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Recent advances in understanding the hydration of limestone calcined clay cements (LC³)

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ABSTRACT

Limestone and calcined kaolinitic clays are unique among supplementary cementitious materials due to their high and widespread availability. Furthermore, their combined reactivity enables substitutions of clinker of 50% (or more), while reaching comparable strength to PC (or pozzolanic cements) and enhanced durability properties. During the last 4 years, our understanding on the hydration mechanisms governing the behavior of these cementitious systems has evolved substantially, opening new possibilities for optimization and further development of the technology. The sulfate requirement of LC³, which is commonly observed to be higher as conventional PC, has been proven to be controlled by sulfate adsorption mechanisms rather than the total reactive alumina content of the system.

The precipitation of hemi and monocarboaluminate in LC³ was directly associated with the third hydration peak observed in isothermal calorimetry. Formation of carboaluminates is enhanced by the reaction of carbonates from limestone and alumina from metakaolin and has a significant contribution to strength gain and porosity reduction at early ages. Carboaluminates precipitate in pores remaining after clinker dissolution and remain stable in the long-term.

At later ages, it has been observed that the reaction of metakaolin slows down due to the lack of large-saturated pores where hydrates can precipitate. However, further reduction of the critical pore entry radius and total porosity was still observed, suggesting that precipitation might also take place in the pore solution film that lines the internal surface of partially saturated pores. In addition, precipitation of strätlingite was observed combined with a substantial reduction in Ca/Si ratio of C-A-S-H, in agreement with trends observed from thermodynamic modeling at equilibrium.

KEYWORDS: *sustainability, hydration, carboaluminates, sulfate requirement, porosity.*

1. Introduction

Sustainability in the cement industry is a major concern (Schneider et al., 2011). The most effective strategy to tackle this challenge on a worldwide scale is to reduce the clinker factor in cements based on Portland cement clinker (K. L. Scrivener et al., 2016). This has accelerated the adoption of blended cements that incorporate supplementary cementitious materials (SCMs) replacing part of the Portland cement (PC) fraction. Nowadays, blended cements are more common than PC. Among commonly used

SCMs are fine limestone, granulated blast furnace slag and fly ash (Lothenbach et al., 2011). Fly ash and slag are together available in amounts close to 15% of cement production (IEA & CSI, 2018). This means that we need to look for other materials to further reduce clinker factor, such as calcined clays.

Limestone calcined clay cements (LC³) are one of the promising alternatives for high performance sustainable cements (K. Scrivener et al., 2017). LC³ incorporates significant amounts of metakaolin, a reactive aluminosilicate phase (Antoni, 2011) formed after calcination of kaolinitic clays, and ground limestone (CaCO₃). Both materials are widely available and therefore are suitable to face the current shortage of SCMs (K. L. Scrivener et al., 2016). LC³ can achieve equivalent strength to OPC at 7 days with a clinker content of only 50% if the kaolinite content of the calcined clay used is above about 40% (Antoni et al., 2012; Avet & Scrivener, 2018a; K. L. Scrivener et al., 2018). The high reactivity of metakaolin contributes to achieve a refined microstructure in LC³ systems at early ages (Avet & Scrivener, 2018a), making LC³ a particularly good cement in terms of resisting chloride ingress (Sui et al., 2019).

2. Sulfate requirement of LC³ and cementitious systems

Calcium sulfate is added to clinker during grinding, to control the reaction of the aluminate phase. This addition is usually referred to as gypsum (Calcium sulfate dihydrate, CaSO₄·2H₂O) although anhydrite and hemihydrates (plaster) may also be present in combination with minor amounts of alkali sulfates from clinker. The optimum sulfate addition is that which gives the highest strength PC (at 1 or 28 days).

The main purpose of adding gypsum to PC and blended cements is to control the reaction of C₃A and thus to prevent flash setting (Lerch, 1946), however it is also known to influence the hydration kinetics of C₃S/alite (Quennoz & Scrivener, 2013; Zunino & Scrivener, 2020a) and the morphology of C-(A)-S-H (Mota et al., 2015; Zunino & Scrivener, 2022a). In the presence of gypsum, the hydration reaction of C₃A shifts from the precipitation of calcium aluminate hydrates and ettringite is formed (RILEM T.C., 1986). The mechanism by which gypsum slows down the reaction of C₃A has been extensively studied but is still a matter of debate. Originally it was suggested that a diffusion barrier is formed of ettringite or Ca-Al hydrates, retarding the dissolution of C₃A (Colleparidi et al., 1978; Corstanje et al., 1974). Recent work shows that there is no diffusion barrier and it is more tenable that the adsorption of sulfate (or Ca-S complexes) on C₃A active sites slows down the C₃A reaction (Geng et al., 2018; Minard et al., 2007; Myers et al., 2016). Usually, the adjustment of gypsum content is made based on the measurement of compressive strength at 24 hours in mortar specimens or by isothermal calorimetry (ASTM C563, 2018).

