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

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Abstract The RILEM technical committee 282-CCL: Calcined Clays as Supplementary Cementitious Materials, investigates all the aspects related to calcined clays, from clay exploration and characterization to calcination process, hydration reactions and concrete properties. This white paper focuses on the hydration mechanisms of calcined clay-blended Portland cements, covering 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.

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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 optimising the 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 6–7% of the anthropogenic CO₂ emissions worldwide [1]. 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 [2]. This has accelerated the adoption of blended Portland cements that incorporate supplementary cementitious materials (SCMs) by replacing part of the Portland cement (PC) fraction [3, 4]. Nowadays, 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 [3, 4]. However, fly ash and blast furnace slag are available in combined quantities close to only 15% of the global Portland cement production [2, 5]. The availability of

fly ash is expected to decrease as electricity production by combustion of coal is transitioning towards the use of cleaner fuels [6]. In the case of blast furnace slag, the production of steel increases more slowly compared to cement; moreover, changes in production methods and the recycling of steel might have an implication on blast furnace 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 [1]. This has been one of the main drivers for exploration of other SCM sources that are widely available globally and have the potential to be used for the production of concretes with different performances [7]. In this scenario, calcined clays and limestone play a key role, as they are the only SCMs available in the quantities required for widespread use and, when combined together, for a significant reduction (30–50 wt%) of the clinker content in Portland cement blends [6, 8–11].

Clay particles are made up of stacks of layers, composed of alternating silica tetrahedral and alumina octahedral sheets [12]. 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) [12]. In the case of kaolinite, two distinct interlayer surfaces coexist, one with aluminate groups and one with silicate groups. A recent review from RILEM TC 282-CCL [13] provides more detailed information about the mineralogy, physical and

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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 [14].

Blended Portland cements incorporating calcined clays, with or without limestone, are technically and economically feasible paths towards a substantial reduction of clinker content [15]. The combination of calcined clay and limestone is sometimes referred to as limestone calcined clay cement (LC³) [9, 10, 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 blended cements, there is a synergetic reaction of the alumina provided by calcined clay with the limestone, leading to the formation of additional hydration products that further contribute to porosity reduction [4, 11, 19, 20].

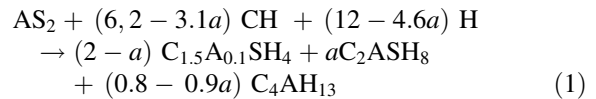
In this paper, the main aspects of hydration, properties, characterisation and blend design of cements incorporating calcined clays or calcined clays and limestone are presented, including 1:1 and 2:1 calcined clays. A critical review of the literature regarding the mechanisms of hydration and performance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

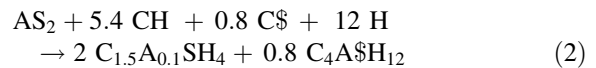
In general, the principal reactive components of calcined clays are silica and alumina which partly or fully dissolve in an alkaline environment, depending on the type and structure of the calcined clay and on other constituents. Considering metakaolin with the ideal composition, Al₂Si₂O₇ (AS₂ in cement oxide notation), as an example, some main reactions can be described depending on the composition of the hydrating system [4]. The pozzolanic properties of

metakaolin can most simply be described through its reaction with a saturated portlandite solution, Ca(OH)₂ (CH), which results in the formation of an aluminium-substituted calcium silicate (C-(A)-S-H) phase, (illustrative composition C_{1.5}A_{0.1}SH₄, i.e., Al/Si = 0.20), strätlingite (C₂ASH₈), and calcium aluminate hydrate phases of the AFm type, C₄AH₁₃. Assuming these ideal compositions for the hydrate phases, this reaction is described in Eq. (1):

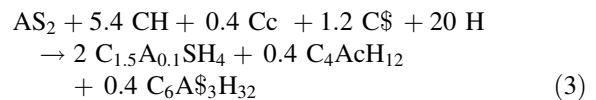


These three reaction products can be identified by solid-state ²⁹Si and ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) analysis as shown in Fig. 1. The C-(A)-S-H phase is the dominant reaction product, as evidenced by the Q¹ and Q² peaks in the ²⁹Si MAS NMR spectrum.

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):



