




Fresh properties of concrete containing calcined clays: a review by RILEM TC-282 CCL

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Received: 8 October 2021 / Accepted: 25 April 2022 / Published online: 23 June 2022
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Abstract This state of the art presents an overview on the effects of calcined clay inclusion on the fresh properties of concrete under the framework of RILEM TC-282 CCL. Progress in recent literature was reviewed to determine the effects of calcined clay, particularly metakaolin and lower grade kaolinite clays, on fresh concrete properties and how to control them using admixtures, particle packing, and mixture proportioning. A summary of recent studies on the use of superplasticizers in modified (or combined form) to

improve compatibility have shown promising outcomes to control the rheological properties of calcined clay binders. Superplasticizer demand required to achieve workable concrete increases with increasing dosage of calcined clay and increases substantially for concrete produced with calcined clay at water-to-cementitious material ratios below 0.40. A comparative analysis of data from several literature shows that the addition of calcined clay could reduce setting time when used without superplasticizers. Addition of

This paper has been prepared by RILEM TC 282-CCL. The paper has been reviewed and approved by all members of the TC.

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superplasticizers could help to control and increase the setting time significantly. Calcined clay can be used to make concrete with similar workability and setting times as concrete containing Portland cement through the use of polycarboxylate-based superplasticizers. However, more studies in future should focus on retention of workability by suitable methodologies for various construction activities. Care should be exercised to avoid long setting times with high dosages of superplasticizers.

Keywords Calcined clay · Fresh properties · Workability · Mixture proportioning

Abbreviations

PC	Portland cement
MK	Metakaolin
LC ³	Cement with limestone and calcined clay
w/b	Water-binder ratio or water-cementitious materials ratio
PCE	Polycarboxylate ether
WRA	Water-reducing admixtures
SNF	Sulphonated naphthalene formaldehyde
HPC	High performance concrete
LC ²	Limestone and calcined clay admixture
LDH	Layered double hydroxide

1 Introduction

Calcined clays were one of the early supplementary cementitious materials (SCMs) used to substitute Portland cement (PC) concrete and were initially used to reduce the heat of hydration and improve durability

[1–6]. Pozzolanic activity of calcined clays has been demonstrated since the early 19th century by Louis Vicat, and, its incorporation in PC-based materials was under investigation from mid 28th century [7, 8]. However, the high fineness and water demand were major obstacles to its use as a mineral admixture in concrete initially when there was limited usage of water-reducing admixtures (WRA). Calcined clay is experiencing a renaissance recently because of the widespread geographic availability of these clays [9, 10], favourable economics for manufacture [11], potential for large reductions in concrete greenhouse gas footprint [12], and suitable fresh state, mechanical and durability properties for use in reinforced concrete systems [13–16]. In the past, a significant portion of the calcined clay used in concrete was primarily metakaolin (MK), which is a purified and highly reactive form of kaolinite-based calcined clay. MK is typically limited to 8–20% cement replacement levels because of concern over workability and cost [17, 18]. Raw clay sources used to make MK are refined and must have a high percentage of kaolinite clay [19]. The availability of such high purity kaolin clay deposits is limited worldwide. Moreover, several industries such as paper, pollution control, coating, and pottery need such high purity kaolin clay materials, which leads to higher demand and cost of MK as a cement substitute. For example, the commercial cost of pure kaolin clay can be twice that of PC, which restricts the use of these materials in construction projects due to economic viability. The additional cost comes from processing required to remove impurities such as quartz sand, iron-based compounds, and other mineral impurities to whiten the clay color and increase the kaolinite

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content. Pure forms of MK has been typically used only in high-performance concrete (HPC) as a premium SCM, at low water-cementitious material ratio (w/b), or in instances where white color is needed for architectural reasons [9].

As an alternative to purer forms of MK, lower-grade calcined clay made from clays with moderate kaolin contents, as low as 40% kaolinite content in raw clay, are explored in the past decade. These lower grade clay sources can also make suitable pozzolanic material with little processing despite the complex chemical and mineralogical composition of clays [20–22]. Such forms of kaolin clays are well-distributed worldwide in large quantities for potential use as cement substitutes. Calcined clay is made by heat treatment, often referred to as calcination, of natural clay source at moderately-high temperatures, typically between 700 and 850 °C [9, 23]. Calcination is usually followed by grinding to reduce particle size suitable for use in cementitious materials. The chemical and physical properties of calcined clay can vary depending on the clay type, clay content, firing process, grinding, and grinding aids used [23–26]. More recently, it has been found that calcined clay and fine limestone powder can be used together as cement substitute to produce a blended binder known as limestone calcined clay cement (LC³) [9, 27, 28]. All components in the ternary limestone-calcined clay-clinker system react synergistically to provide enhanced strength and durability to concrete [29, 30]. Powdered limestone is considered to be an ideal component for increasing clinker substitution level [31], specifically with alumina rich—SCMs like calcined clays due to improved chemical reaction.

The role of calcined clay on workability, setting and fresh properties has been a subject of concern for the research community and concrete producers [32–34]. In the last decade, considerable work has been performed to assess the effects of calcined clay on fresh concrete properties, including rheology, stability, setting, and workability retention. These efforts have led to the development of solutions to tailor the fresh properties of concrete containing calcined clay, allowing it to be used successfully in most concrete applications. Furthermore, the increasing complexity of clay type, its variation, composite ternary formulations composed of calcined clay has produced some new challenges in controlling the behavior of fresh concrete, which is pointed out in this review. This

paper reviews advances in the use of chemical admixture used to control the properties of concrete made with calcined clay, the effects of calcined clay on fresh properties of concrete, how to use chemical admixtures to control them, and incorporating calcined clays in mixture design.

2 Admixture use with calcined clays

Polycarboxylate ether (PCE) polymers have been used in concrete construction since the late eighties. There has been a noticeable improvement over former technologies such as lignosulphonate or sulphonated naphthalene formaldehyde (SNF) condensates over the years. The intrinsic dispersing ability of PCE is noticeably higher and helps to achieve the target workability while reducing the water content in concrete beyond what was previously possible, opening the way to high performance and self-consolidating concrete [35, 36].

All PCE molecules share a common branched structure which is known by various names such as ‘bottle-brush’ [37–39] or ‘comb-copolymer’ [40–42]. A basic description of PCE structures would be a main anionic chain made of acrylic or methacrylic acid from which protrude side-grafts usually made of methoxy-terminated poly(ethylene glycol) (PEG) polymers. They are usually obtained either by esterification of the main chain acids by the terminal alcohols of the methoxy-PEG, or by free-radical copolymerization of the unsaturated carboxylic acid with a PEG-ester of the same acid. Over the years, some variants were produced, with the insertion of maleic acid or acrylamidomethyl propane sulphonic acid into the main chain. However, only subtle changes were brought to graft chemistry mainly for the sake of polymerization efficiency or cost-reduction with PEG-tethered isoprenyl, vinyl or methallyl alcohols [43].