In LC³ cements (and blended cements in general), the total sulfate content is lower due to the partial replacement of PC by SCMs. In some cases, undersulfation of the system is observed, where the aluminate peak occurs before the alite (main) hydration peak (Quennoz & Scrivener, 2013; Zunino & Scrivener, 2020a). The balance of the system can be restored by the incorporation of additional gypsum to retard the aluminate reaction (Antoni et al., 2012; Avet & Scrivener, 2018a; Zunino, 2020). 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 (Zunino & Scrivener, 2020a):

- **Adsorption of sulfate on surfaces**, mainly C-(A)-S-H, during the induction and acceleration period (before the onset of the aluminate peak) (Zunino & Scrivener, 2019b). In LC³ (and blended cements), an increased amount of C-(A)-S-H forms due to the enhanced reaction of alite (filler effect), leading to an earlier depletion of solid gypsum and thus an earlier aluminate peak (Bentz et al., 2017; Zunino, 2020; Zunino & Scrivener, 2020a, 2019b).
- **The formation of ettringite before gypsum depletion** (i.e., before the onset of the aluminate peak). The amount of ettringite formed depends on the reaction rate of C₃A and the solubility of the sulphate source (Zunino & Scrivener, 2020a). In a recent study, the authors showed that the contribution of alumina from SCMs to sulfate balance is second order compared to the effect on

alite hydration and C-(A)-S-H precipitation rate. Particularly, the contribution does not seem to be related to the alumina content of the SCM (Zunino & Scrivener, 2022c).

This mechanism has been extended to cementitious systems in general, including PC and blended cements with limestone (PLC) and slag (Zunino & Scrivener, 2022c), and it has been validated far beyond the original scope of the study, for example, with the addition of alkali salts as accelerators (Yan et al., 2021). It highlights that, in addition to dissolution and supersaturation, adsorption of species (sulfate complexes) in surfaces can also influence the hydration kinetics of cementitious systems.

3. Precipitation of carboaluminates and relationship with mechanical properties

A major factor contributing to this good performance is the higher amounts of carbo-AFm ($\text{CO}_3\text{-AFm}$) phases, which will be referred as carbo-aluminate phases. These carbo-aluminate phases are hemicarboaluminate ($\text{C}_4\text{Ac}_{0.5}\text{H}_{12}$, Hc) and monocarboaluminate ($\text{C}_4\text{AcH}_{11}$, Mc), which are formed in LC^3 systems due to the reaction between metakaolin and limestone (Antoni, 2011; Avet & Scrivener, 2018a).

As shown in Figure 1, carboaluminates precipitate in pores left after clinker hydration, significantly contributing to space filling and mechanical properties development. In a recent study (Zunino & Scrivener, 2021a), the authors showed that the precipitation of carboaluminates is related with a feature observed in calorimetry curves of LC^3 systems, namely the third peak of hydration. This peak relates to the reaction of metakaolin with limestone and occurs with a maximum between 2 and 4 days of hydration depending on the metakaolin content of the system. By comparing the total heat released (proportional to the overall reaction degree) and in-situ ultrasound pulse velocity (proportional to elastic modulus/strength), a relationship between strength development in LC^3 and the third peak of hydration was established. Moreover, a fundamental/mechanistic explanation for well-known relationship (Avet & Scrivener, 2018a) between metakaolin content (which influences the kinetics of the third peak) and compressive strength between 3 and 7 days was provided.

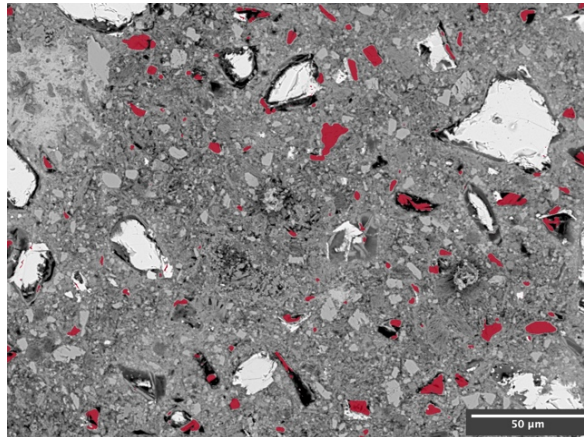
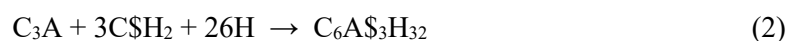
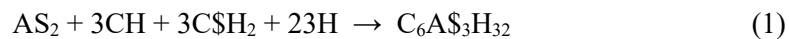


Figure 1: BSE maps of a typical LC^3 system sealed-hydrated for 3 days with $\text{CO}_3\text{-AFm}$ phase highlighted in red.

