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Calcined clay – limestone cements: hydration processes with high and low-grade kaolinite clays

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Abstract. The development of ternary binders based on limestone and calcined clays appear as a promising way to increase the substitution of clinker. Their production is likely to remain limited if highly kaolinitic clays are required, but calcined clays with low metakaolin content are less reactive in a binary binder, as shown in many previous studies. This study focused on the difference, regarding hydration degree and products, between several binders containing calcined clay and limestone filler. Two calcined clays were studied, coming from two very different raw clays. The first calcined clay contained more metakaolin than the second one. In addition to ordinary Portland cement, four binders were analysed: two binary blends with 25% of cement substitution by the two calcined clays. Two ternary binders, composed of 30% of calcined clay and 15% of limestone filler, were also studied, using both calcined clays. Binary binders showed strong differences between the two calcined clays. However, this work showed that in a ternary binder, significant pozzolanic activity and synergy between calcined clay and limestone filler were observed even for the composite calcined clay with minor metakaolin content. From this comprehensive study on hydration, it can be concluded that calcined clay with low metakaolin content is likely to result in the same degree of hydration and products at long-term as high metakaolin calcined clay in a ternary system.

Keywords: metakaolin, illite, calcined clay, supplementary cementitious materials, ternary blend, hydration.

1. INTRODUCTION

Supplementary cementitious materials (SCMs) are a well-known alternative to partially substitute clinker and reduce CO₂ emissions related to cement production. Fly ash, blast furnace slag or silica fume have been widely studied ([1]–[5]), hydration mechanisms are now quite well understood ([6]) and they are the most commonly used SCMs. However, the use of these SCMs becomes limited worldwide due to the lack of availability of these materials. More attention has been given recently to calcined clays, and more specifically obtained from kaolinite-rich clay, in order to reduce clinker factor ([7]–[10]). These materials are widely available on the earth crust and they show relatively high reactivity, depending on their chemical and mineralogical composition. Calcined kaolinite, called metakaolin, reacts with the portlandite from cement hydration to form new hydration products which enhance, in some cases, mechanical properties and durability. Many studies have already reported results about these binary binders (cement and calcined clay). Ternary binders have also been developed for most SCMs as a combination of cement, SCM and limestone filler ([4], [5], [8], [11], [12]). Limestone filler is likely to induce several physical and chemical interactions between clinker phases, hydration products, and SCMs. Limestone particles fill in the empty spaces so they improve the packing density and create more nucleation sites for hydration products to grow. A chemical effect can be observed as well which can also promote the formation of new hydrates. Instead of forming monosulfoaluminate, the presence of limestone would allow the formation of carboaluminates by favouring the insertion of aluminates brought by the SCMs ([8]).

The most studied calcined clay so far is metakaolinite, resulting from the calcination of kaolinite clay ([13], [14]). However, pure kaolinite clays are relatively scarce and they are expensive because of the use of kaolinite in paper and ceramic industry [11]. Natural soils are generally composed of different types of clays. In this paper, the term “calcined clay” is used and it refers to a complex material resulting from the calcination of a natural soil containing different clayey minerals and other phases. When the raw material has a low content of kaolinite (before calcination), it can be called “low-grade” kaolinitic clay. Such a material can also contain illite or montmorillonite for example. The term “composite” clay is also used to refer to this raw (or calcined) material containing different types of clays. For the past few years, several studies have focused on the use of soils containing different types of clayey minerals, with a low kaolinite content as calcined clays in binary and ternary binders. Other clayey minerals, such as illite or montmorillonite ([15]–[19]), and the corresponding products after calcination, have been studied and their use as SCMs is quite promising.

The recent studies on “low-grade” calcined clay mainly focused on the hydration and performances of binary binders ([16], [18], [20], [21]) with relatively low proportions of calcined clay. Such results on binary binders containing low-grade kaolinitic or natural calcined clays are very promising and

encouraging ([18], [22], [23]). Ternary binders based on calcined clay and limestone are likely to lead to different results. Low-grade calcined clays combined with limestone filler are likely to approach the same properties as highly kaolinitic calcined clays ([24], [25]) but ternary binders need further investigations ([26]–[28]) as proposed in the present study.

Besides, it has been demonstrated that the reactivity of blended cements is highly correlated to the clinker hydration. If calcined clay with high metakaolin content is used in low clinker system, the availability of portlandite actually becomes an issue, and lower degree of hydration of clinker has been observed ([19]). It is not easy to generalize on the behaviour on calcined illitic clays, as their reactivity depend on the proportion, calcination temperature ([18]) and calcite content of raw clay ([20]). The behaviour of mixed kaolinitic-illitic clay is all the more complex as the optimal calcination temperatures of both clays are not the same. Comprehensive studies on the hydration of binary and ternary systems with composite clays cannot be easily found, however understating the behaviour of these complex systems is necessary to develop efficient low-clinker binders.

The use of illitic clays or composite clays (with mixed kaolinite and illite), is interesting in order to adapt and create alternative ternary blends depending on the available clay deposit. To carry on the investigations on the use of low-grade and composite calcined clays as SCMs, this work focuses on the comparison between one mainly kaolinitic clay and another clay containing kaolinite and illite. Both clays were calcined at 850°C even though kaolinite and illite do not have the same activation temperature. It has to be noted that the choice of 850°C may not allow to take the most out of the illite potential ([16], [29]), but beyond 900°C kaolinite turns into mullite and reactivity is then lower. This study aims at comparing and understanding the reactivity of calcined clays originating from two significantly different natural clays, namely: a composite clay containing both kaolinite and illite, and a mainly kaolinite clay. Synergistic effect between limestone filler and low-grade kaolinitic calcined clay is studied to demonstrate that such clays can be as valuable as pure metakaolin clays in ternary binders.

In order to study the hydration processes of alternative binders (binary and ternary) containing Portland cement, calcined clays and limestone filler in the case of ternary binders, advanced characterization techniques were used in this study such as X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), and solid-state Nuclear Magnetic Resonance (NMR). These techniques, among others, allow the characterization of hydration products and help to investigate the consequences of using a low-grade or composite calcined clay over a more kaolinitic calcined clay. A multi-method approach is then adopted and hydration reactions of five mixtures can be monitored, from early-age behaviour to long-term phase assemblage.

2 MATERIALS AND METHODS

2.1 Materials

Grey Portland cement of type CEM I 52.5R was used in all mixtures. Two different calcined clays were used, both calcined between 800 and 850°C but from different raw clays. The first clay, called “CC1”, contained 68% of metakaolin, and was produced in a rotary kiln calciner ([30]). The second one, called “CC2”, contained 21% of metakaolin (determined by TGA) and it was obtained through flash calcination. Chemical composition measured by X-Ray Fluorescence and physical properties of the powders are given in Table 1. In the chemical characterization, *Others* refers to minor oxides (or impurities) present in relatively low quantities in the materials.

Table 1: Chemical composition and physical properties of anhydrous materials

	Cement (PC)	CC1	CC2	Limestone filler (LF)
Chemical composition [wt%]				
SiO ₂	20.1	59.2	55.8	4.2
Al ₂ O ₃	5.5	33.8	24.5	1.5
Fe ₂ O ₃	3.2	1.2	7.2	0.8
CaO	62.5	0.2	4.7	51.4
Na ₂ O	0.2	0.1	0.3	0.1
MgO	2.0	0.1	3.4	0.8
<i>Others</i> ¹	5.6	2.4	4.3	-
LOI	0.93	1.87	2.44	40.8
Physical properties				
d ₅₀ [μm]	11.5	5.9	11.0	6.0
BET surface [m ² /g]	1.2	18.2	19.3	5.3

¹SO₃, K₂O, SrO, TiO₂, P₂O₅ and MnO

The mean particle diameter d₅₀ was determined using a particle sizer with laser diffraction in ethanol. The specific surface area of the powders was obtained through an analysis from Brunauer, Emmett and Teller (BET) theory.

The mineralogical compositions of studied materials are given in Table 2. The composition was assessed using X-Ray Diffraction coupled with Rietveld external standard method (detailed further). A large amount of calcined illite, hard to quantify by TGA, has to be considered in CC2. A proportion of the difference between metakaolinite content and amorphous phase content calculated by XRD comes from calcined illite, which allows to distinguish CC2 from CC1.

Five different binders were studied: one based on Portland cement (PC₁₀₀) and the four others containing calcined clay. The composition of the five different blends is given in Table 3. The sulfate content was not adjusted. This will be discussed in section 3.3 from the study of early-age hydration.