2.1 PCE incompatibility with calcined clays

The interaction between clays and PCE dispersants has been extensively studied due to the observed loss of dispersion efficiency, leading to higher demands of those admixtures content. Such problems usually arise when the aggregates, especially sands, are poorly or not washed and contain natural clays [44, 45]. In some instance, PCE molecule was found to be incorporated



with interlayer space of aluminosilicate, as shown in [45]. Cases in which dehydroxylation is not complete could experience some of these same incompatibility issues.

Many studies agree on the primary mechanism of PCE consumption, namely the intercalation of macromolecules in the interlayer space of phyllosilicates [46–50], also named as chelation mechanism. Even if small amounts of surface adsorption could be measured, it appears that intercalated PCE induces a deformation of the clay sheet-like structure, easily observed by X-ray diffraction through increasing the interlayer thickness. This indicates that the clay platelet stacked structure deforms to accommodate large molecules. A comprehensive review on the subject is reported in Ma's article [51].

Most authors observed that only the side grafts of the PCE macromolecules, namely poly(ethylene oxide) (PEO) chains, produce an intercalation effect. However, a study reported in [46] demonstrated that this intercalation induces a decrease of the interlayer water amount, according to a dehydration-like mechanism. Another study by Lu et al. [52] proposed that the units of the PEG chains interact with interlayer cations in a crown-ether-like fashion, replacing the hydration water of the said ions (Fig. 1).

It was shown that intercalation is more pronounced for longer PEO chains than for the shorter ones [48, 49], which led to the design of very short side-graft PCE molecules to improve clay tolerance [50, 53]. Other modifications involved the insertion of amide groups [54] or substitution of PEO by β -cyclodextrin [55], leading to mixed results in mitigating the intercalation, the total polymer consumption and the cementitious material workability. No intercalation of PCE was reported for kaolinite and illite; it

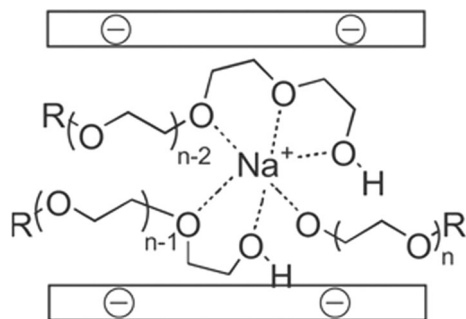


Fig. 1 Sketch of the crown-ether-like configuration of PEG units needed for sodium interaction [52]

is argued that their structure naturally leads to such behavior [51]. The kaolinite interlayer space is devoid of any cation, which eliminates the basic PEO chelation mechanism described previously. This leads to the conclusion that most PCE interactions with kaolinite or illite would merely involve surface adsorption. It was indeed shown that PCE molecules are efficient dispersants of kaolinite suspensions [56].

2.2 Compatibility of PCE with calcined clays

Calcination is reported to have different effects based on the mineralogy of clay. First, it was shown that 800 °C calcination induces a decrease in the specific surface of montmorillonite and illite while kaolinite seems to be far less sensitive [57, 58]. It is then expected that surface adsorption would be noticeably decreased after calcination for the first two, while kaolinite will retain much of its adsorption capacity.

Most compatibility studies seem to be devoted to kaolinite-rich calcined clay, pure calcined kaolin and more recent studies have a focus on lower grade calcined clay and calcined clay-limestone combination. A comprehensive study with commercially available PCE polymers was conducted by Nair et al. [59], comparing OPC, a 30% fly ash-blended cement and LC3, a blend of Portland clinker gypsum, calcined clay and limestone. The extensive experimental program involved paste and concrete testing, in both fresh and hardened state. It was observed that PCEs needed to be added at a higher dosage than required for PC or the fly ash-blended cement for equivalent performance. Interestingly, the correlation of optimum dosage in concrete versus paste followed a peculiar trend, with almost no change in required dosage for concrete when the water-binder ratio (w/b) was above 0.40 and a sharp increase below 0.40 shown in Fig. 2.

Original polymer structures were also explored for compatibility with calcined clay-limestone blends, as described in [34]. They consisted of very sparsely (less than 1%) grafted acrylic acid-acrylamidomethyl propane sulfonic acid (AA-AMPS) copolymer main chain, obtained by free radical terpolymerization. The side chains were roughly 23 units long, and the molecular weight was typically five to ten times as high as typical PCE weights. This resulted in polymers with a very high ionic character, yielding a robust calcium-chelating property and a dispersing effect that

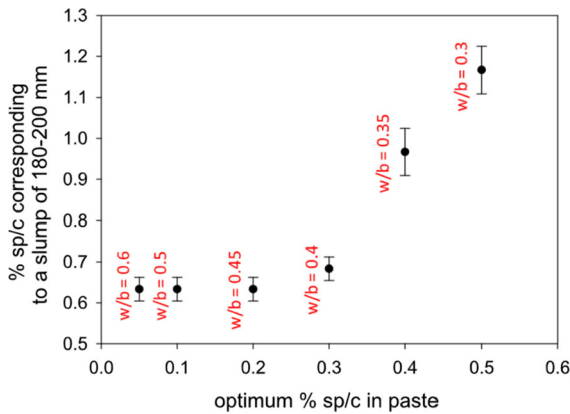


Fig. 2 Optimum dosage in concrete versus the superplasticizer saturation dosage in paste made of limestone calcined clay, used with permission from Nair et al. [59]. sp/c is the superplasticizer-to-cement ratio obtained using Marsh cone tests after which the flow does not increase based on flow time versus superplasticizer dosage curve. w/b: water-binder ratio

uses electrostatic repulsion, as shown by zeta potential measurements in Fig. 3.

