalcium aluminate in the presence of calcined clays. *J Am Ceram Soc* jace.17745. <https://doi.org/10.1111/jace.17745>
111. Krishnan S, Emmanuel AC, Bishnoi S (2019) Hydration and phase assemblage of ternary cements with calcined clay and limestone. *Construction and Building Materials* 222:64–72.
<https://doi.org/10.1016/j.conbuildmat.2019.06.123>
112. Palou M, Kuzielová E, Žemlička M, et al (2018) The effect of metakaolin upon the formation of ettringite in metakaolin–lime–gypsum ternary systems. *J Therm Anal Calorim* 133:77–86.
<https://doi.org/10.1007/s10973-017-6885-0>
113. Shah V, Parashar A, Mishra G, et al (2020) Influence of cement replacement by limestone calcined clay pozzolan on the engineering properties of mortar and concrete. *Advances in Cement Research* 32:. <https://doi.org/10.1680/jadcr.18.00073>
114. Antoni M, Rossen J, Martirena F, Scrivener K (2012) Cement substitution by a combination of calcined clay and limestone. *Cement and Concrete Research* 42:1579–1589
115. Yu J, Wu HL, Leung CKY (2020) Feasibility of using ultrahigh-volume limestone-calcined clay blend to develop sustainable medium-strength Engineered Cementitious Composites (ECC). *Journal of Cleaner Production* 262:121343. <https://doi.org/10.1016/j.jclepro.2020.121343>

116. Avet F, Scrivener K (2018) Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3). *Cement and Concrete Research* 107:124–135. <https://doi.org/10.1016/j.cemconres.2018.02.016>
117. Parashar A, Bishnoi S (2021) Hydration behaviour of limestone-calcined clay and limestone-slag in ternary blended cement. *Rilem Technical Letters* 7:17–34
118. Li X, Snellings R, Antoni M, et al (2018) Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1. *Mater Struct* 51:151. <https://doi.org/10.1617/s11527-018-1269-x>