Table 2: Mineralogical composition of the main components (wt%)

	PC	CC1	CC2	LF
Alite	57.0	-	-	-
Belite	17.1	-	-	-
Tricalcium aluminate	7.6	-	-	-
Tetracalcium alumino ferrite	11.1	-	-	-
Anhydrite	4.3	-	-	-
Portlandite	0.7	-	-	-
Sulfurs	1.3	-	-	-
Quartz	0.1	18.0	13.0	2.4
Calcite	0.5	-	1.2	93.3
Dolomite	-	0.1	-	-
Chlorite	-	2.3	1.2	0.8
Kaolinite	-	3.6	0.6	-
Muscovite / illite	-	1.3	11.4	0.7
Hematite	-	-	1.4	0.1
Periclase	0.4	0.3	0.2	-
Microcline	-	3.1	5.3	-
Anatase	-	1.6	0.0	-
Ankerite	-	-	-	1.5
Magnesite, siderite	-	-	-	1.2
Amorphous	-	69.7	65.5	-

Table 3: Composition of studied binders (in wt%)

	PC	CC1	CC2	LF
PC ₁₀₀	100	-	-	-
PCC ₁₂₅	75	25	-	-
PCC ₂₂₅	75	-	25	-
PCC ₁₃₀ LF ₁₅	55	30	-	15
PCC ₂₃₀ LF ₁₅	55	-	30	15

2.2 Mixtures and preparation of samples

The study was performed on pastes with a water to binder ratio of 0.50. For all analyses, except for isothermal calorimetry, a batch of 800g of binder was mixed with water for 3 minutes at 140 rpm and then cast in small plastic containers sealed for 24 hours. After demolding, samples were kept in water at 20°C until the stoppage of hydration to allow TGA, XRD and NMR analyses. The sample was first ground at 1.25 mm and immersed in acetone for 30 minutes. A vacuum filtration was performed and the sample was immersed in diethyl ether for 30 minutes before a second vacuum filtration. The sample was then dried at 40°C and ground at 100 µm to perform the analyses. This protocol was executed following the study of Schmitt ([31]) knowing that it can generate some modifications on a microstructural level, especially on calcium hydroxide ([32]). However, as seen in the first chapter of [33], all the different protocols for hydration stoppage can cause some alterations.

2.3 Testing procedures

2.3.1 Isothermal calorimetry and degree of reaction

Isothermal calorimetry was performed at 20°C with a TAM Air 3-channel device from TA Instrument. Heat flow $q(t)$ and cumulated heat $Q(t)$ were recorded for seven days. Around 600 grams of binder was mixed with water (water to binder ratio of 0.5) in a mixer compliant with the EN-196-1 standard [34]. 90 grams of paste were weighed and put in a glass pot which was sealed and put inside the channel. The first 45 minutes were not recorded as the opening of the device impacts the signal. Heat flow and cumulated heat were normalized regarding the mass of Portland cement present in each mix.

The degree of reaction can be estimated from the results of isothermal calorimetry tests. It can be approximated as the ratio of the heat of hydration $Q(t)$ to the ultimate heat of hydration Q_∞ [35]. An extrapolation of the curve to 0 on the Y axis provides the Q_∞ value. The illustration of this method is shown in figure 1.

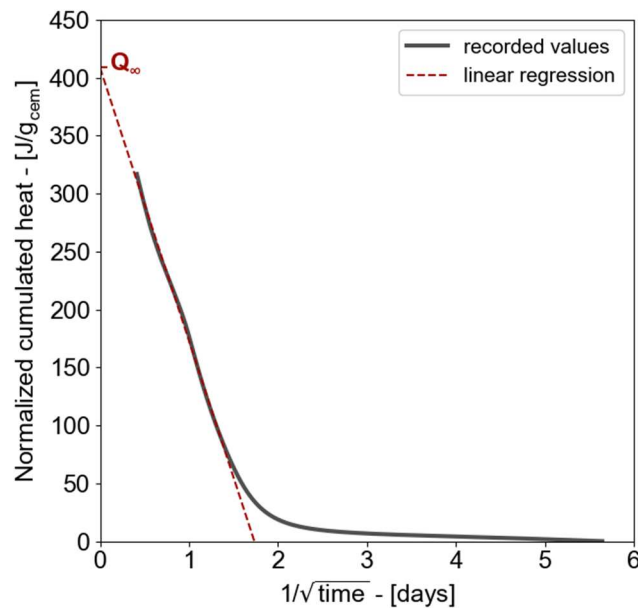


Figure 1: Graphical method to determine Q_∞ for PC₁₀₀

The degree of hydration α is then approximated by the extent of reaction ξ following equation (1).

$$\alpha(t) \approx \xi(t) = \frac{Q(t)}{Q_\infty} = \frac{\int_0^t q(t)dt}{Q_\infty} \quad (1)$$

Minimum 2 tests were carried out for each of the different blends. Due to the high sensitivity of the device, standard deviation of Q_∞ is estimated between 2 and 15 J/g.

2.3.2 Thermogravimetric analysis – determination of bound water and portlandite content

TGA was used to determine the amount of bound water and CO₂ released while heating. Analyses were performed on Netzsch STA 449 F3 instrument. 100 mg sample were put into alumina crucible for each experiment. The temperature increased from 30 to 1000°C at the rate of 10 °C/min.

Bound water and portlandite contents are determined from TGA results. Bound water represents the amount of water released by hydration products during the heating of the sample. Bound water content is calculated by adding mass loss between 40°C and 400°C (using the stepwise method) and water loss between 400 and 550°C approximately (using tangent method). The choice of starting the measurements at 40°C has been made as some monocarbonate can start to decompose around 45°C, some C-S-H can decompose around 50°C and ettringite starts to decompose around 80°C (Lothenbach et al. [36]).

Portlandite content value (found with tangent method between 400 and 550°C) must be corrected for binary binders with the mass loss between 550 and 850°C corresponding to the CO₂ released by the decomposition of CaCO₃ formed from carbonated portlandite. Portlandite content CH_{tot} is calculated using the formula suggested by Kocaba [37] (equation 2).

$$CH_{tot} = \Delta CH \times \frac{M_{Ca(OH)_2}}{M_{H_2O}} + C\bar{C}_{Ca(OH)_2} \times \frac{M_{Ca(OH)_2}}{M_{CO_2}} \quad (2)$$

where ΔCH is the mass loss corresponding to dehydration of portlandite, $M_{Ca(OH)_2}$ molar mass of portlandite, M_{H_2O} water molar mass, $C\bar{C}_{Ca(OH)_2}$ the content of carbonated portlandite and M_{CO_2} molar mass of carbon dioxide.

For ternary binders, equation (2) cannot be used as carbonated portlandite must be distinguished from calcite brought by initial limestone filler. In this case, average amount of carbonated portlandite is calculated from the other samples (assuming that all the samples are kept under the same conditions before analysis) and this amount is taken into account for ternary binders.

The results are expressed in g per 100g of anhydrous binder. Standard deviation of bound water and portlandite content is estimated around 0.15 g/100g of anhydrous binder.

2.3.3 X-Ray diffraction

XRD analyses were carried out on a Bruker D8 Advance instrument in a θ - θ configuration using CuK α source. Scanning program consisted in rotating between 5 and 80°2 θ with a step size of 0.005°2 θ and a time per step of 0.5s. Phase quantification was made on the software Topas 5.0 from Bruker with Rietveld analysis using rutile as external standard. Rutile XRD analysis was systematically performed the same day as the samples analyses to ensure the same environmental conditions and scanning program. Rutile analyses are needed to determine k-factor which is then applied to the

studied sample for the determination of the amorphous phase amount (also called non-diffracting phase).

2.3.4 Solid-state nuclear magnetic resonance

Solid-state ^{29}Si NMR spectroscopy was performed on a 300 MHz Bruker NEO. ^{29}Si magic-angle spinning (MAS) spectra were obtained with a single $\pi/2$ pulse excitation using a 7mm MAS probe. MAS frequency was set to 5 kHz. The repetition time was checked and 2s was found sufficient for full relaxation between scans. Solid-state ^{27}Al NMR spectroscopy was performed on a Bruker Avance III 500 MHz spectrometer. Spectra were acquired with a single pulse excitation of $\pi/13$ using a 2.5 mm MAS probe. MAS frequency was set to 30 kHz and repetition time at 1 second. ^1H decoupling was systematically used during acquisitions. Spectra were referenced against TMS (tetramethylsilane) and an $\text{Al}(\text{NO}_3)_3$ aqueous solution for ^{29}Si and ^{27}Al respectively. It should be noted that the significant iron content in the materials (both Portland cement and calcined clay) made the experimental data more difficult to analyze. The presence of iron can cause magnetic disturbances, especially in ^{27}Al solid-state NMR, and it alters the shape of the peaks (Maia et al. [38], Alujas et al. [16]).

The results from MAS NMR analysis cannot be used for absolute quantification. The iron content in grey cement and calcined clay has a large impact on NMR analysis. The presence of iron in the tested materials decreases the resolution of the spectrum but it does not affect the position of the peak.

3. RESULTS AND DISCUSSION

3.1 Hydration products

The products of hydration reactions can be observed and quantified with XRD analyses. Depending on the type of calcined clay used in the binder and on the type of binder (binary or ternary), hydration products are different. Figures 2a, b and c show the XRD patterns for the studied systems after 2, 28 and 90 days of hydration.