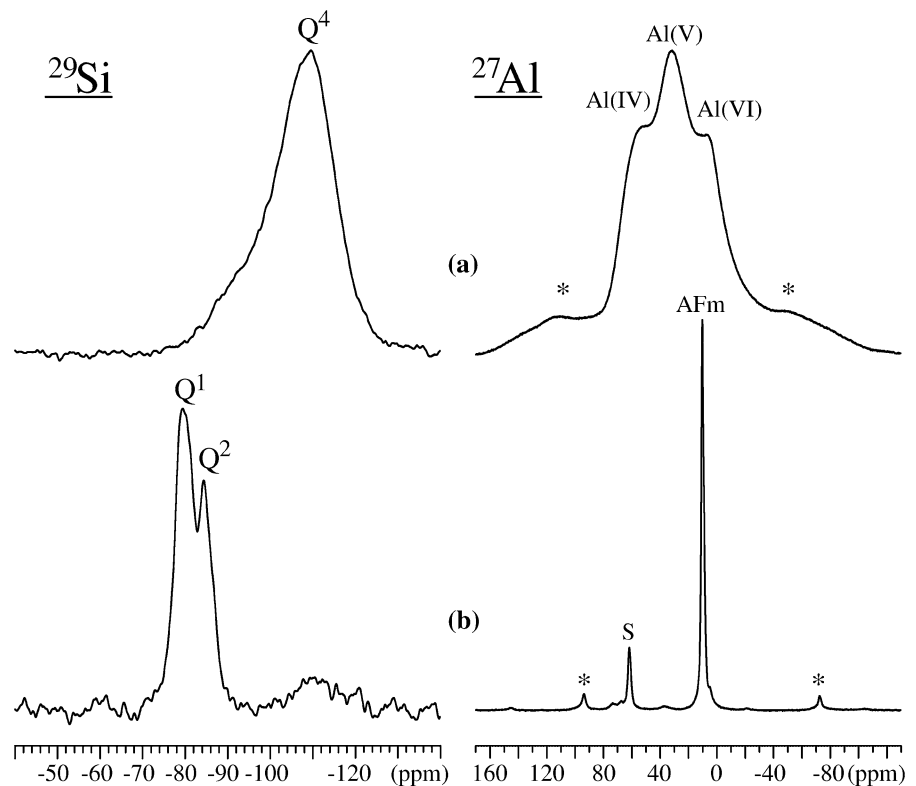
In ternary systems with large fractions of limestone (Cc), the carbonate ions will result in the formation of monocarbonate (C₄AcH₁₂) instead of monosulphate [21, 22], resulting in the retention of ettringite (C₆A\$₃H₃₂), according to the Eq. (3):



The synergetic effect of limestone and an aluminosilicate-rich SCM in ternary Portland cement-limestone-SCM systems has also been reported for systems including fly ashes [23], blast furnace slags [24], and calcined smectite [17] as SCMs.

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

Fig. 1 ^{29}Si and ^{27}Al MAS NMR spectra of metakaolin before **a** and after **b** pozzolanic reaction with portlandite in solution for 16 days. The spectra show the formation of hydration products C-(A)-S-H, strätlingite (S) and AFm phases upon the reaction of metakaolin with portlandite. The ^{27}Al NMR spectrum presents 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), respectively



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, it has been reported that the Ca/Si ratio decreases from 1.8 to 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 alumino-silicate tetrahedra (MCL). This parameter generally increases with hydration time and with higher clinker 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 5–6 for composite cements with smectitic clays [32, 33] and 8–11 [25, 29] for blends with metakaolin.

The amount of Al incorporated in the C-(A)-S-H phase increases 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]. ^{27}Al and ^{29}Si MAS NMR studies have shown that the $\text{Al}_{\text{IV}}/\text{Si}$ ratio of the C-(A)-S-H phase is nearly constant with

hydration time for Portland cement—metakaolin blends [25], similar to that observed in hydrated pure Portland cements. Conversely, other studies applying energy dispersive X-ray spectroscopy (EDS) have indicated that this ratio increases with hydration time [20, 28]. 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 mixture design) with clays that contain different kaolinitic contents and for different curing ages.

Although strätlingite is observed as a reaction product in pure metakaolin-portlandite systems (Fig. 1), this phase is not observed in all blended cements incorporating calcined clays. This reflects that strätlingite and portlandite are thermodynamically

incompatible in the ternary $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram, implying that strätlingite is theoretically formed when portlandite is fully consumed [34]. The presence of limestone also suppresses the formation of strätlingite, since a larger fraction of aluminium is consumed in the formation of monocarbonate and hemicarbonate AFm phases (Eq. 3), retaining ettringite [34]. Strätlingite has been identified in calcined clay blends at late ages, when the degree of hydration is high [25, 35, 36]. 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 [36]. 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 with respect to portlandite when the amount of this phase decreases in the system due to the ongoing pozzolanic reaction [28]. It has been postulated 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 (Fig. 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.

2.2 Influence of clay type and impurities on reactivity

The chemical 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 compressive strength development of binary blends is observed for calcined kaolinite, compared with calcined illite or calcined montmorillonite, for clays with similar grades, i.e. for similar kaolinite, illite or montmorillonite content and for similar levels of clinker replacement [39–41]. A large study was carried out on about 70 clays and pointed out the key