Adsorption featured sharper initial slopes and pronounced saturation plateaus on limestone and calcined clay when compared to PC, as shown in Fig. 4. The expression of the results in mg adsorbed by the unit weight of mineral misled the authors on the relative capacities to accommodate polymers at the surface: the specific surface being 5 times higher for limestone and calcined clay compared to PC, their saturation occurs at lower levels per unit surface area. The main finding of that study is that much polymer

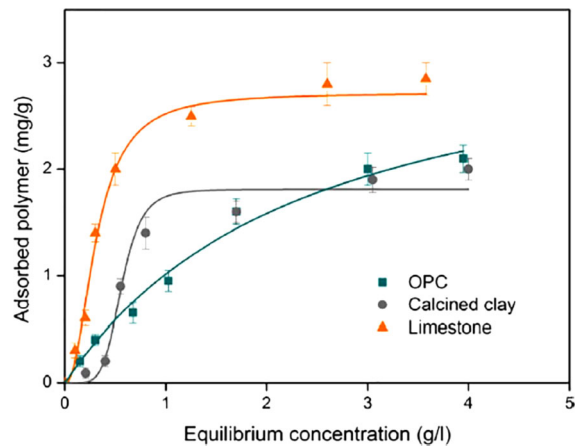


Fig. 4 PCE adsorption by material type in synthetic pore solution, used with permission from Akhlaghi et al. [34]

remains in solution to fuel further adsorption over time. Hence good workability retention was achieved [34].

A study devoted to different chemistries of grafts was performed by Schmid and Plank [43]. They used free radical polymerization with macromonomers bearing different unsaturated functions to assess their relative influence on the dispersion of blends of OPC with calcined kaolinite. Namely, the functions involved were ω -methoxy PEG methacrylate (MPEG), isoprenyl PEG (IPEG) and α -methallyl- ω -methoxy PEG (HPEG). IPEGs are usually produced by ethoxylation of isoprenol and should probably not bear an ω -methoxy group shown on Fig. 5. The HPEG-based polymers are commercially available

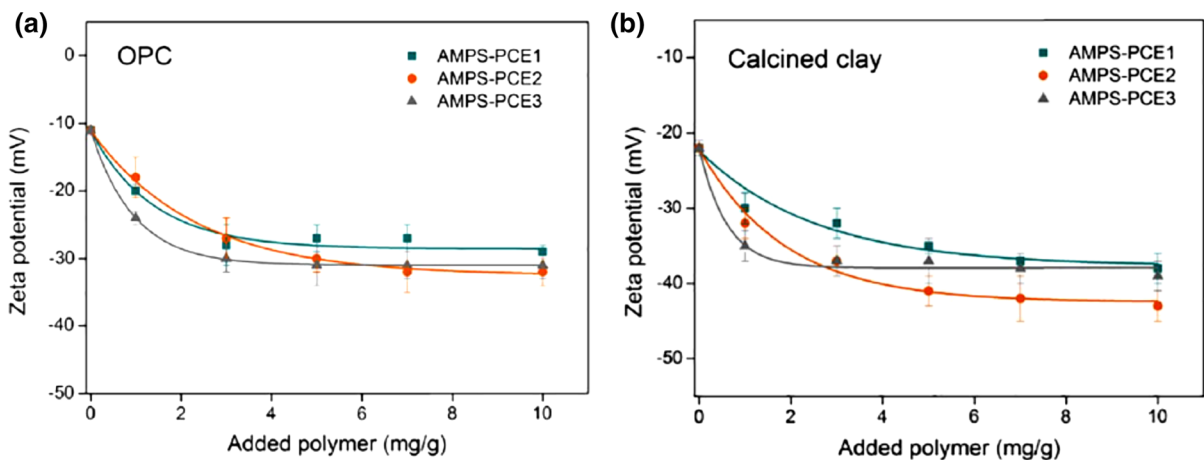


Fig. 3 Zeta potential in a synthetic pore solution of **a** OPC and **b** calcined clay with PCE dosage, used with permission from Akhlaghi et al. [34]

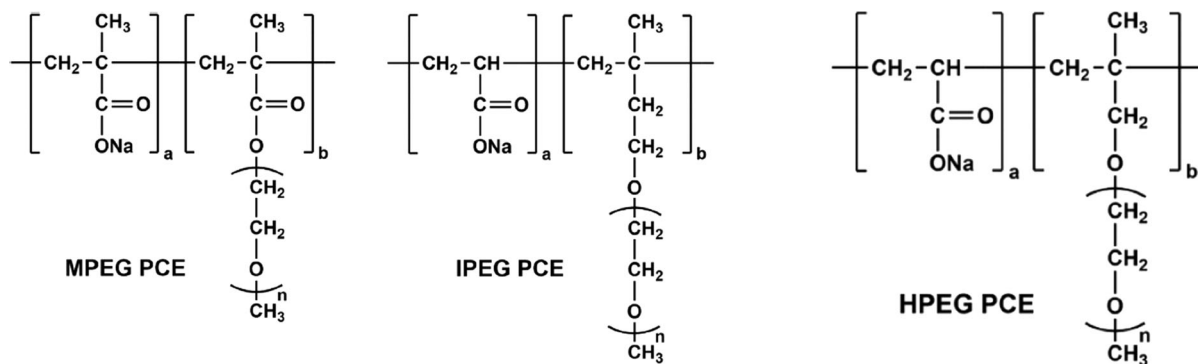


Fig. 5 Macromonomers used in the study of Schmid et al., used with permission from Svhid and Plank [43]

products. The polymers were synthesized with variable molar amounts a and b and variable graft ethylene glycol units. The comonomer used with MPEG was methacrylic acid for better reaction conversion, while acrylic acid was used with the other two shown in (Fig. 5).

A natural clay was calcined from a source containing low amounts of kaolinite (23%), with illite-smectite (32%) and quartz (20%) present as the other main components in the material. After calcination at 750 °C for 30 min, 60% of amorphous phases were achieved with a specific surface four times as high as PC. The behavior of all polymers was then assessed in combination with increasing amounts of calcined clay in a blend with a PC. The required dosages for a targeted paste flowability and adsorption isotherm were measured. All the dispersants used in the study required dosages that increased with the proportion of calcined clay in the blend. The IPEG-based polymers required the highest dosages, while the HPEG-based commercial polymers demonstrated to be the most efficient. Whenever applicable (i.e. on IPEG and MPEG based polymers), the grafting ratio had a mild influence on the dosage required except on the pure calcined clay, for which the lowest grafting ratio provided the best efficiency in terms of dosage needed to disperse the solid particles [43].

Adsorption was only investigated with MPEG-based polymers and showed a similar trend on calcined clay cement and just PC; the higher the grafting ratio and the graft length, the lower the adsorption. Interestingly, adsorption onto calcined clay features a more pronounced plateau than onto PC for all structures. Nevertheless, some adsorbed

amounts seemed similar for calcined clay and PC; hence adsorption seems barely responsible for the differences in fluidity, which they attribute to a different mixing protocol in the two tests. However, the authors may have been misled by comparing their results in terms of polymer mass adsorbed per unit weight of the material, neglecting the four-fold higher specific surface of calcined clay, as measured by the BET method. When considering this, adsorption by unit surface area of calcined clay was lower than for PC, providing a more convincing explanation for the fluidity difference [43].