After two days of hydration, the two main phases detected by XRD are portlandite and ettringite; the peaks associated to monosulfoaluminate and hemicarboaluminate can be slightly identified in both binary blends. In both ternary binders, PCC₁₃₀LF₁₅ and PCC₂₃₀LF₁₅, combining calcined clay and limestone, hemicarboaluminate and monocarboaluminate can be distinguished. This can be explained by the presence of limestone, which prevents the formation of monosulfoaluminate from ettringite, as confirmed by 28-days results (figure 2b).

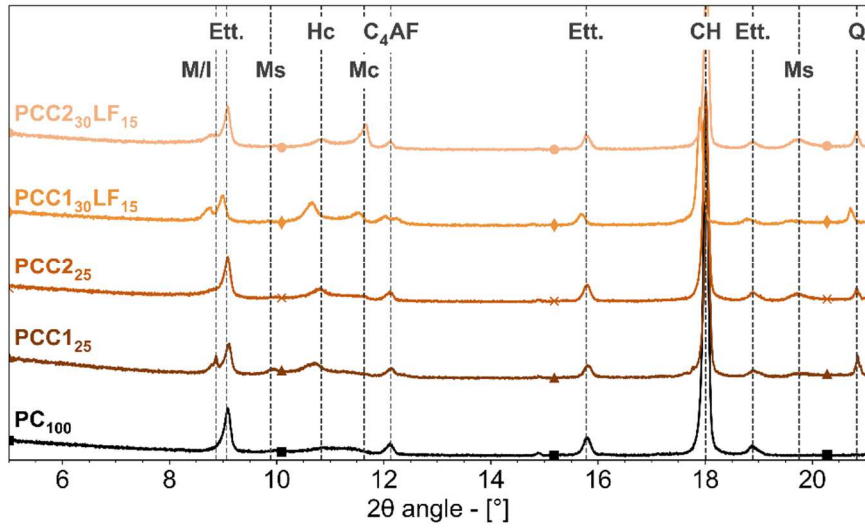


Figure 2a: XRD pattern after 2 days of hydration

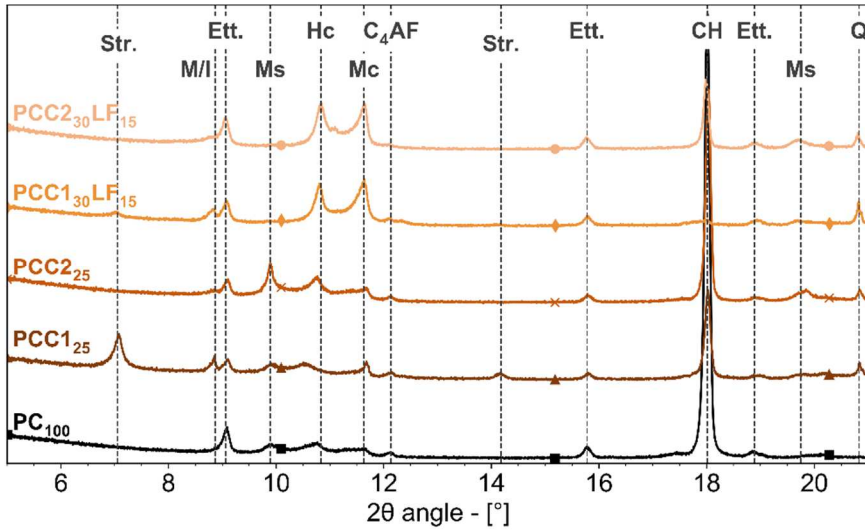


Figure 2b: XRD pattern after 28 days of hydration

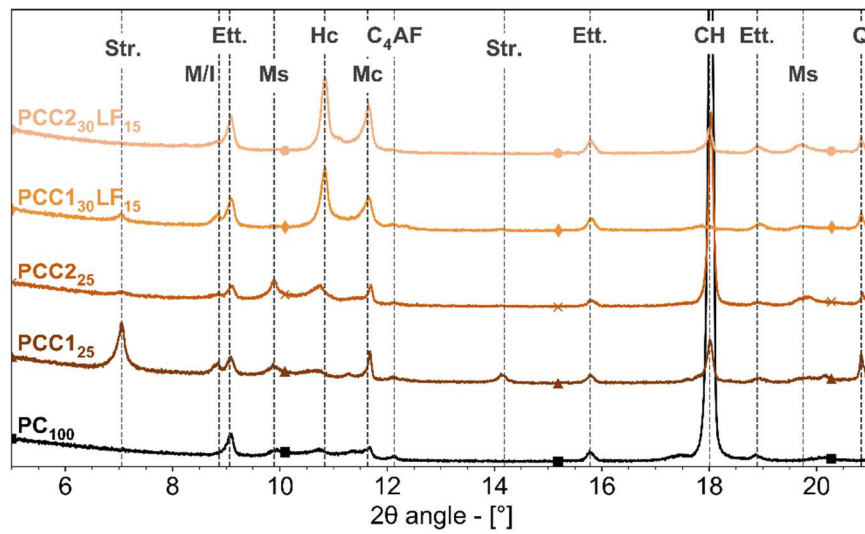


Figure 2c: XRD pattern after 90 days of hydration

Figure 2: XRD pattern for the three different blends at 2, 28 and 90 days of hydration
 (Str. – strätlingite, M/I – muscovite/illite, Ett. – ettringite, Ms – monosulfate, Hc – hemicarboaluminate, Mc – monocarboaluminate, C₄AF – tetracalcium aluminate iron, CH – portlandite, Q – quartz)

Carbonate-rich phases are actually more stable than sulphate-rich hydration products, due to the chemistry of solutions based on carbonate and sulphate ions. Although not clearly visible on figure 2, portlandite content was always higher for PC₁₀₀. As showed later in figure 3b, portlandite content was lower in PCC1₂₅, PCC2₂₅, PCC1₃₀LF₁₅ and PCC2₃₀LF₁₅ due to clinker dilution effect and secondary hydration reactions and thus the TGA and XRD results seem consistent.

After 28 days of hydration, the chemical effect of limestone filler clearly appears with the large formation of hemi- and monocarboaluminate in PCC1₃₀LF₁₅ and PCC2₃₀LF₁₅. The formation of carboaluminates instead of monosulfates sets more sulphates free and available to form more ettringite [8]. This is observed in figure 2b where ettringite content seems to be slightly higher in PCC1₃₀LF₁₅ and in PCC2₃₀LF₁₅ than in the other blends. At 28 days, in the binary blend PCC2₂₅ monosulfoaluminate was largely formed, more than in PCC1₂₅. However, the blend PCC1₂₅ shows the formation of strätlingite (C₂ASH₈)¹. This result can be explained by the composition of the calcined clay used in PCC1₂₅, with higher alumina content. Strätlingite also slightly appeared in PCC1₃₀LF₁₅ from 28 days. In presence of limestone the content seems lower than in a binary binder containing the same calcined clay. Such results are confirmed by Antoni et al. [8]. At this stage of the reaction, PC₁₀₀ started to form monosulfoaluminate.

After 90 days of hydration, the trends observed at 28 days are reinforced. The chemical effect of limestone filler favoured the formation of more carboaluminates instead of monosulfate in PCC2₃₀LF₁₅ and strätlingite kept growing in PCC1₂₅. Ettringite content remained significant for PCC2₃₀LF₁₅.

The PC₁₀₀ mixture showed the highest portlandite content (figure 3b). All the blends containing calcined clay indicate portlandite consumption. When comparing both 25% substitution binary blends, PCC2₂₅ had a higher portlandite content which suggests that CC2 has a lower pozzolanic potential than CC1. Concerning ternary binders, the results on figure 3b show that both binders PCC1₃₀LF₁₅ and PCC2₃₀LF₁₅ had the lowest portlandite content during hydration. The decrease of portlandite content was slower for PCC2₃₀LF₁₅ than PCC1₃₀LF₁₅ but both binders resulted in the same ultimate portlandite content. Pozzolanic and secondary hydration reactions seem to be as effective for a blend containing a lower mekaolinitic calcined clay as for a blend containing a higher content of metakaolinite. In general, limestone filler present in ternary blends interacts with calcined clay and promotes secondary reactions (such as the formation of carboaluminates) inducing the consumption of portlandite. The use of a mainly kaolinitic clay in ternary blends is not necessarily required from the point of view of hydration. The interaction and synergy between calcined clay and limestone filler was significant even for a composite clay.

¹ Notations: C – CaO, A – Al₂O₃, S – SiO₂, H – H₂O

From figures 2, it can be observed that the behaviours during hydration are different when using on the one hand a mainly metakaolinitic calcined clay and on the other hand a composite calcined clay. Hydration products are also different from binary and ternary binders. Bound water and portlandite contents deduced from TGA can help identifying the impact of mineral additions and quantifying hydration products in every blend.