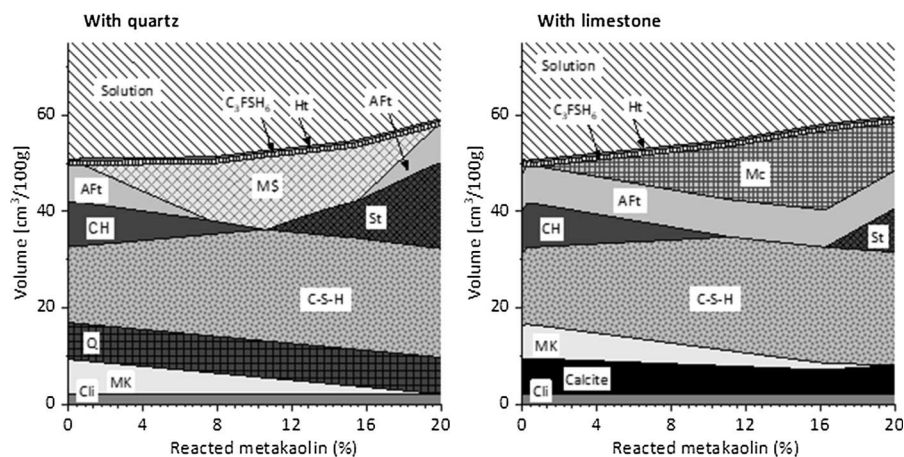


Fig. 2 Thermodynamic modelling of 60% cement and 20% metakaolin with left: 20% Quartz and right: 20% Limestone (Adapted from [27]). “Cli” refers to unreacted clinker, “MK” to

unreacted metakaolin, “Q” to quartz, “AFt” to ettringite, “St” to strätlingite, “MS” to monosulphate, “C₃FSH₆” to hydrogarnet and “Ht” to hydrotalcite

influence of the calcined kaolinite content on the strength development of calcined clay blends [20]. Other parameters such as calcined clay 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 Portland 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 [9, 10, 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 combination of 1:1 and 2:1 clays, with one clay being dominant. For instance secondary illite and Ca-montmorillonite can be observed in kaolinite rich deposits, and vice versa [43]. The degree to which the secondary clays affect the chemical reactivity of the overall system 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 kaolinitic 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. It should be noted that his effect could vary depending on the size of the feed raw material before calcination.
- (c) Dolomite decarbonation temperature can cover a range from 500 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 [47]. 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 increase the overall reactivity of calcined clay. A 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 clay compositions.
- (d) Quartz is a very common mineral found in clay deposits. Quartz is often used in research studies as a reference with no reactivity. The separation of quartz from clay is a fast-developing field. Separation could come from density or grindability difference between quartz and clay. This could 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 be present in the raw clay or formed due to the transition of anatase during clay calcination [49]. No influence on calcined clay reactivity has been reported.
- (g) Clays may contain muscovite or mica [50, 51] and other presumably inert crystalline phases such as feldspars, cristobalite, and hematite [39, 44, 52]. Some of these phases may



decompose or structurally rearrange during calcination, depending on the calcination temperature, potentially increasing the perceived reactive clay content [52].

- (h) Sulphides such as pyrite and pyrrhotite can also be present in natural clay deposits. These minerals are known for causing expansion in concrete [53]. 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 [54].

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 deceleration were investigated by Briki et al. [55]: 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 Fig. 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 fraction of calcined clay with silica fume, an Al-free SCM. The remaining fraction of calcined clay excluding metakaolin was replaced by quartz. The reaction degree of silica fume follows a similar trend to metakaolin. A similar reaction deceleration 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-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 capillary pores 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, 56]. As hydration continues, the internal relative humidity of the material decreases, and pores

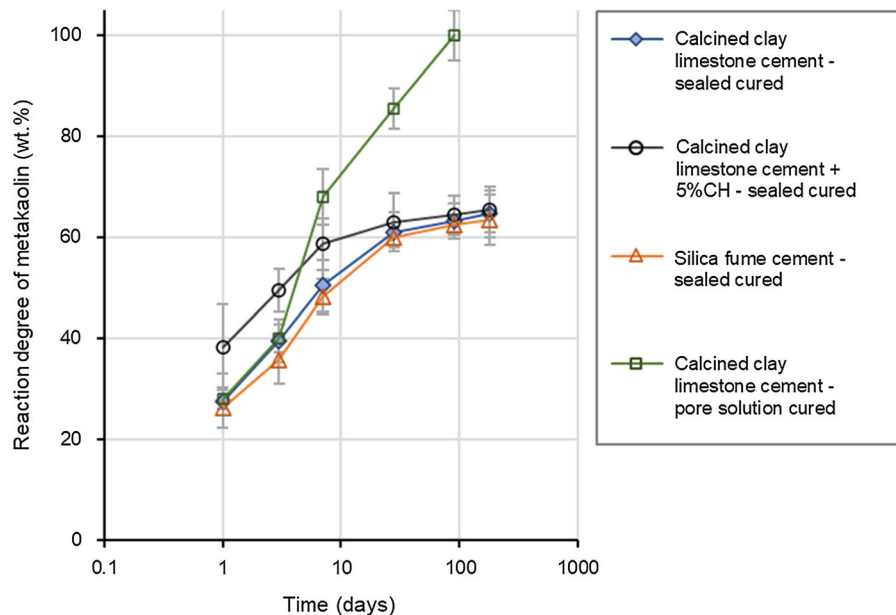


Fig. 3 Reaction degree of metakaolin in calcined clay limestone cement pastes. The influence of portlandite addition, a comparison to the reaction degree of silica fume, and the influence of sealed versus pore solution curing are shown. (Adapted from [55])