2.3 Other admixtures

A few studies are available on other admixtures, and most of them are about retarders, usually associated with a polymer dispersant of some sort and never alone. For instance, in Nair et al. [59], a designated ‘lignosulphonate-based’ retarder helped recover some workability retention. Since lignosulphonates are usually classified in the plasticizer category and retard mainly when they contain sugars (see e.g. [60, 61]), it is inferred here that a special unrefined grade was used and that sugars are also suitable retarders for calcined-clay systems. More recently, a combination of PCE with layered double hydroxide (LDH) has been proven to improved fluidity retention in calcined clay blended cement [62]. The PCE molecules in LDH were gradually exchanged with sulfate ions to produce improved flow retention in the cementitious systems containing calcined clay. More such combined formulations needs to be explored in future studies.

3 Rheology

The rheological properties of cementitious materials are a key consideration when designing the formulation of cementitious products. Assessment of rheological properties can be undertaken using different test methods and give information on the different physical properties of paste, including yield stress, viscosity, thixotropy, flowability and viscoelasticity. Cement paste rheological properties are influenced by many different factors. These parameters include particle size distribution, solid volume fraction or packing density, particle shape and texture, and interparticle forces [63]. Interparticle forces can occur from surface charge [64, 65]. C–S–H nucleation and build up during hydration can also increase rheological parameters [65]. Chemical admixtures are often used to control interparticle forces as previously described.

Calcined clay particles can change the cement paste parameters that govern the rheological properties and warrants further discussion. [66–68].

3.1 Controlling rheology with chemical admixtures

The work of Vance et al. [68] showed that including fine particles of limestone significantly decrease the plastic viscosity of cement paste. However, a decrease in the limestone particle size to 0.7–3.0 μm , was found to cause an increase in the plastic viscosity and yield stress of pastes. The sole use of limestone can lead to the segregation of PC pastes (when mixed with a PCE superplasticizer) [68]. The inclusion of calcined clay materials can reduce this segregation and, when used in conjunction with limestone, reduce the workability of the paste. By mixing a PC-limestone blend with MK, the yield stress decreases with the increase in limestone content compared to that of PC and MK due to the packing effect of fine limestone and the electrostatic effects between MK and limestone particles [69].

Superplasticizers are required to control workability and setting times when calcined clays are used as SCMs [14, 59, 70]. Ferreiro et al. [70] showed by comparing 1:1 and 2:1 clays that the water demand is significantly lower for 2:1 clays. That study also showed that delayed addition of superplasticizer, a few minutes after the water, improved workability. The use of WRAs increases the workability of concrete

containing calcined clay-based cementitious materials. Comparison between slump and concrete rheology results were reported by Paiva et al. [71] and showed that yield stress and viscosity decreased as slump increased with MK. The results also showed that WRA dosage increased significantly as MK dosage increased [71]. The use of these materials is governed by ASTM C494 [72], with specific consideration given to Type A and Type F admixtures [73]. Zaribaf and Kurtis [73] have assessed various WRAs on ternary blends of PC-limestone-MK, with up to 30% replacement, using polycarboxylate ethers (PCE), lignosulfonates, naphthalene and polymelamine sulfonate based admixtures. For high MK content ternary blends, PCEs were the most efficient to increase the workability. Moreover, both powdered and liquid based PCE were effective, which could allow to produce pre-mixed MK/PCE blends. The work of Nazario-Santos et al. [69] has shown that keeping the superplasticizer content below 0.5 wt% is ideal for controlling the workability of all MK blended cements.

The inclusion of PCE-based superplasticisers can significantly affect the rheological properties of cement paste [74]. The authors reported a significant reduction in yield stress when PCE was added to a calcined clay paste. This reduction in viscosity was attributed to better dispersion of the calcined clay particles within the cement paste. However, the type of clay was reported to impact the behavior of calcined clay-based paste significantly. Calcined phyllosilicates have shown shear thickening behavior, whilst MK has shown higher yield stress without any associated shear thickening behavior [74].

3.2 Yield stress and viscosity

The inclusion of MK within different cementitious systems was found to drastically increase both plastic viscosity and yield stress of paste [66–68, 75]. In addition, the incorporation of MK increased both water demand and Vebe time and systematically decreased slump and compacting factor [76, 77].

Calcined clay particle size and presence of impurities have been found to have a considerable effect on the resulting cementitious system rheological properties. A study by Lorentz et al. [63] showed that the yield stress and the viscosity could be related to the material particle size and zeta potential. However,

these issues were overcome through the use of additional (excess) chemical admixtures. Calcined clay surface area is a function of the calcination process, mainly temperature and grinding. The particle size distribution increases as the calcination temperature increases up to 800 °C. Sintering likely starts to occur at calcination temperatures above 800 °C, increasing the particle size. The workability and reactivity of the clays are then dependent on the surface area after grinding. The finer the particle size distribution, the higher the pozzolanic reactivity, and the higher the water demand [20].

Sonebi et al. [66] researched the rheological parameters of cement grouts with MK content ranging from 6 to 20% of PC. The results indicated that for a given dosage of viscosity-modifying agent (VMA) and superplasticizer (SP), an increase in MK content caused a significant increase in the yield stress, plastic viscosity, cohesion plate and flow time, and a reduction in mini-slump. Cassagnabère et al. [78] investigated the slump, flow, and apparent viscosity at different shear rates of cement/MK-based mortars. The results showed that both slump and viscosity are strongly dependent on the morphology of MK. A decrease in roundness and increase in the angularity of particles caused a decrease in slump and an increase in viscosity values. The influence of the size and shape of particles on viscosity is dependent on shear intensity. The nature and content of impurities such as quartz, illite, or uncalcined kaolinite are the main parameters that affected the morphology of particles, the water demand, and flow properties (viscosity values) of the MK mortars.

Vance et al. [68] demonstrated that increasing the MK content in the paste significantly increased both yield stress and plastic viscosity. For example, when the MK content increased from 0 to 10%, the plastic viscosity doubled, and the yield stress increased by 1.75 times (Fig. 6). This observation is attributed to MK's very high surface area and the tendency of MK fines to agglomerate. Agglomeration of particles causes water to become trapped, preventing it from lubricating particles and causing significant elevations in the measured yield stress and plastic viscosity.