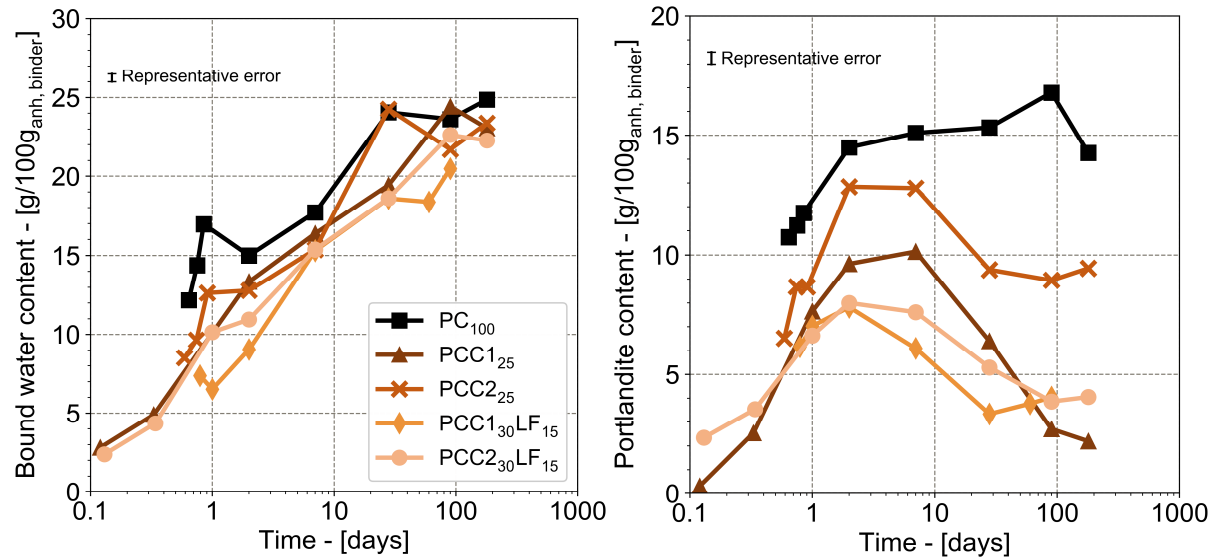


Figure 3a: Bound water content

Figure 3b: Portlandite content

Figure 3: Bound water and portlandite content (per g of anhydrous binder)

Figure 3a shows the evolution of bound water content for the five different binders. This graph shows that bound water contents were similar for all the blends. The amount of hydrates formed during hydration reaction was actually the same at long-term. However, the comparison between figures 3a and 3b demonstrates that blended systems such as PCC1₂₅, PCC1₃₀LF₁₅ and PCC2₁₅LF₃₀ probably had different hydration products than PCC2₂₅ or PC₁₀₀. As bound water content was almost the same but portlandite contents were significantly different, different sets of hydration products were formed.

Calcined clay contains a non-negligible amount of amorphous material, coming from the calcined kaolinite and illite. The amount of amorphous phase present in the anhydrous blend as well as the amorphous phase forming during hydration (primary C-A-S-H and secondary forming after pozzolanic reaction) are difficult to distinguish in XRD. That is why solid-state NMR is a useful technique as it allows the detection and analysis of amorphous phases. The following results give an overview of ²⁹Si and ²⁷Al NMR analysis made on some of the blends at different stages of hydration.

Figure 4 shows ²⁹Si MAS NMR spectra of three blends: PC₁₀₀, PCC1₂₅ and PCC2₂₅ after two days of hydration. As described in Engelhardt ([39]) study, the local environment of one SiO₄ tetrahedra can

be deduced from the chemical shift data, extracted from NMR spectrum. One SiO_4 tetrahedra linked to n other tetrahedra is conventionally described as follow: Q^n ([39], [40]). In hydrated cement pastes, the Q^0 peak on figure 4 corresponds to unreacted cement in the mix, as showed by Richardson et al. ([40]–[42]) while Q^1 and Q^2 generally refer to the C-S-H ([40], [43]).

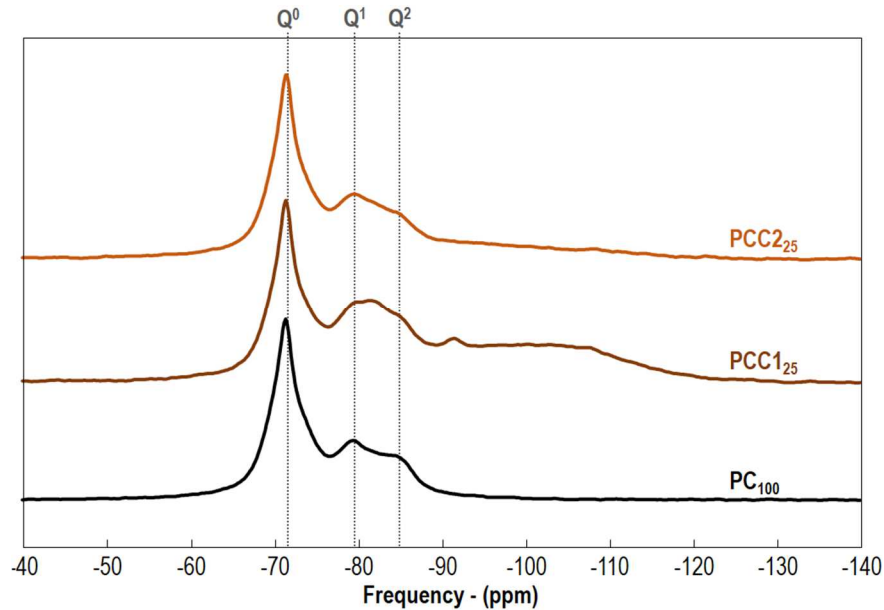


Figure 4: ^{29}Si MAS NMR spectra after 2 days of hydration

After two days of hydration, PC_{100} and PCC_{25} tend to have similar ^{29}Si signatures whereas PCC_{125} is slightly different. The results presented in figure 3.b actually show a lower contribution of CC2 to secondary reactions than CC1 at early age. Differences can be seen mainly around -82 ppm where $Q^2(1\text{Al})$ sites are visible in PCC_{125} . The presence of $Q^2(1\text{Al})$ (explained in more details further) transcripts the incorporation of aluminate into silicate chains. In PCC_{125} this could be due to the higher quantity and availability of aluminate in CC1 thanks to the higher aluminium content (Table 1). The influence of a less metakaolinitic calcined clay on cement hydration is not significant from ^{29}Si NMR results. The broad small peak between -90 and -115 ppm illustrates the presence of metakaolin ([14], [44], [45]). This peak is largely visible on PCC_{125} signature meaning that at two days there was still some metakaolin in PCC_{125} , in a larger quantity than in PCC_{25} . It is important to recall that the initial metakaolin content was higher in CCA. If metakaolin was detectable this means that it had not fully reacted yet. These results come to confirm previous results from figure 3b as this one showed that pozzolanic reaction was still low after 2 days of hydration. Metakaolin has just started to react with portlandite and thus it is still largely present in hydrated pastes, more especially PCC_{125} .

Figure 5 shows the three blends ^{29}Si MAS NMR signatures after 180 days of hydration.