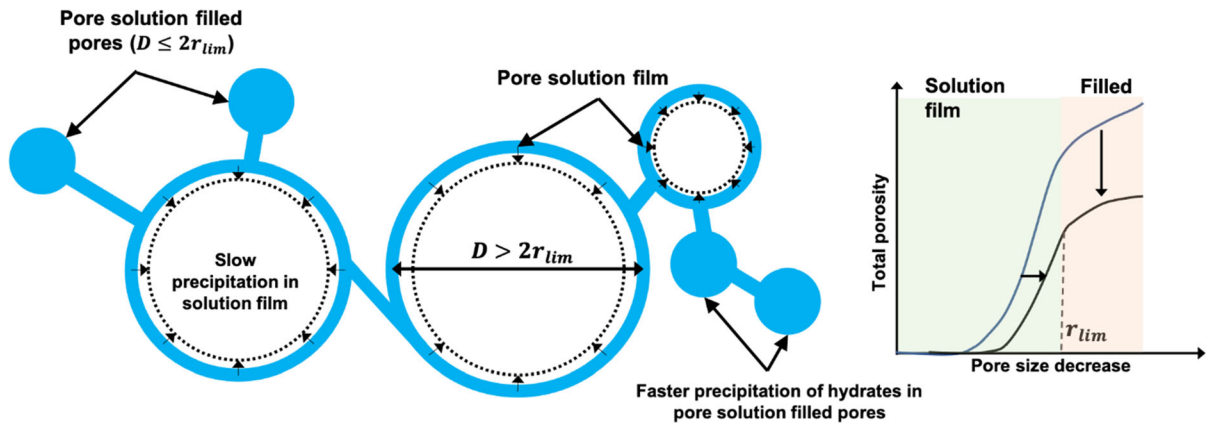


Fig. 4 Schematic representation of the proposed mechanisms controlling the kinetics of precipitation at later ages. Adapted from [28]

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}) [57, 58].

In saturated pores, the extent of reaction leads to further porosity reduction. As reaction progresses and microstructure refines, a higher degree of supersaturation towards the precipitated phase is required to stabilize the smaller (higher curvature) crystal [57]. 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, 20]. 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 Fig. 4, illustrating the difference in water saturation with pore size, and its influence on the progress of hydration reactions and porosity reduction over time.

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 pore structure development 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 summarized.

At this point, it is convenient to define two terms that are used throughout this section with reference to the testing procedure and outputs: the threshold pore entry radius and critical pore entry radius. 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 have 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), ^1H NMR, micro-tomography and electrical impedance spectroscopy. A detailed overview of the observation of pore structure features, as a function of the type of

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

| Method | Main features of techniques | Main 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 blended cements with metakaolin and lower grade calcined kaolinite clays Total porosity is similar due to an increase in gel porosity but significant pore refinement was observed Limited change in critical pore diameter after 7 days for metakaolin and blends produced with calcined clays with > 50% kaolinite content | [59–61, 70, 71] |
| 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 identified for sample cured in sealed conditions Signal from capillary porosity continuously reduced in sample cured in moist conditions A major increase in the fractions of gel pores between initial 10 days could be identified for sample cured in sealed and cured conditions | [26, 55] |
| Micro tomography | Volumetric analysis of pore structure revealing its pore morphologies such as shape and connectivity | Metakaolin containing binders have a 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. Studies were conducted using synchrotron micro tomography | [72] |
| SEM-BSE imaging | Spatial distribution of the phases and porosity can be observed in the microstructure | Kaolinite clay produces 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 of curing. However, 28 day microstructures were similar for calcined clay with 50% and 95% kaolinite content Calcined clay produces a compact microstructure compared to fly ash binder | [39] [19] [65] [68] |
| 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 a major rise in resistivity by 3 days compared to PC and 35% fly ash binder Electrical conductivity was 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 the electrical response was found to identify pore refinement by 3–7 days and identified the difference in microstructural development of calcined clay and calcined-limestone combinations in long term | [74] [62, 68] [75] |

Table 1 continued

| Method | Main features of techniques | Main observations on the performance of calcined clays containing materials | Reference |
|-------------------------------------|--|--|-----------|
| 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] |

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 kaolinitic clays and metakaolin, showing this refinement between 3 and 7 days of curing. The distribution of different pore fractions was studied by Avet et al. [26] using ^1H NMR. While PC showed a 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 content up to 15% was studied in [59], 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 the pozzolanic reaction of metakaolin. Frias et al. [60] 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 portlandite in the system. It has also been reported [61] 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 a higher degree of metakaolin reaction.

The clay purity and type strongly influence the pore structure of blended 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) [62]. Cement paste systems with calcined clay with metakaolin contents of 93% and 73% had significantly finer pore structures compared to Portland cement [63], most notably with calcined clay with lower contents of metakaolin. This is consistent with the results reported by Avet et al. [20] who 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 [20].