Paiva et al. [71] investigated the effects of MK on concrete workability. With the increase in MK content, both water content and admixture content had to be increased to keep the workability at a constant slump of 90 ± 10 mm. Janotka et al. [67] reported

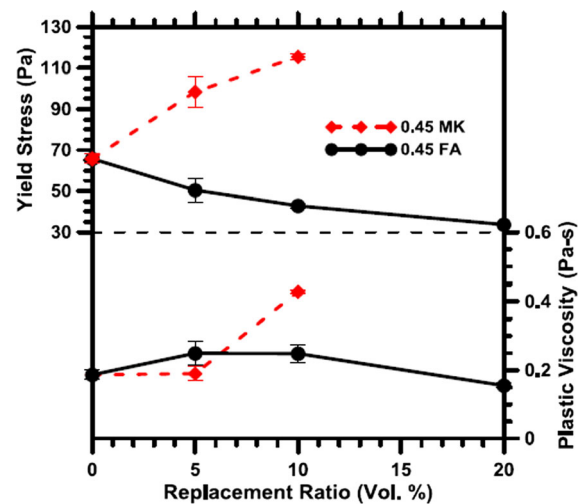


Fig. 6 Influence of fly ash and MK on the rheological properties of binary pastes from Vance et al., used with permission from Vance et al. [68]

that mortars with MK fit the Herschel–Bulkley model much better than the Bingham mode, with the yield stress increasing as the MK content increased. MK with the highest pozzolanic activity and highest specific surface induced the highest increase in yield stress.

3.3 Thixotropic and dilatant effects

Thixotropic behavior within cement paste is often described as the need to apply strong shear to a cement paste in order to bring the paste back to its reference state [79]. Cement pastes containing MK and a superplasticizer have been shown to display an increase in the thixotropic behavior with an increase in MK content [80, 81]. The increasing dilatancy of the cement paste has been attributed to interaction? (or jamming) of the angular, plate like MK particles [80]. Calcined clays thixotropic effects have been shown to be caused by negatively charged calcined clay surfaces as measured by zeta potential and layered particles. This increases particle flocculation, reducing water availability. This mechanism is different than seen in Portland cement pastes, where thixotropy is caused by C–S–H nucleation and buildup [64, 82]. In the context of an extrusion-based 3D-printing study [83], the quick and intense structural build-up was observed in the cementitious material produced with calcined clays from two different origins, being more

pronounced for clays with higher kaolin content. However, looking at the initial slump flow diameter results, for the same water content, the mixture that presented higher thixotropy also showed lower flow, pointing to the water adsorptivity of calcined clays as the main factor for the behavior of the mixture.

3.4 Pumpability and extrudability

Calcined clays can be used to produce shotcrete characterized by low dust generation and reduced rebound, therefore suitable for the application of thin layers on dry substrates [84]. It was also referred that shotcrete with calcined clay led to a denser concrete with lower water penetration depth.

A lab-scale extrusion test method based on a ram extruder was proposed in a recent study [85] to efficiently observe the extruded filaments of the fresh mixture and quantify the required extrusion pressures at different ages. Mixtures with calcined clays showed good shape stability before their initial setting. Although pointing to the content of MK as the main factor, the large variation of particles fineness could also impact on the studied rheological properties. Namely, using finer calcined clay may increase the extrusion shear strength of fresh mixtures, which may bring difficulties for extruding and reduce the printability window/open time. However, the buildability and structural build-up behavior of mix designs for 3D concrete printing could be enhanced by using finer calcined clays [86, 87].

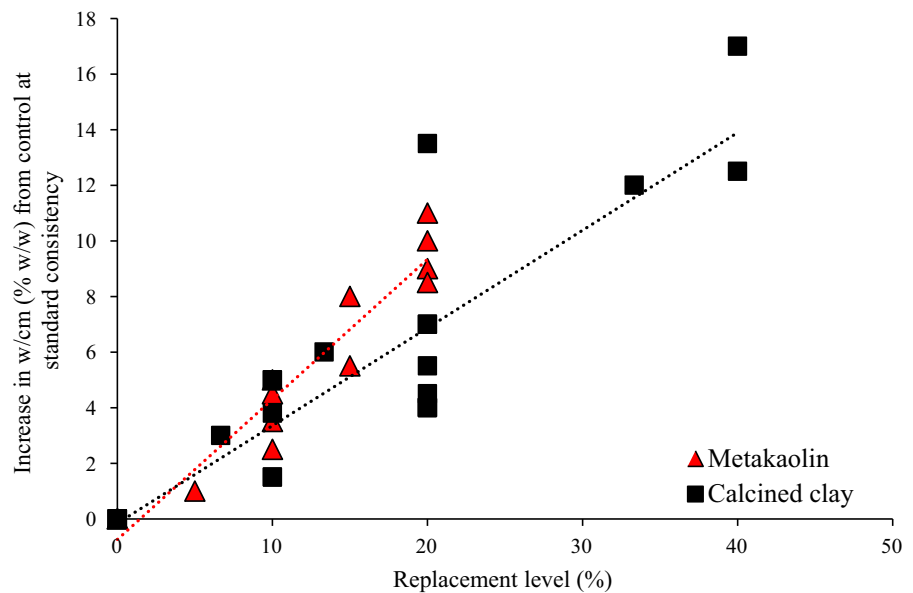
4 Mixture cohesion

Limited work has been reported on the segregation resistance of concrete mixes produced using calcined clay. Caldarone et al. [76] reported that although the slump of concrete mixes reduces with the addition of MK, the superplasticizer dosage required is 25–35% lower than that required for similar doses of silica fume. In addition, mixes with MK were less sticky because of the lower superplasticizer dosage required than mixes with silica fume and could have a better surface finishability. This study also reported that although the mixes with lower w/b seemed to have poor workability when prepared using MK, good compaction was achieved upon vibration.

Bai et al. [77] reported that the addition of MK to mixes with fly ash reduces the sensitivity of the mixes to superplasticizers and the tendency of the mixes to bleed upon water-reducing admixture overdosing. This was attributed to the blocking of the capillary channels by MK particles. It has also been reported that despite the higher surface area of MK particles, the increase in compactability and VeBe time was relatively small. This has been attributed to the ease of flow of the mixes under vibration due to the thixotropic nature of clay suspensions and improved packing of calcined clay particles between the cement particles. Paiva et al. [71] reported that the agglomeration of MK particles has a significant influence on the workability of concrete and that superplasticisers can effectively break these agglomerates. Perlot et al. [88] reported that MK increases the cohesion and robustness of self-compacting concrete mixes as bleeding and segregation were reported to be reduced. This was attributed to the high thixotropic nature of the mixes containing MK, as reported by Vejmelková et al. [89].