In addition to the total metakaolin content of the system, the precipitation of carboaluminates is also influenced by the sulfate content of the system and the water to binder ratio (Zunino & Scrivener, 2021a). In LC^3 systems, the formation of ettringite is only limited by the availability of sulfate (gypsum), as alumina from metakaolin is generally present in excess. When the amount of sulfate in the system is increased so it is the amount of ettringite formed. Eventually, C_3A is depleted, and the reaction is then sustained with alumina from metakaolin. This pathway to ettringite (Eq. 1) is deficient in calcium compared to the classical reaction involving C_3A (Eq. 2) and therefore CH is consumed in the process. As a result, the formation of carboaluminates is suppressed until sulfate depletion.



4. Long-term hydration of LC³ cements

In general, studies on LC³ systems have focused on early-age performance, i.e., from mixing up to about 90 days (Avet & Scrivener, 2018b; Zunino & Scrivener, 2021a). Different aspects on raw material processing (Zunino et al., 2020; Zunino & Scrivener, 2020b, 2021b), blend design (Antoni et al., 2012) and sulfate balance (Zunino & Scrivener, 2019a, 2020c), rheology (Hou, 2021), hydration kinetics (Avet et al., 2018; Avet & Scrivener, 2018b), morphology and properties of hydrates (Avet et al., 2019; Zunino & Scrivener, 2021a), and the synergic reaction of metakaolin and limestone (Zunino & Scrivener, 2021a) have been described in detail over this period. Most of the studies concerning later-ages are related to durability aspects of LC³ (Dhandapani et al., 2018, p. 3; Nguyen, 2020), rather than a detailed phase assemblage and microstructural assessment focused on hydration. In this regard, thermodynamic modelling is a useful tool to predict and extrapolate the phase composition of cements towards later ages (Lothenbach & Zajac, 2019). However, the complexity of LC³ systems makes this process challenging, information on reaction kinetics is still required to accurately predict the phase assemblage over time (Lothenbach et al., 2019; Lothenbach & Zajac, 2019).

In a recent study (Zunino & Scrivener, 2022b), a systematic look on the microstructural development of LC³ systems in the long term provided new insights in this regard. Strätlingite was observed for the first time in these types of binder in addition to Mc and Hc. More importantly, evidence for a continued (slow) reaction of metakaolin in the long term was provided, leading to an increased reduction in porosity between 90 days and 3 years. Based on CH consumption rates, it was estimated that the long-term reaction of metakaolin proceeds 10-to-20 times slower than at earlier ages.

Interestingly, the reaction of metakaolin seems to continue beyond depletion of CH. In this case, the required calcium to sustain the reaction is sourced from C-(A)-S-H, leading to a decrease in Ca/Si ratio. This observation, predicted by thermodynamic modeling before (Kunther et al., 2016), was confirmed experimentally for the first time in (Zunino & Scrivener, 2022b). The study also confirmed the long-term stability of Hc, despite the absence of this phase in thermodynamic modeling results. In a subsequent study, this stability is linked to the incorporation of sulfate in Hc (Georget et al., 2022). By comparing the pore size distribution with internal relative humidity, an hydration mechanism considering precipitation in the pore solution film lining the surface of larger pores was proposed (Zunino & Scrivener, 2022b).

5. Conclusions and perspectives

During the last 4 years, significant advances in the fundamental understanding of the hydration of LC³ cements have been achieved. Clear answers have been provided to some outstanding questions regarding binder formulation and long-term hydration performance. Based on these findings, the following concluding remarks can be drawn:

- The sulfate requirement of LC³ cements is associated with the surface area of the clay and limestone used, and not with the reactive alumina content of the system. Isothermal calorimetry appears as the most reliable method to assess and correct sulfation issues in complex binder formulations.
- Carboaluminates, as C-A-S-H, play a key role in the development of compressive strength in LC³ binders. The kinetics of the carboaluminate precipitation was described and explained the relationship between metakaolin content and strength of LC³ at early-age.
- The reaction of metakaolin continues in the long-term, leading to a decrease in the critical entry radius and a reduction in total porosity. While some conversion of Hc to Mc is observed, Hc is still present in significant amounts highlighting the long-term stability of this phase.

While progress has been significant, some open question remains. In general, our understanding on reaction kinetics and phase assemblage during the first 24 hours of hydration is limited compared to later ages. Shading light over this period is crucial to unveil outstanding issues for practice, such as workability (thixotropy, structural build-up, surface/admixture interactions) and early-age strength.

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