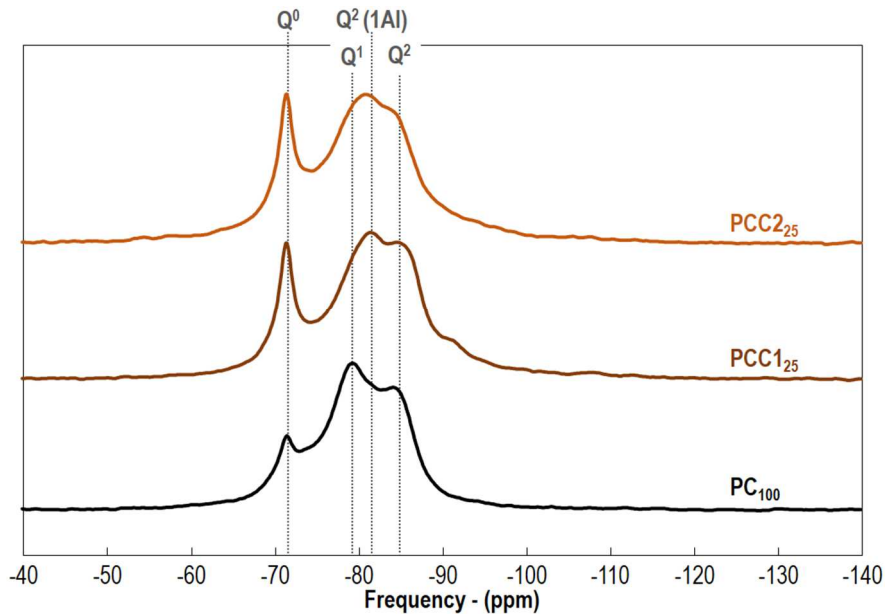


Figure 5: ^{29}Si NMR signature after 180 days of hydration

At 180 days, the apparition of Q^2 (1Al) in both PCC₁₂₅ and PCC₂₅ is a strong indicator of the impact of calcined clay on the hydration products ([46], [47]). As explained in previous studies ([47]–[49]), Q^n (1Al) represents a SiO_4 tetrahedron linked to n other tetrahedra in which one is a AlO_4 tetrahedra (silicium replaced by aluminium). Q^2 (1Al) could be detected on PCC₁₂₅ sample at 2 days as a shoulder between Q^1 and Q^2 peaks (figure 4) and at 28 days for PCC₂₅ (appendix). Aluminates from the calcined clay are actually incorporated into C-S-H during the hydration reaction to form aluminium-modified calcium silicate hydrate (C-A-S-H). As demonstrated in Dai et al. ([45]), $\text{Al}(\text{OH})_4^-$ ions are incorporated in the silicate structure of C-S-H by bridging SiO_4 tetrahedra. The chemical composition of metakaolin allows to increase the total Al/Si ratio of the blend and facilitate the $\text{Al}(\text{OH})_4^-$ ions incorporation into C-S-H chains, especially when using a material with a large amount of metakaolin (Avet et al. [50]). The presence of Q^2 (1Al) confirms the formation of C-A-S-H in both blends PCC₁₂₅ and PCC₂₅, either from a mainly kaolinitic clay or with a less kaolinitic clay. This result is promising for the use, after calcination, of a less kaolinitic or composite raw clay in such systems. Relative quantities of belite, identified from Q^0 peak, and C-S-H (Q^1 and Q^2), between 2 and 180 days of hydration in all the systems tend to show that belite has a slower reactivity in binary binders than in the reference binder. Results will be further discussed in this paper (section 3.2).

Besides ^{29}Si MAS NMR, additional information on the hydration of studied binders can be provided by the aluminium environment through ^{27}Al MAS NMR. It allows the distinction of the different coordination sites of aluminium. Results on figure 6 show spectra for both calcined clays and both binary blends PCC₁₂₅ and PCC₂₅ after 28 days and 180 days of hydration.

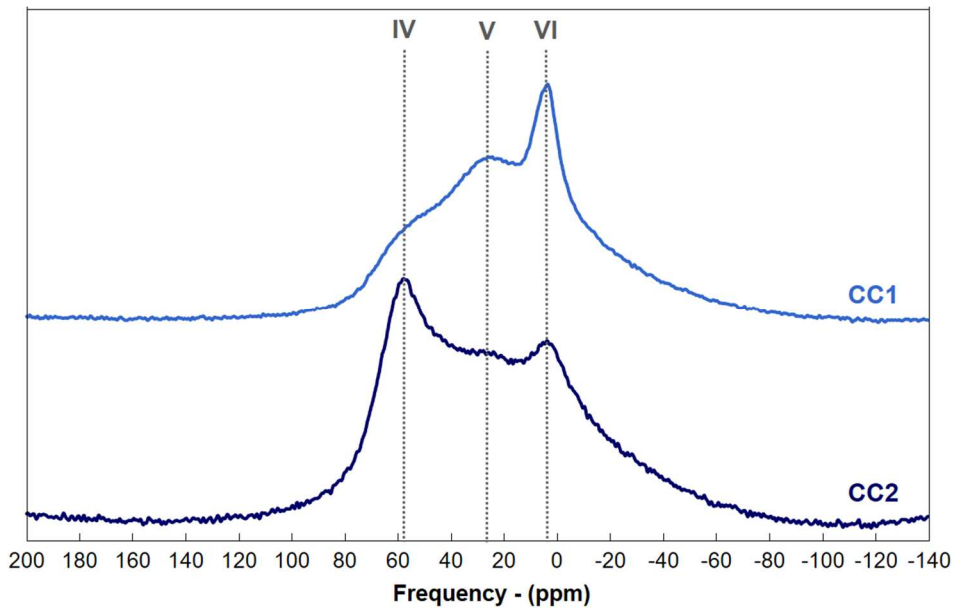


Figure 6a: ^{27}Al MAS NMR signature of CC1 and CC2

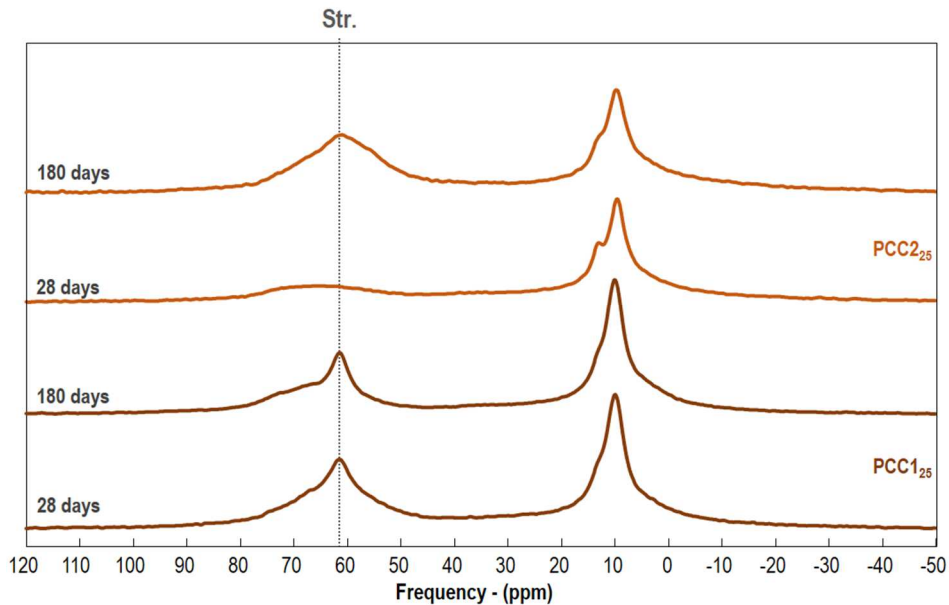


Figure 6b: ^{27}Al MAS NMR spectra of pastes at 28 and 180 days

Figure 6: ^{27}Al MAS NMR spectra for both calcined clays and hydrated pastes

On figure 6a, differences between the two calcined clays are clearly visible. Three main peaks can be distinguished, corresponding to the three aluminium coordination: tetra-, penta- and octahedral. The position of the peaks on ^{27}Al spectra are consistent with previous studies on calcined clays. The ^{27}Al spectra of kaolinite mainly shows Al[VI] (Coudert et al. [51]). After calcination at 800°C , Al[V] is mainly produced in kaolinite whereas Al[IV] appears in illite and montmorillonite. The peaks with the highest amplitude in CC1 and CC2 are respectively assigned to aluminium in octahedral (Al[VI]) and tetrahedral (Al[IV]) coordination (Alujas et al. [16]). The calcination of clays actually results in lower Al[VI] peak and higher Al[IV] and Al[V] peaks (Fernandez et al., [29]). The heating of illite-riche clay

above 800°C induces a transition from Al[VI] to Al[IV] due to the dehydroxylation without any other strong modification in the crystallographic structure. The calcination of kaolinite is characterized by a different decomposition process with significant disorder in the crystal structure. Fernandez et al. observed that Al[V] peak prevailed at 800 °C for calcined kaolinite, whereas for CC1 the amplitude of Al[V] peak was lower than the Al[VI] peak. Results on figure 6a are consistent with kaolinite-rich clay for CC1 and mixed kaolinite and illite clay for CC2. Fernandez et al. also concluded that the presence of 5-coordinated aluminium is a key parameter for the pozzolanic activity of calcined clay. CC1 actually induced higher portlandite consumption (figure 3b), especially at long-term in binary binders.

Figure 6b shows the formation of strätlingite at 28 days for PCC1₂₅. As detected in XRD, strätlingite formed earlier for PCC1₂₅ than PCC2₂₅. Later strätlingite formation has actually been associated with slower pozzolanic reaction (Cyr et al. [52]), which is consistent with TGA results in terms of portlandite consumption (figure 3b). The formation of AFm-type phases prevailed over ettringite in blended systems, especially for CC1. This result can be related to the additional alumina content brought by the calcined clay in the system increasing the overall alumina-to-sulphate ratio. High pH and calcium-rich binders favour the formation of stable C-A-S-H and strätlingite. These data confirm the results obtained by Garcia-Lodeiro et al. ([53]) on synthetic materials.

3.2 Clinker hydration

Figure 7 shows the correlation between heat flow curves and XRD-Rietveld phase evolution during the first two days of hydration. Figures 7a and 7b refer to PC₁₀₀ and PCC2₂₅ respectively. Heat flow curves can be divided into 4 different stages, well described for example by Hesse et al. ([54]), and plotted on figures 7a and 7b.