The influence of the limestone and calcined clay combination on stability has also been investigated. Perlot et al. [88] found the combination of limestone and calcined clay to be highly suitable for self-consolidating concrete industrial production as they were found to reduce mixing sequence time and improve cohesion. While there is some consensus on the influence of MK on cohesion, the influence of limestone is not clear. While Larsen and Naruts [90] reported an improvement in the cohesion of concrete mixes containing limestone, Muzenda et al. [75] reported that the presence of limestone in the blend binders reduces the cohesion of the mixes in the tack test. However, it may be considered that limestone has long been used as an additive to improve cohesion in self-compacting concrete mixes. Vardhan et al. [91] reported a lower admixture dosage requirement for the production of self-compacting concrete with 45% cement replacement by a blend of limestone and calcined clay than a similar replacement level by fly ash. This has been attributed to the higher robustness of the mix with limestone and calcined clay. Another study by Nair et al. [59] reported bleeding in mixes containing calcined clay and limestone when admixture dosages were increased to achieve initial workability levels similar to mixes with PC. However, this was controlled by modifying the fine aggregate

Fig. 7 Increase in standard consistency of cement pastes with CC or MK. CC—if $A/S < 0.7$; MK if $A/S > 0.7$. [6, 95–99]



contents in the concrete mixture as reported in that study.

5 Plastic shrinkage

Very limited and conflicting findings on the influence of MK on early-age shrinkage and cracking have been reported in the literature. Branch et al. [92] reported that the shrinkage strain in mixes containing MK is higher than mixes containing fly ash or blast-furnace slag. This could partly be explained by the lower bleeding capacity and rate that has been reported for mixes with calcined clays [93]. Still, due to the faster strength development with MK (compared to fly ash and slag concretes), cracking was not observed in the restrained ring test. However, Niknezhad et al. [94] reported a reduction in free shrinkage, restrained shrinkage stress and crack width in concretes containing MK. Much more work is needed in this area to understand the bleeding and plastic shrinkage of concrete containing calcined clay.

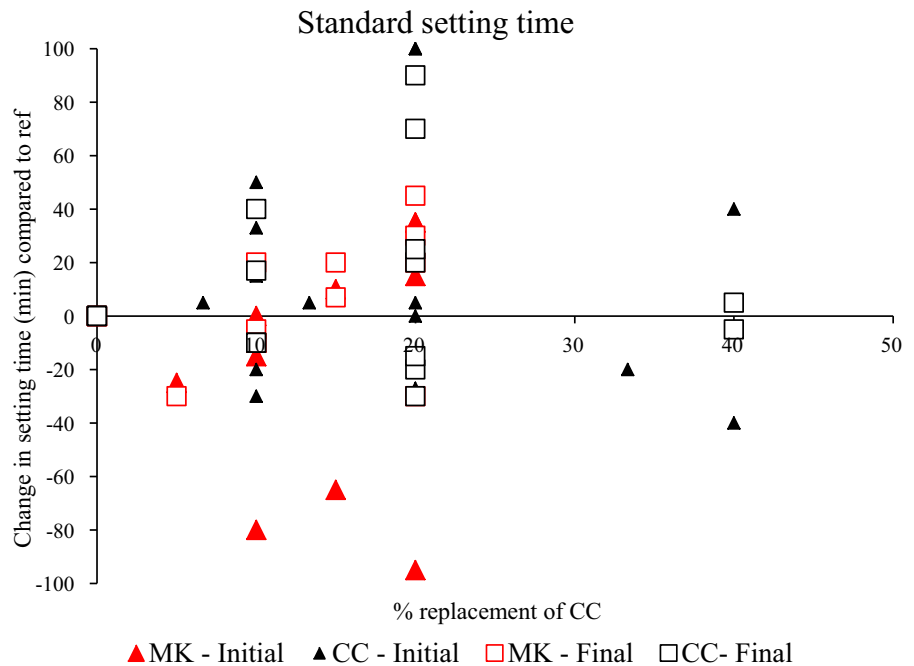
6 Setting

Setting is the time duration required for the concrete/mortar/pastes to lose its workability and start to harden. Setting time of cement pastes is typically

measured by the Vicat needle test. The result of this test is mainly dependent on the consistency of the cement paste, so in this test cement paste mixtures are made at a standard consistency. Figure 7 plots the increase in the standard consistency reported in the literature for a blended binder containing calcined clays [6, 95–99]. An increase in cement replacement by calcined clay increases paste standard consistency, requiring a higher w/b in the setting test, leading to increased setting time at lower dosages, as shown in Fig. 8. Use of MK increases the standard consistency more than calcined clay because of the higher kaolinite content in MK and its accompanying increase in surface area.

Figure 8 shows the change in the initial and final standard setting time (measurement based on standard consistency) for data compiled from the literature at different replacement levels of calcined clay [6, 95–99]. Lower-grade calcined clay and MK are demarcated in the analysis. It can be seen that the data points are scattered, although MK is more likely to have a lower setting time compared to lower grade and alternative calcined clay. On the other hand, Fig. 9 compiles data taken from the literature on setting time at the same w/b ratio with and without the addition of a superplasticizer (SP). It should be noted that the classification between MK and calcined clay was not shown in this figure. Comparing the data with and without SP, it is clear that the replacement with

Fig. 8 Change in standard setting times of cement pastes with CC or MK. CC—if A/S < 0.7; MK if A/S > 0.7. [6, 95–99]



calcined clays reduces the setting time and large increases in setting time are typically caused by the admixture [100]. As superplasticizers are generally added to improve workability with the addition of calcined clay, its retarding effect may, in practice lead to an increase in setting time.