There is a limited number of studies evaluating the pore structure of non-kaolinitic calcined clays-PC binders. Martirena-Hernandez et al. [39] identified that cement pastes with calcined kaolinite clays had lower capillary porosity than PC reference samples, while calcined illite or montmorillonite clay-containing cement pastes had higher capillary porosity than PC. 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]. This 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 [11]. Studies have shown that the calcined clay-limestone system produced with clays containing 20–60% kaolinite formed a higher amount of monocarbo- and hemicarbo-



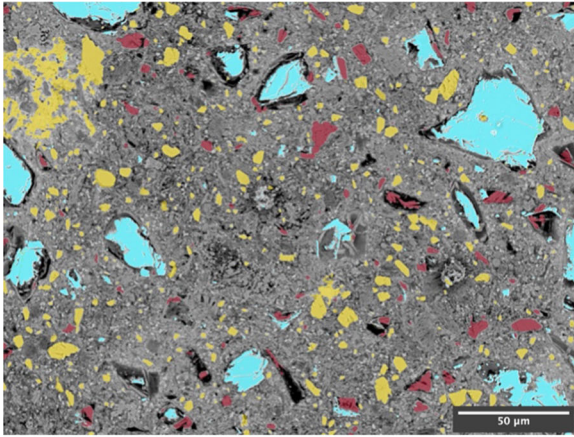
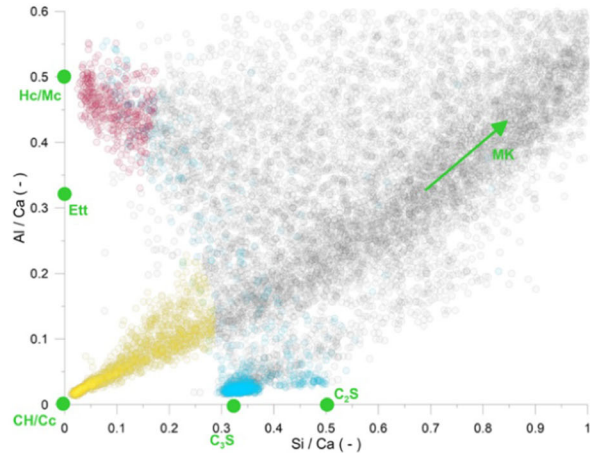


Fig. 5 Left: Pore filling due to formation of carboaluminate production in limestone-calcined clay-PC combination. Right: corresponding chemical composition of the microstructure, as

aluminates than PC alone [65]. Thus, the carboaluminate phases produced in a higher amount when using a lower grade calcined clay benefits from the calcined clay-limestone interaction and refine the porosity. Another study [19] revealed that deposition of these CO_3 -AFm phases occurs along with large pore spaces, as shown in Fig. 5. There is a lower tendency to form such hydrate phase at later ages or at lower water to binder ratios. This is due to the significant porosity refinement which 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, irrespective of limestone addition, was found to refine pore structure in cement mortar (w/b of 0.60–0.75) [66] and in concretes [67, 68] 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 [69]. This could have a direct effect on the pore structure development in ternary binders containing calcined clay.

The effect of metakaolin-limestone (or dolomite) ratio on pore structure of blended cements was reported in [76]. Up to 25% addition of limestone or dolomite did not induce any increase in porosity or critical pore size in a cement containing 60% PC and 15–30% metakaolin [76]. The effect of metakaolin – limestone ratio on pore structure development was



reported in [19]. Note: Portlandite + limestone in yellow, Hc + Mc in red, anhydrous cement grains in cyan

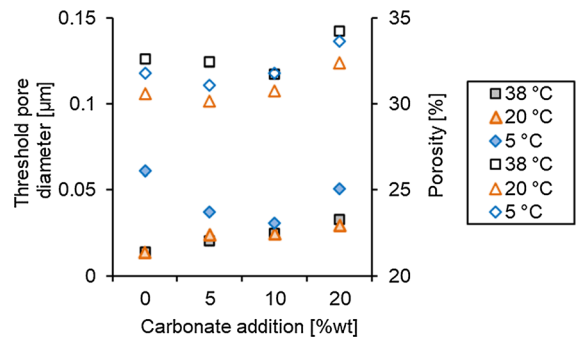


Fig. 6 Threshold pore diameters of PC-metakaolin systems with the addition of limestone at different curing temperatures at 90 days (Adapted from [79]). Filled markers represent pore diameter, emptied markers represent porosity

studied by Tang et al. [77], and the results showed that about 10% metakaolin is sufficient to compensate for the substitution of 30% of clinker by limestone. 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 [78]. 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 [79]. 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 Fig. 6. The change in porosity and threshold pore sizes were limited up to 10% carbonate addition; the effect of a lower amount of reactive was clearly visible at 20% limestone addition.

In summary, a significant pore refinement in cements containing calcined kaolinitic clay has been confirmed by numerous studies using multiple techniques. Calcined kaolinitic 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 is above 40%. Studies on other alternative clays are limited and non-exhaustive compared to kaolinitic clays.