As described by Hesse et al. [54] on synthetic cement, the total dissolution of anhydrite matches with the second peak observed on heat flow curves occurring during stage III. In figure 7a and figure 7b, anhydrite is the main sulphate source in the system and aluminate peak corresponds to the full dissolution of anhydrite. However, two observations differ from Hesse et al. [54] concerning aluminate peak. On figure 7a, even though total dissolution of anhydrite is clearly observed, C₃A content is decreasing but never reaches the total dissolution after 48 hours of hydration. The complete dissolution of C₃A appears later. Besides, ettringite formation does not seem to accelerate during the period corresponding to aluminate peak, which is in accordance with the results of Jansen et al. ([55]) on ordinary Portland cement. Even after 48 hours of hydration ettringite has not reached yet its maximum content.

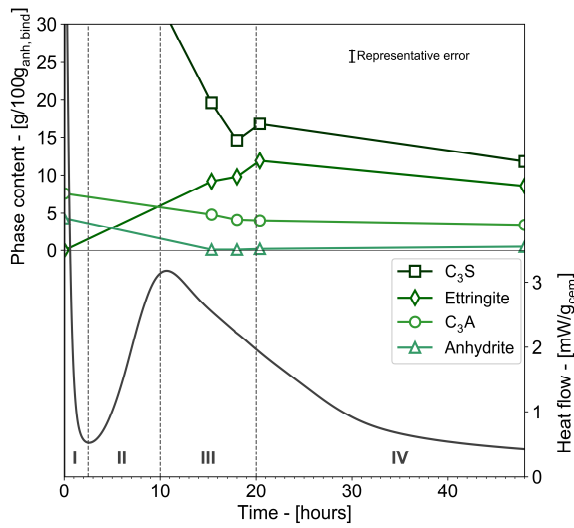


Figure 7a: Results for PC₁₀₀

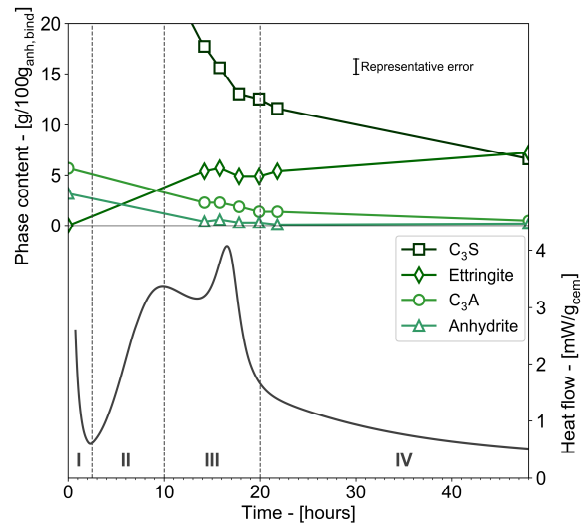


Figure 7b: Results for PCC₂₅

Figure 7: Correlation between XRD results and calorimetry

When looking at both figures 7a and b, there are no fundamental differences in the evolution of phase content. Both evolutions show that the aluminate peak coincides with a slowdown of alite dissolution. Heat flow curves show significant differences with a more intense aluminate peak for PCC₂₅ but this cannot be attributed to differences between PC₁₀₀ and PCC₂₅ in terms of phase content evolution. The values are different but trends are similar. Correlation between isothermal calorimetry and XRD analyses confirm that the substitution of cement by calcined clay does not affect the hydration of main clinker phases at early age. The ternary binder with CC2 does not result in undersulfation as previously observed with pure metakaolin ([8]). The use of CC2 even results in higher cumulated heat at 24 hours, as seen later in section 3.3 (figure 12). This higher cement hydration heat can be partly attributed to the significant aluminate peak (Jansen et al. [55]). Calcined clay also results in better hydration of cement during the silicate peak. Thus the results allow to assume a coupling between the enhanced hydration of silicate and aluminate at short-term.

The values of Q_{∞} (given later in Table 4) allow calculating the degree of hydration of the studied binders at different times (figure 8). The overall hydration degree estimated from calorimetry is similar for all the blends. This result seems consistent with the evolution of bound water presented in figure 3.a, as the values were similar especially from 7 days.

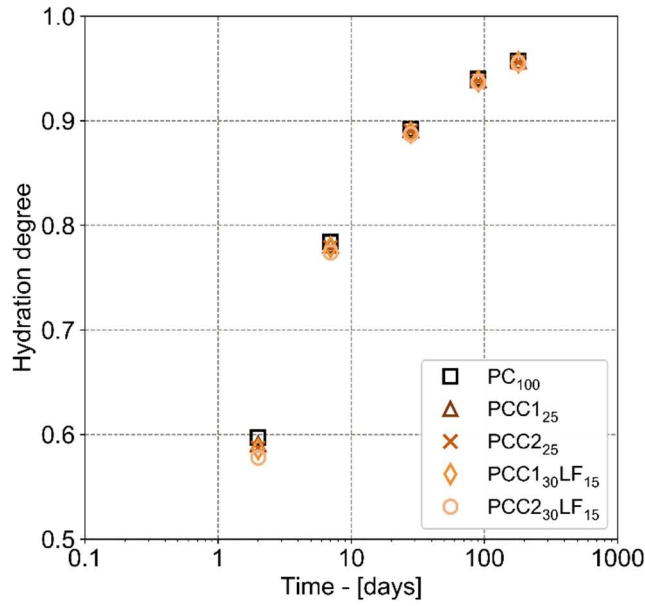


Figure 8: Hydration degree deduced from isothermal calorimetry

The clinker degree of hydration DoH can also be calculated by XRD. For each clinker phase (C_3S , C_2S , C_3A and C_4AF), DoH is found according to equation (3), where W_j refers to the weight of each phase j , the index 0 refers to anhydrous state and t corresponds to the time considered for the calculation:

$$DoH_{j,t} = \frac{W_{j,0} - W_{j,t}}{W_{j,0}} \quad (3)$$

As indicated on figure 9a C_3S hydration degree is similar for the three blended systems PCC₁₂₅, PCC₂₂₅, PCC_{130LF15} and PCC_{230LF15}. At early ages it seems that C_3S hydration degree in PC₁₀₀ was lower. The C_2S hydration shows a similar trend at early age for all blended systems, PCC₁₂₅, PCC₂₂₅ and PCC_{230LF15}. In PCC_{130LF15} the C_2S hydration degree is similar than in PC₁₀₀. At early ages, the hydration of C_2S slowed down for the blended systems but it caught up with PC₁₀₀ at later ages. As demonstrated by Krishnan and al. ([56]), belite hydration degree is lower in presence of calcined clay. This result seems in contradiction with previously shown data (section 3.1, figure 5). It is actually difficult to assess belite hydration degree in such systems without further investigations. However, as NMR and XRD analyses do not operate at the same scale, the comparison can be biased. Besides, it is also possible that belite particles are too small to be clearly detected by XRD. As shown later in figure 10, XRD seemed less reliable to assess the long-term hydration degree. In figure 9c, blends seem to have the same hydration degree for C_3A except PCC_{130LF15} and PCC₂₂₅, but the values of this mixture remain relatively high. This difference may be due to the reactions involving aluminate. As shown in figure 9d, C_4AF hydration rate was impacted by the presence of CC1 (i.e. more kaolinitic calcined clay) in PCC₁₂₅ and PCC_{130LF15} and the combination between CC2 and

limestone filler in PCC2₃₀LF₁₅. The presence of the composite calcined clay CC2 in binary binder PCC2₂₅ does not seem to impact the reaction of C₄AF, when comparing to PC₁₀₀. The short-term hydration degree of C₄AF has already been reported to be relatively low (Choudhary et al. [57]).