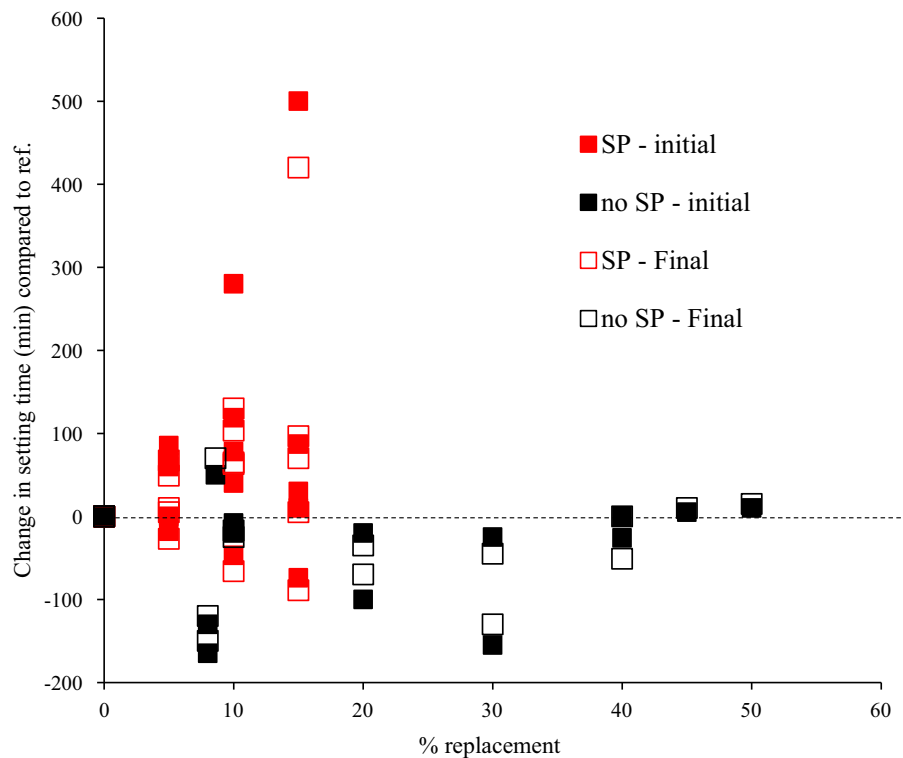
7 Mix design

As discussed in the previous sections, calcined clay can significantly influence the fresh properties of concrete and affect its placement onsite. Concrete mix design must therefore be adjusted to account for this influence. For concrete mixes with similar water content and superplasticizer (SP) dosage, the slump was found to decrease with increasing MK replacement level [16, 110]. This increased water-demand can be compensated by using a higher water content or increasing the water reducer dosage. While studies have shown that polycarboxylate based admixtures are the most effective, calcined clay based concrete can be more sensitive to the dosage of this type of admixture, with some studies indicating the possibility of bleeding upon over-dosing [59]. The effect of water content on SP demand to produce a similar slump was investigated by Nair et al. [59]. Concrete mixes with

water content below 160 kg/m^3 required a significant increase in the superplasticizer dosage to produce a similar initial slump. To separate the effect of water content from the influence of calcined clay, some studies considered concrete mixes with similar water content (per m^3 of concrete) to focus on superplasticizer requirement [111–114]. The studies reported that an increase in calcined clay content required an increase in SP% to produce a similar target slump.

In cement paste, the relative increase in admixture dosage required to maintain the same flow with the addition of calcined clays was higher than that required in concrete due to the influence of aggregates [32]. Additionally, since fine aggregate is also known to contribute to the stickiness of mortar and concrete, reducing fine aggregate content has been suggested to compensate for the influence of calcined clays on water demand and cohesion. A similar reduction in fine aggregate content was adopted for concretes with MK together with a reduction in w/b [112] (See Table 1). Table 1 lists typical concrete mix designs with calcined clays. In all cases, SP dosage increased when the PC replacement level increased or the w/b was reduced. Güneysi et al. [115] used a SNF-based water reducer. Most of the other studies adopted PCE-based superplasticizer.

Fig. 9 Changes in setting time with respect to reference at constant w/b ratio with and without superplasticizer [101–109]



It is possible to interfere with the concrete workability characteristics by controlling paste content and aggregate proportions [116]. In calcined clay systems, this method can be suitable to produce desirable slump characteristics in concrete systems by tailoring mixture proportioning including controlling paste and fine aggregate content along with SP dosage. In some cases, SP dosage above 1–2% is reported for concrete containing calcined clay to produce a suitable initial slump, as shown in Table 1. Hence, it is important to develop a rational mixture proportioning approach to address potential slump issues in concrete with calcined clay. The tradeoff between increasing superplasticizer dosage and effectiveness of mixture proportioning needs to be explored further to facilitate widespread industry adoption of calcined clay-based binders for diverse concrete applications. Table 2 presents the influence of mixture proportioning by accommodating binder content to improve both slump and slump retention characteristics in calcined clay systems. The Q value denotes the distribution coefficient as per the modified Andreassen model. The value typically varies from 0.21 to 0.37 depending on slump or workability requirements of the concrete mixture [117].

Concrete mixtures designs need to be developed considering the influence of calcined clay on the rate of strength development. The high superplasticizer content typically used with calcined clay can significantly affect the early age hydration and alter strength development rates. Despite the higher superplasticizer addition, the early age strength of calcined clay-based concretes can be significantly improved by 7 days [30, 119]. Both mix design procedure and quality control should be adjusted in accordance with the time-dependent strength development observed for these concretes.

Self-compacting concrete (SCC) mixtures with calcined clays have been shown to be more viscous than other concretes, requiring higher superplasticizer dosage. An increase in V-funnel time was reported for self-compacting concrete containing MK [33] and calcined clay-limestone combinations [32]. However, compared to other cements, the higher cohesion requires the fine aggregate content to be reduced, partially compensating for the increased admixture demand. Also, the use of calcined clay was found to reduce the segregation tendency in SCC concrete mixes without the use of viscosity modifying admixtures.

Table 1 Concrete mixture proportioning strategies adopted in recent studies containing metakaolin or calcined clay-limestone combinations

References	MK,CCL *	Replace- ment level (%)	w/b	Water content (l/m ³)	FA:CA (%)	Slump (mm)	SP (%)	Remarks
[115]		0	0.35	158	53–47	140 ± 20	1.75	•SNF used.
	MK	10					2.24	•Aggregate volume adjusted with metakaolin dosage
	MK	20					2.75	•Aggregate proportion maintained
	MK	0	0.55	193	53–47	180 ± 20	1.00	
	MK	10					1.25	
	MK	20					1.74	
[112]		0	0.4	185	45–55	100	0.56	•PCE used
	MK	10					0.67	•Aggregate proportion adjusted for different w/b.
	MK	15					1.12	
	MK	20					1.34	• Similar water content for all w/b by adjusting binder content
		0	0.5		48–52		0.42	
	MK	10					0.57	
	MK	15					0.85	
	MK	20					0.94	
		0	0.6		49–51		0.04	
	MK	10					0.13	
	MK	15					0.26	
	MK	20					0.34	
[59]		0%	0.5	155	50–50	195	0.40	•w/b adjusted to produce similar strength.
		0%	0.45	162		200	0.34	Binder content was modified to produce a similar initial slump
		0%	0.4	168		210	0.27	
	CCL	30%	0.5	225		200	0.49	
	CCL	30%	0.35	122.5		200	0.80	
	CCL	30%	0.3	126		215	1.20	
	CCL	45%	0.5	175		200	0.60	
	CCL	45%	0.35	147		210	0.85	
	CCL	45%	0.3	126		210	1.25	
[32]		0	0.4	162	35–65	75–100	1.01	•SP dosage adjusted to obtain similar initial slump
	CCL	20					1.60	
	CCL	35					1.82	
	CCL	50					2.20	

*MK: metakaolin, CCL: Calcined clay-limestone combinations

8 Research needs/recommendations for future research

Several areas of concrete fresh property performance when calcined clay is used have been identified as areas in need of further research. They can be summarized as follows:

- PCE consumption of concrete containing calcined clay is high when compared to PC applications. A better understanding of the physical chemistry, the ionic conditions of the pore solution and the microscopic phenomena at the origins of workability loss (agglomeration, thixotropy, yield stress increase) may lead to more efficient molecules, thus a lower admixture cost.