3 Methods for determining the reaction degree of calcined clay

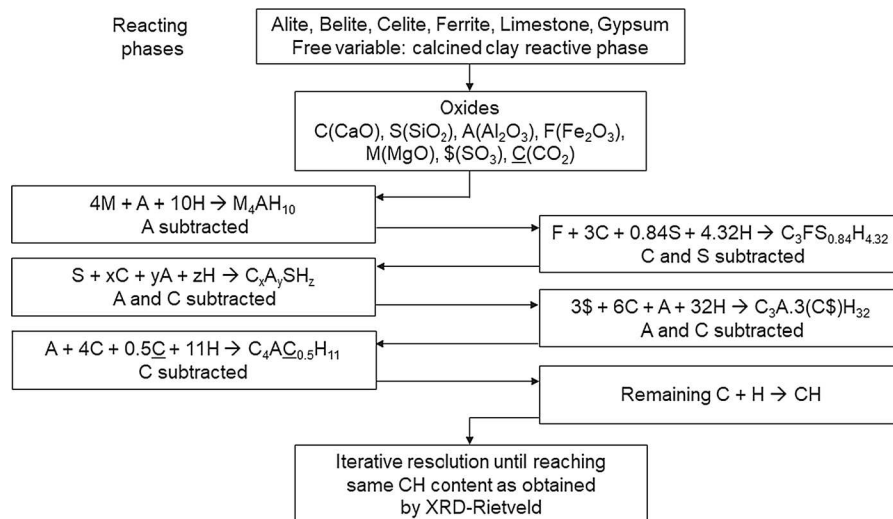
During the hydration of calcined clay-blended cements, the calcined clay minerals (metakaolin, calcined montmorillonite, etc.) are the dominant reactive phases. The determination of the reaction degree of the calcined clay minerals is essential to better understand their contribution to the phase assemblage and consequently performance evolution of calcined clay-blended cements. A wide range of methods have been used to determine the reaction degree of supplementary cementitious materials (SCMs) [7, 80]. 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 cement 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 is not generally known.
2. Selective dissolution [71] 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 [71]. 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, 34, 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 a 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 the 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 Fig. 7. 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. For example, 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 [56]. The chemistry of the reactive compound in the clay can be adjusted depending on the composition of the clay. Thus,



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 cements |
| Selective dissolution | Not recommended | | Deviations due to remaining undissolved phases | Vacuum filter | [71] |
| Image analysis | Not possible | | Too high fineness of calcined clay particles | SEM | Not on calcined clay cements |
| ^{27}Al and ^{29}Si NMR | Recommended | Direct quantification | Issue with paramagnetic iron | NMR | [25, 34, 86] |
| Mass balance | Recommended but reliable inputs needed | Full assessment of hydration | Indirect method | XRD + SEM | [27, 56, 87–89] |
| Thermodynamic modelling | Recommended but reliable inputs needed | Full assessment of hydration | Indirect method | XRD | [34, 56, 71] |
| PONKCS | Possible | Equipment widely available | Low accuracy Complex for mixed clay | XRD | [36, 56, 90] |

**Fig. 7** Mass balance procedure, adapted from [56]

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.

- Thermodynamic modelling is also suitable for estimating 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 so that it considers aluminium incorporation and accurate Ca/Si. The Al incorporation may have to be implemented manually in the modelling software.
- 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 the 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

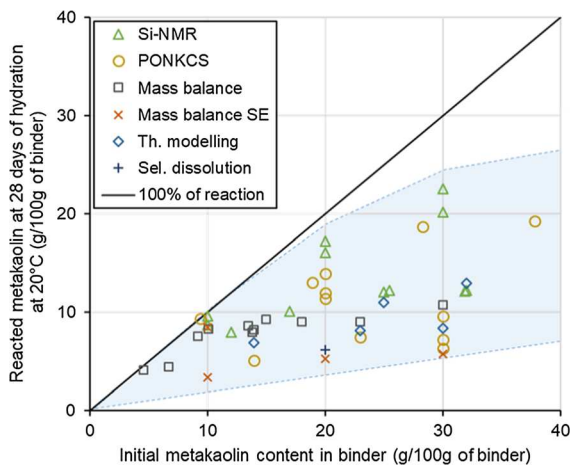


Fig. 8 Range of measured reacted metakaolin in blended paste at 28 days of hydration at 20 °C, compared with the initial metakaolin content of the blends. The solid line indicates full reaction of metakaolin. Collected data are based on Si-NMR [25, 34, 86], PONKCS [36, 56, 90], mass balance [27, 56, 87–89], mass balance single-equation (SE) approach [11, 91], thermodynamic modelling [34, 56] and selective dissolution [71]

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 [56] and decreasing replacement levels.

Figure 8 summarises published data on the amount of reacted metakaolin determined by 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 remains 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 MAS NMR was successfully used [32, 33], demonstrating that a lower reaction degree is reached for 2:1 clays compared with 1:1 clays.

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:

- 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 databases.
- 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. [92] tested the performance of 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 expected considering

the complex, simultaneous reactions occurring during the hydration of cements. However, some correlations have been observed between the C_3A , C_4AF , SO_3 contents and the strength development in calcined clay blended systems [92].