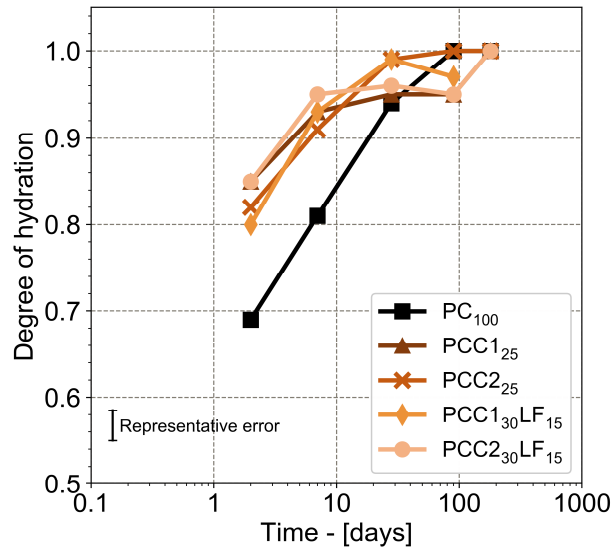


Figure 9a: C₃S hydration degree

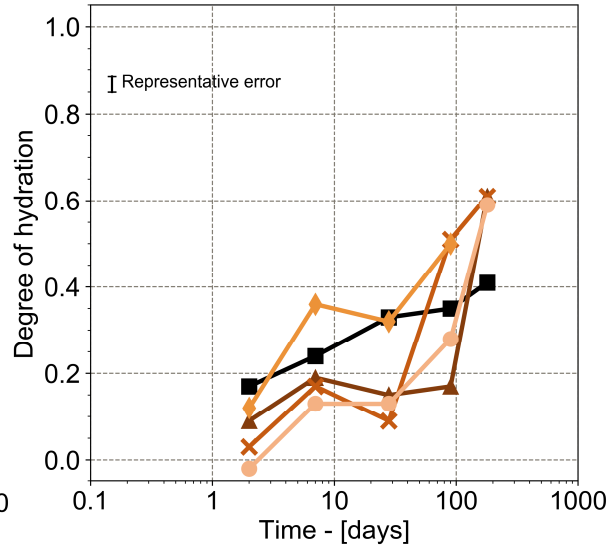


Figure 9b: C₂S hydration degree

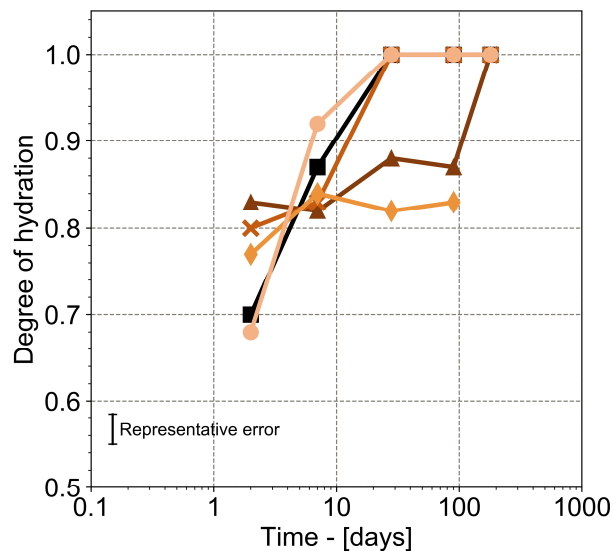


Figure 9c: C₃A hydration degree

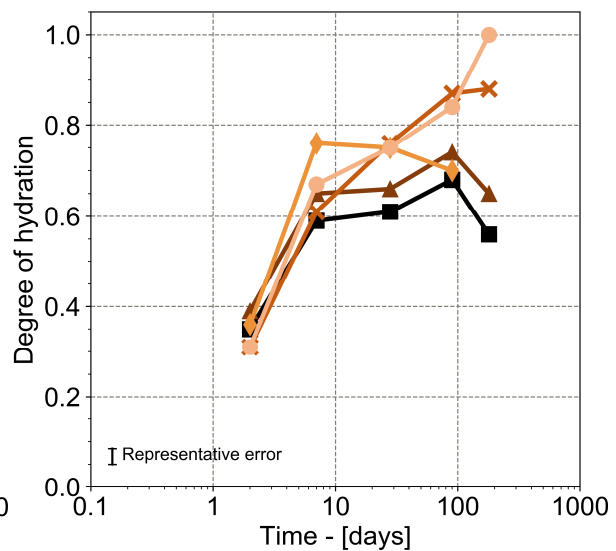


Figure 9d: C₄AF hydration degree

Figure 9: Degree of hydration of clinker phases calculated by XRD

The hydration degree of clinker can be obtained by combining the values of the four main clinker phases and their content. The DoH of clinker in the paste PC₁₀₀ is compared with calorimetry results in figure 10. The correlation is relatively good at short-term but then the difference increases to reach 15% at 180 days. The difference between calorimetry and XRD results can be attributed to uncertainties in XRD results due to the sample preparation or phase identification and quantification and also uncertainties related to the extrapolation of calorimetry data. The calculus from XRD

measurements takes into account only clinker phases hydration degree while isothermal calorimetry gives the overall reaction hydration degree. Differences between the two results in figure 10 may come from this point. Hydration degree calculated by XRD is related to clinker phases hydration degree.

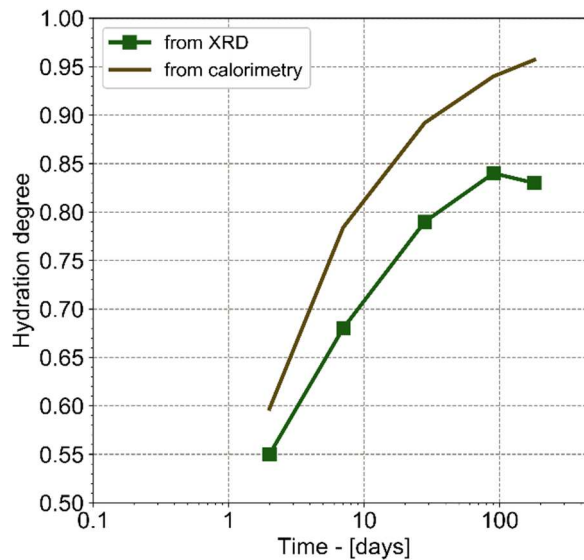


Figure 10: Hydration degree of PC₁₀₀ calculated by calorimetry and XRD

3.3 Reaction rates

The heat release normalized per gram of cement is shown in figure 11. The onset of the acceleration period occurred earlier with the increase of the substitution rate and the amount of metakaolin in the system. The intensity of the silicate peak was higher for the blended binders, especially when Portland cement was substituted by CC1 and calcined clay combined with limestone. This observation was already made by Antoni et al. [8]. The presence of mineral additions, here calcined clay and limestone filler, provides more nucleation sites which allow hydration products to grow faster, especially C-S-H. Limestone actually induces higher degree of undersaturation with respect to alite and faster reaction [58]. The fine particles also reduce the inter-particle distance, which leads to an increase of the shearing rate during mixing, and an enhancement of early-age hydration.

The second peak cannot be easily distinguished in every blend. The heat flow curve of PC₁₀₀ has only a slight shoulder on the decreasing side of the silicate peak. For the four other mixes, the second peak occurred right after the silicate one. As the relative position of the aluminate and silicate peak was not affected, it was not considered necessary to adjust the sulphate content in binary and ternary binders. The aluminate peak, triggered by the total depletion of initial calcium sulphate, corresponds to high rates of tricalcium aluminate (C₃A) dissolution and ettringite formation, as

shown by Hesse et al. [54] and Jansen et al. [55]. The presence of calcined clay and limestone also affected the sulphate depletion time. Early aluminate peak indicates a lack of sulphate in the system at this time (Antoni et al. [8]). When substituting cement by mineral additions the initial sulphate content is lower than the plain cement mix. The sulphate to C_3A ratio remains the same but aluminates can be also provided by metakaolin in calcined clay, as this is evidenced by NMR data (Fig. 10).

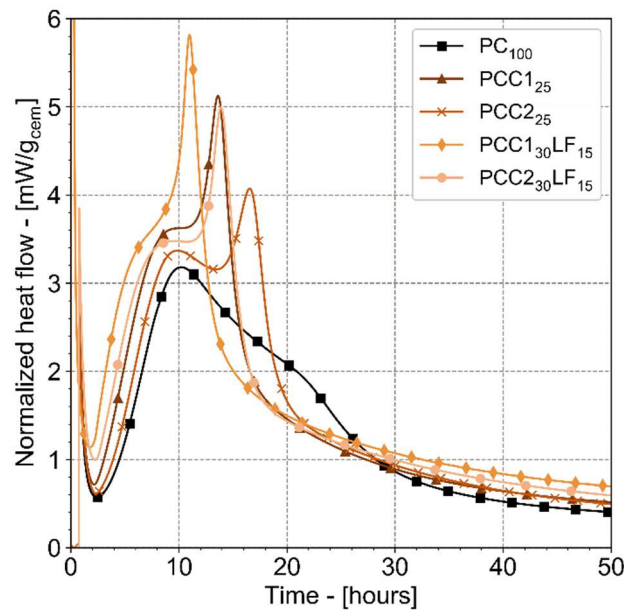


Figure 11: Normalized heat flow (per gram of cement) over hydration time

The intensity and shape of the aluminate peak depend on the substitution rate of the cement but also on the nature of calcined clay. The graph on figure 11 shows that the second peak was more intense and occurred earlier for PCC1₂₅ and PCC1₃₀LF₁₅ than for PCC2₂₅ and PCC2₃₀LF₁₅. CC1 was produced from a more kaolinitic and purer clay than CC2. The aluminate content and the proportion of amorphous phase of CC1 was higher but the specific surfaces of both calcined clays were approximately the same (table 1). At this stage it can be deduced that the position and intensity of aluminate peak are mainly influenced by the reactivity of the calcined clay, as previously observed by Antoni et al. ([8]) and Avet and al. [59], and not associated with the specific surface area increase as suggested by Zunino et al. [60].