Table 2 Slump characteristics of two concrete mixes containing limestone-calcined clay (LC²) produced at similar mini-slump saturation dosage [118]

Q value	w/b	Binder content (kg/m ³)	SP dosage (%*)	Water content (kg/m ³)	Paste Volume (%)	FA:CA** (%)	Slump (mm)	Slump after 1 h (mm)	28th day compressive strength (MPa)
0.26	0.36	410	0.5%	147.6	29	52:48	100	30	56.6
0.23	0.36	450	0.5%	162	31.8	55:45	160	60	54.6

* Saturation dosage of PCE based superplasticizer from cement paste studies using mini-slump was used

** FA corresponds to fine aggregate and CA corresponds to coarse aggregate

- The response of calcined-clay-blended cements to admixtures other than dispersants is not well documented. Research is needed in air entrainers, and a more chemically precise study of retarders seems necessary to obtain an improved compromise in terms of workability retention and early age strength. In addition, research on the mechanism of slump loss in concrete is needed, including if thixotropic or yield stress growth is responsible.
- Calcined-clay can accelerate concrete setting, mixture proportioning should be adjusted based upon the application to achieve suitable setting times. Although initial studies have shown that lignosulphonates, in combination with PCEs, can act as retarders, a more detailed study is required on the subject
- Information on the effects of calcined clay on concrete pumpability is still needed.
- Systematic work on the effects of calcined clay on bleeding is needed. This should include a fundamental understanding of the interaction of calcined clays and water, including agglomeration.

9 Conclusions

Calcined clay has great potential as a supplementary cementitious material to improve concrete properties. One of the biggest concerns concrete users have with calcined clay-based concrete is the control of fresh state properties. Increases in calcined clay particle size and surface area, internal porosity in sintered particles, and presence of incompletely calcined 2:1 clays or mineral impurities have been found to decrease slump, and increase the yield stress, viscosity, and thixotropy of cementitious systems. Common PCE structures

may be considered efficient enough to provide PC-calcined clay blends to control initial fresh state properties. However, new variants of PCE in modified forms were found to produce improved retention behavior. This could future pathways to obtain sufficient control on concrete workability for diverse construction applications. It was shown that polymer structure has the same influence as on straight PC systems; hence an adsorption-electrosteric repulsion dual mechanism is still involved. As a result, polymer efficiencies seem to rank in the same order as on PC. However, most studies show that the polymer consumption is higher than for PC systems, most probably a result of the much (several times) higher specific surface and faster reactivity of calcined clays. There remains a need to optimise dispersant efficiency to reduce dosages, hence cost, and future research should be carried out in this direction.

Calcined clay systems have produced conflicting changes in setting time compared to straight PC systems as measured by the Vicat needle test. However, this is primary due to higher w/b than control mixtures to achieve a standard consistency. When measured on mortar or concrete, calcined clay without any superplasticizers can reduce setting time. Superplasticizer could be used to control setting behaviour of calcined clay and calcined clay-limestone binders.

Calcined clay mixtures can be proportioned for a range of strength and workability classes. Superplasticizer demand required to achieve workable concrete increases with increasing dosage of calcined clay and increases substantially for w/b below 0.40. In order to improve workability, users can either (1) increase SP dosage, (2) use a retarder, (3) increase the paste content, (4) design particle size distribution in the mixture to improve packing, or (5) adjust the mixing and hauling procedure. In addition, calcined clay can



significantly increase mixture segregation resistance and reduce bleeding in SCC.

Acknowledgements TC Membership: Chair: Fernando Martirena-Hernandez, Cuba; Deputy Chair: Manu Santhanam, India; Regular Members: Eduardo Irassar, Argentina; Arnaud Castel, David Law, Sumaiya Afroz, Taehwin Kim, Vinh Dao, Australia; Jan Elsen, Ruben Snellings, Belgium; Silvia Vieira, Brazil; Arezki Tagnit-Hamou, William Wilson, Canada; Kequan Yu, Tongbo Sui, Zengfeng Zhao, China; Oscar Oswaldo Vásquez, Colombia; Adrian Alujas, Roger Samuel Roger, Cuba; Joergen Skibsted, Mariana Canut, Sergio Ferreira Garzón, Wolfgang Kunther, Denmark; Fabrizio Moro, François Avet, Gabriel Pham, Gilles Escadeillas, Pascal Dion, Pascal Boustingorry, Victor Poussardin, France; Alisa Machner, Elsa Qoku, Frank Dehn, Karl-Christian Theinel, Matthias Maier, Mohsen Ben Haha, Germany; Luis Velasquez, Guatemala; Anuj Parashar, Sri Kalyana Rama Jyosyula, Ravindra Gettu, Shashank Bishnoi, Talakokula Visalakshi, Tushar Bansal, Yuvaraj Dhandapani, India; Laith Al-Jaberi, Iraq; Luca Valentini, Italy; Joseph Mwit Marangu, Kenya; Sol Moi Park, Korea; J Ivan Escalante-Garcia, Mexico; Hassan Ez-Zaki, Morocco; Roman Jaskulski, Poland; Angela Maria Nunes, Karyne Ferreira do Santos, Manuel Vieira, Portugal; Guoqing Geng, Singapore; Franco Zunino, Karen Scrivener, Switzerland; Alastair Marsh, Daniel Geddes, Hoda Beltagui, Wenzhong Zhu, Fragkoulis Kanavaris, John Provis, Shiju Joseph, Susan Bernal Lopez, Theodore Hanein, UK; Claire White, Katelyn O'Quinn, Kyle Riding, Maria C.G. Juenger, USA

Author contributions All authors contributed to the review paper conception and design. The first draft of the manuscript was written by YD, SJ, DAG, ZZ, PB, SB, MV, and KA. Riding and was edited by FM, AC, FK, and KA. Riding. All authors read and approved the final manuscript.

Funding No funding was provided for this work. This work was performed by a volunteer working subgroup of RILEM committee 282-CCL.

Availability of data and material All data cited in this review paper is available in the referenced sources.

Declarations

Conflict of interest None. This paper was prepared by a working subgroup of RILEM committee 282-CCL.

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