Calcined clay particles also influence clinker hydration through physical effects [3, 23, 93–95]. These physical effects lead to the enhancement of the hydration of clinker compared to plain cement [96–98]. 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, i.e. the distance between particles. The shearing of particles during mixing is increased by this closer distribution [99].

Calcined clay may also negatively influence the hydration of clinker. In some specific cases, especially with high-purity 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 the calcined clay reaction. The reasons for this slowing down are likely to be similar to the ones explained in Sect. 2.3 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 on early-age strength

Alkalis influence the reaction kinetics of alite [100], 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

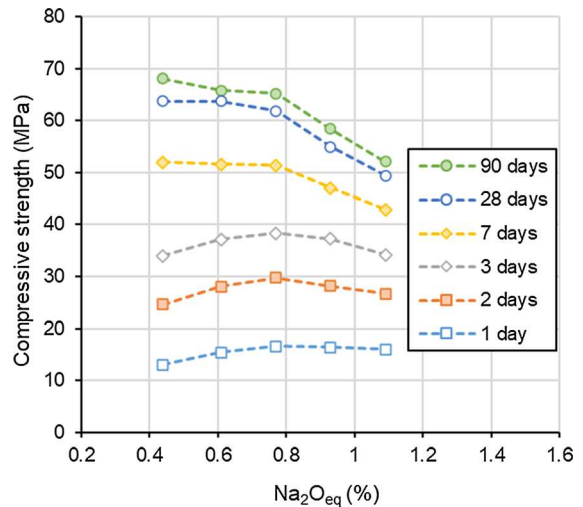


Fig. 9 Compressive strength of calcined clay cements having limestone addition with different levels of alkali content adjustment (adapted from [8]). The lowest level refers to a mix design without alkali addition, i.e. alkalis only come from the clinker

cements with higher alkali content [101], 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 [92].

As shown in Fig. 9, an increase of the total alkali content can lead to an increase in the early-age strength of mortar [8, 10]. In this case, the alkali content was adjusted by the addition of KOH to the mixing water. However, for Na_2O_{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 the 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 [58]. 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 [102]. It is important to note here that the alkali contents of cement systems, in most 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, is not necessarily similar to the effect of the soluble alkalis present in the clinker. As such, the methodology presently used to ascertain the effect of alkalis on cement hydration may not be a realistic representation of the actual hydration process.

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. 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 reaction present in the Portland cement—calcined clay—limestone system also exists in the Portland cement—calcined clay—dolomite system [78, 79]. 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 Fig. 10. In addition to these common phases, the Mg-bearing hydrotalcite-like ($\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 3\text{H}_2\text{O}$) 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 [76, 78]. Formation of strätlingite is observed in systems where the reactivity of dolomite is limited [27, 103]. The slower reaction of dolomite 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%

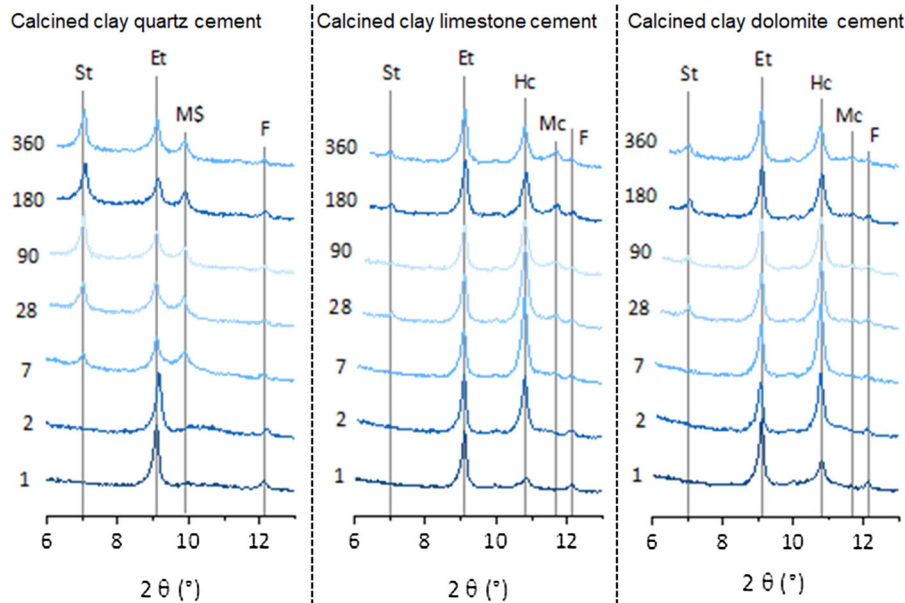


Fig. 10 XRD patterns for the ternary blends containing calcined clay with quartz, limestone and dolomite. The main peaks of ferrite (F), ettringite (Et), monosulphate (MS), possibly

a sulphate and carbonate containing hydroxy-AFm(Hc-M\$), and stratlingite (St) are indicated (Adapted from [27])

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 [11]. 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, 103]. It is expected that these secondary minerals will remain as unreactive in the microstructure in these systems.