However, PCC1₂₅ and PCC1₃₀LF₁₅ and PCC2₂₅ and PCC2₃₀LF₁₅ had different shapes and intensities of the aluminate peak, although they were based on the same calcined clay. This result shows that the binder composition and limestone filler content also significantly influence the reaction rate of

sulphates and aluminates. It also shows that the ternary blends – where the mineral addition is a combination of calcined clay and limestone filler – with a lower kaolinitic clay, tend to react approximately at the same rate as the binary blend PCC1₂₅ containing a purer clay.

The cumulated heat per gram of cement is shown in figure 12. The two systems with 25% of calcined clay (PCC1₂₅ and PCC2₂₅) tend to have similar heat of hydration over time while a large shift can be observed between PCC1₃₀LF₁₅ and PCC2₃₀LF₁₅ and the rest of the blends. The difference between the different binders increase with hydration time.

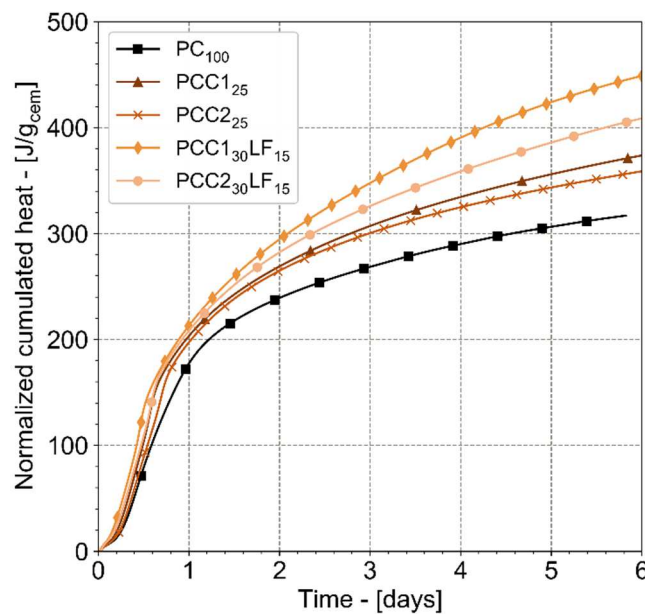


Figure 12: Normalized cumulated heat (per gram of cement) versus hydration time

The higher the substitution of cement, the higher the cumulated heat per gram of cement. In addition to taking advantage of the calcined clay reactivity, binary and ternary binders studied here tended to promote the reactivity of clinker. Whereas the substitution of cement resulted in earlier aluminate peak (figure 11), this does not slow down the hydration reaction of clinker at early age, as the cumulated heat of binary and ternary binders were higher even during the first 24 hours (figure 12).

For each blend, total cumulated heat at later ages can be calculated by extrapolation, as explained in section 2.3.1. Table 4 gives the value of ultimate heat of hydration Q_{∞} per gram of cement and per gram of total binder for the studied blends.

Table 4: Maximal cumulated heat of hydration Q_{∞}

	PC₁₀₀	PCC₁₂₅	PCC₂₂₅	PCC_{130LF15}	PCC_{230LF15}
Q_{∞} [J/g_{cem}]	402.1	476.4	462.7	562.7	520.4
Q_{∞} [J/g_{bind}]	402.1	357.3	347.0	297.4	286.2

Similar values of Q_{∞} for PC₁₀₀ have been reported in previous studies ([35], [61]). As observed in figure 12, and confirmed in Table 4, total cumulated heat per gram of cement increased with the substitution rate. This confirms the beneficial effect of the studied mineral additions on clinker hydration. This effect is largely due to the chemical effect of limestone filler and probably to the new nucleation sites provided by mineral additions and secondary reactions involving the phases formed from calcined clays and limestone filler, as evidenced through TGA and NMR analyses. Lower cumulated heat per gram of total binder means that blended cements release less heat during hydration than plain cement mixes. As the binder content was the same for all mixes, cumulated heat in PC₁₀₀ was higher than PCC₁₂₅, PCC₂₂₅, PCC_{130LF15} and PCC_{230LF15}. Portland cement hydration reaction is an exothermic reaction and when cement is replaced by a mineral addition, the reaction between this addition, cement and water generally releases less heat. The influence of this dilution effect prevails, even if secondary reactions take place. Both calcined clays seem to result in the same ultimate hydration heat of binary binders. As explained in Msinjili et al. [18], heat of hydration is not always a good indicator of the clay reactivity. Cementitious blends containing illitic calcined clay may have similar heat of hydration than blends containing low-grade kaolinite calcined clay even if the compressive strengths are different.

The differences observed between PCC_{130LF15} and PCC_{230LF15} can highlight the effect of metakaolin and limestone filler in a cementitious matrix. The blend containing the highest level of metakaolin has the highest cumulated heat per gram of cement and the highest cumulated heat per gram of total binder.

4. CONCLUSION

The studied binary and ternary binders are based on Portland cement, calcined clays and limestone filler. Low metakaolinitic calcined clay obtained from illite-kaolinite composite raw clay is compared with high kaolinite raw clay, which is mainly composed of metakaolin after calcination. The study aims at investigating the influence of composite calcined clay on the hydration of cement in binary

and ternary systems. Advanced experimental techniques were combined to identify and quantify the hydration products at different ages.

- At short term, the first calcined clay containing mainly metakaolin showed a higher reactivity than the second composite calcined clay obtained from illite and kaolinite. Even though the first calcined clay reacted faster in a cementitious matrix, it was demonstrated that the composite calcined clay did not slow down the hydration reactions of clinker.
- In a ternary blend, the composite calcined clay combined with limestone had a very positive impact on hydration. Pozzolanic reaction was actually improved in the ternary blend when comparing with the binary blend with the highly metakaolinitic clay. The ternary blend with the composite clay (illite/kaolinite) finally had a higher pozzolanic activity than the ternary blend with the highest metakaolin content. This shows that pure kaolinite raw clay is not necessarily required as the synergy between limestone filler and illite-kaolinite calcined clay can clearly be observed.
- The hydration of clinker phases and the phase assemblage of the cementitious matrix are influenced by the substitution of cement by calcined clay and limestone filler. The reactivity of belite is lowered but other phases are generated, such as aluminium-modified calcium silicate hydrate (C-A-S-H), strätlingite, and carboaluminates in presence of limestone and composite calcined clay. These phases can be expected to enhance the engineering properties of the materials for a given cement content.
- At longer term, it was showed that behaviours tend to be similar even though pozzolanic activity was slightly higher for metakaolin than composite calcined clay. Binary binder with metakaolin and ternary binder with illite-kaolinite calcined clay tended to have similar pozzolanic activity. The phase assemblage at long-term is approximately the same for both calcined clays, the kinetics of formation of some phases being slower for the composite clay.

The combination of Portland cement, calcined clay and limestone filler has been confirmed to be a promising way to optimize the potential use of composite clays in cement-based materials. The properties of raw clays can be considered as input data for a given region but other parameters such as the temperature of calcination and the limestone to clay ratio should also be investigated to maximize the potential reactivity of a given clay.

5. APPENDIX

As showed in figure 13, after 28 days of hydration $Q^2(1A)$ had already appeared for PCC1₂₅. As seen earlier, calcined clay in PCC2₂₅ tended to react slower than CC1 in PCC1₂₅. The peak $Q^2(1A)$ started to appear in PCC2₂₅ after 28 days and it was more pronounced after 180 days (see figure 5).

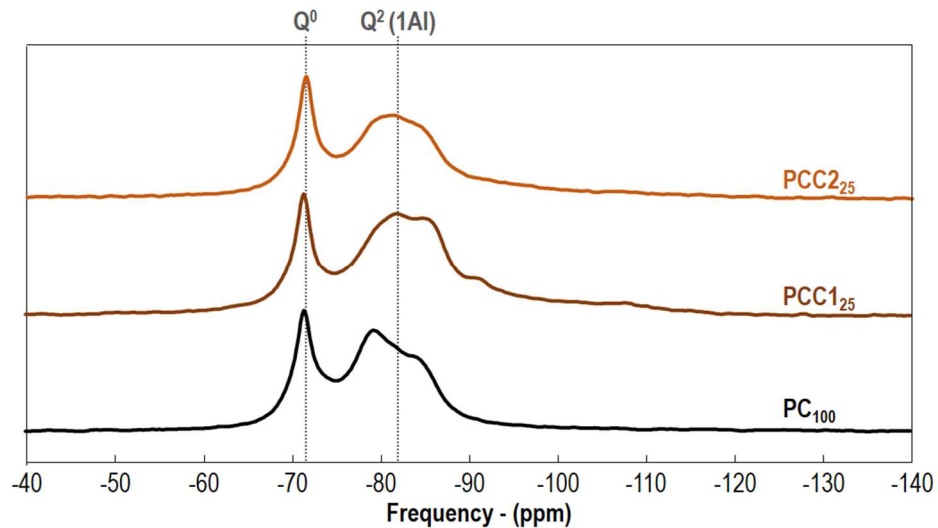


Figure 13: ^{29}Si MAS NMR for pastes after 28 days of hydration

6. ACKNOWLEDGEMENT

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