5 Blend design optimisation—Guidelines for producing 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 [104, 105]. The balance of the system can be restored by the incorporation of additional sulphate (gypsum or another sulphate salt able to control the reaction of C_3A) to retard the aluminate reaction [8, 11, 20]. The distinction between the silicate and the aluminate peaks becomes 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 [105]:

- 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 forms due to the enhanced reaction of alite (filler effect), which leads to an earlier depletion of solid gypsum and consequently, an earlier aluminate peak [8, 96, 97, 105]. Some studies suggest that other surfaces can contribute to the sulphate adsorption process. A recent study [106] 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). Beyond the discussion regarding contribution of different surfaces, most studies concur on adsorption of sulphate ions/complexes as the main factor explaining the sulphate balance of cementitious systems.

- 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 [105]. Although the reaction of calcined clays is much slower, the alumina dissolved in the first hours of hydration is not negligible. Skocek et al. [36] report hydration of $\sim 3\text{--}8$ (g/100 g binder) of metakaolin depending on the replacement level after 6 h. 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 [107].

The requirement of additional gypsum in calcined clay cements, and other binary or ternary cementitious systems, 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 [96].

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, 69, 108]. 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 addition of activated clay in a cement requires an adjustment of the sulphate source to optimise hydration and early strength development.

The dilution of sulphate by the incorporation of calcined clay should be partially compensated. The optimum of gypsum content can be determined (i) by isothermal calorimetry, with the separation between the silicate peak and the aluminate peak, or (ii) evaluating compressive strength.

5.2 Clinker factor

The clinker replacement level in calcined clay cement can influence the engineering properties of the resulting concrete [109]. The need for producing more sustainable concretes is pushing towards reduction of the clinker factor further. Some studies have evaluated the production of calcined clay-based (clay and limestone) cement with 50–80% clinker replacement, resulting in compressive strength between 30 and 65 MPa for water to binder ratios varying between 0.3 to 0.5 [110, 111].

Such a high clinker replacement level can help improve sustainability by reducing the embodied CO₂ [111]. The phase assemblage does not significantly vary with different clinker replacement levels. Still, their quantities, especially for carboaluminates, can vary [19, 20]. The conversion of Hc to Mc occurs later [112]. The formation of C₂ASH₈ at higher replacement levels is also reported [11]. The appearance of C₂ASH₈ can be observed at lower clinker replacement levels when a high purity clay is used [11]. The increased Al concentration in the pore solution leads to more Al ion uptake by C-A-S-H [20].

Overall, a limitation of using calcined clay in cements comes from the slower reactivity of calcined clay compared with clinker. Consequently, 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, do not significantly influence early-age strength [113]. The required strength at early age does not mainly depend on calcined clay type, but on the clinker replacement level and clinker reactivity.

The optimal clinker content must be put in perspective with the desired application of calcined

clay cements. The clinker factor and the calcined clay cement formulation have to satisfy the strength values required in standards, or by the market. For example, the early strength requirements for masonry or unreinforced foundations are much lower compared to those of precast concrete. It follows that depending on the application, the clinker substitution level can vary significantly.

Guideline: the optimum clinker replacement needs to be determined in order to achieve a compromise between sufficient strength for a given application, especially at early age, sufficient workability, and the maximum ecological and/or economic benefits during the entire service life of the cement/concrete.

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 strength development. The differences are mainly associated with the reactions kinetics 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 the 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 satisfactory properties are achieved when using impure sources, which allows the utilisation of large resource of lower grade kaolinite clays for cementitious materials production. It is worth noting that the amount of studies evaluating calcined illite or smectites is very limited compared with kaolinitic clays, therefore further studies of cementitious systems with such clays need to be developed.

The reaction of calcined clay slows down because of the lack of (large) solution-saturated pores. The



precipitation of hydrates continues but much more slowly in the fine saturated pores. The growth of hydrates is controlled by the supersaturation level. Higher supersaturation is required to compensate for 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 may be 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 Research gaps

Although there is a growing interest in calcined clays containing cements, this review highlights that there remain many open questions for future proof this technology. From this study, it is concluded that the following areas of research require further investigation:

- Much more literature is available on kaolinitic clays compared with 2:1 clays. Despite their lower reactivity, 2:1 clays are of interest in many areas where kaolinitic clays are not available. The overall calcined clay reactivity can also be influenced by the secondary phases, as observed with dolomite. These interactions are very interesting to investigate to broaden the range of calcined clays suitable for clinker substitution.

- 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 Portland 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.
 - 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.
 - Development of specific admixtures (accelerators/activators) designed to enhance reactivity of calcined clays.
 - Enhancing clinker reactivity could also allow to offset the decrease in early age strength at a low clinker factor.
 - Accelerating the dissolution of calcined clay at early age.
- The development of other cement 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), calcium aluminate cements (CACs) and alkali-activated cements (AAC).
- 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.

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Declarations

Conflict of interest The authors declare no competing interest.

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