The impact of calcite impurities in clays containing kaolinite on their reactivity in cement after calcination

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Abstract The use of supplementary cementitious materials as a partial replacement for Portland cement is the most effective way to reduce the carbon footprint of the concrete industry. Raw clays containing kaolinite (kaolin) are promising substitute materials. In the field, raw clays are often mixed with calcite and this is thought to affect their behaviour after calcination. This study explores the influence of calcite impurities on the mineralogy and reactivity a kaolinitic clay. A kaolin sample was blended with different quantities of calcite. The results show that during calcination calcite is decomposed, but no significant amount of free lime or amorphous calcium carbonate are formed. A granular deposit was observed that partially covers the kaolinite particles. The decomposition of calcite and formation of the deposit is associated with a reduction in specific surface area, which increases with the amount of calcite that is intermixed in the raw clay. TEM-EDS analysis showed that the deposit corresponds to a new phase formed from the interaction of kaolinite and calcite, with an Al/Si ratio ranging from 0.74 to 0.88 and Ca/Si ratio between 0.86 and 1.65. Reduction of the calcination temperature to 700 °C reduces the calcite decomposition and the negative impact on reactivity.

Keywords Portland cement · Calcination · Hydration · Transmission electron microscopy · Metakaolin

1 Introduction

Mineral additions, commonly referred as supplementary cementitious materials (SCM), are widely used either in blended cements or added to concrete separately in the mixer [1, 2]. The use of SCM, leads to a reduction of CO₂ emissions per unit volume of concrete, and provides a beneficial use for wastes and by-products [3–5].

Clay minerals are unique among supplementary cementitious materials because of their abundance worldwide [6–8]. Clay mineral particles are made up of tens to hundreds of layers composed of tetrahedral silica and octahedral alumina sheets. The three most abundant clay mineral types are kaolinite, illite and montmorillonite [9]. Kaolinite is dehydroxylated in the temperature range 400–600 °C. The dehydroxylation of kaolinite leads to a more disordered material known as metakaolinite [10–12]. Usually, raw clay is calcined in the range 700 and 800 °C to maximize the amount and degree of disorder of metakaolinite in the calcined clay. The reactivity of calcined clay is strongly related to its metakaolinite content [11, 13]. Higher temperatures lead to reduced reactivity due to sintering and eventually recrystallization [11].

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In some regions, raw clays are naturally combined with limestone (calcite). Calcite decomposes between 600 and 800 °C into free lime and carbon dioxide (gas), so if calcite is present some decomposition may occur during the calcination process. The interaction of calcite with clay minerals such as kaolinite has been studied for calcination temperatures above 900 °C, where the formation of metastable calcium aluminosilicate phases such as wollastonite ($\text{CaO} \cdot \text{SiO}_2$), anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) were reported [14–16]. Inclusion of calcium in an amorphous aluminosilicate phase has also been reported previously in systems with small amounts of limestone incorporation [17].

El-Didamony only observed the formation of gehlenite above 850 °C, and in increasing amounts up to 1000 °C [15]. Other studies reported the crystallization of gehlenite and anorthite in kaolinite–calcite mixes sintered at 1100 °C [14]. Snellings et al. reported incorporation of calcium into the amorphous fraction of clay–limestone residues calcined between 820 and 905 °C, indicating the formation of a Ca-aluminosilicate amorphous phase [17]. Hollanders observed positive effects on the pozzolanic reactivity of calcined clays for calcite additions above 10% and after regrinding the material [18].

Despite the abundant literature regarding the calcite–kaolinite system at higher temperatures, there is lack of systematic studies exploring these interactions at temperatures of 800 °C or lower, which is the usual range for calcined clay production for use as a substitute in blended cement. This study explores the effect of calcite impurities below 10% by mass on mineralogy, morphology and pozzolanic reactivity, calcined under typical conditions intended for metakaolinite production.

2 Materials and methods

2.1 Experimental design

A raw clay (kaolin) from China was used in this study, with 71% kaolinite content as measured by thermogravimetric analysis (TGA). The clay was selected due to its high kaolinite content and as it did not contain any limestone. The main associated minerals found in the clay are quartz and anatase. The raw clay was ground in a laboratory jar mill until a homogeneous

powder was obtained with a D_{V50} below 5 μm . Different amounts of limestone (Durcal 5; $D_{V50} = 6.9 \mu\text{m}$, 98.9% calcite by TGA) was added to the raw clay. The particle size distribution (PSD) of the raw materials by laser diffractometry (Fig. 1). The chemical composition determined by X-ray fluorescence (XRF) (Table 1). No illite or muscovite were detected in the raw clay by XRD, so weight loss between 400 and 700 °C was only due to the dehydroxylation of kaolinite.

The raw clay and limestone powders were blended and intermixed in 150 g batches using a Turbula blender (with simultaneous shaking and rotating action) for 15 min, in order to obtain a homogeneous sample. The limestone content of the batches was checked by TGA after blending, it was within $\pm 10\%$ of the nominal limestone content defined in the experimental design (see Fig. 12 in “Appendix”). As the limestone used was nearly pure calcite, both terms are used interchangeably in this paper to refer to the impurities incorporated in the material. The particle size distribution of the raw materials, measured by laser diffraction, are shown in Fig. 1.

Calcination was conducted in a laboratory furnace. About 50 g of powder was placed in flat alumina crucibles to maximize the exposed surface of the material. The heating ramp was in all cases 20 °C/min. After completing the calcination process, the crucibles with the material were left inside the furnace until reaching 200 °C before removing them. After

Fig. 1 Particle size distribution of raw materials measured by laser diffractometry

Table 1 Chemical composition of raw clay and limestone expressed as oxides mass%

	Raw clay (kaolin)	Limestone
SiO ₂	58.16	0.11
Al ₂ O ₃	37.63	0.00
Fe ₂ O ₃	0.79	0.04
CaO	0.17	54.96
Na ₂ O	0.09	0.06
K ₂ O	0.08	0.01
MnO	0.05	0.00
TiO ₂	1.13	0.01
MgO	0.19	0.15
P ₂ O ₅	0.41	0.00
SO ₃	0.35	0.03
LOI	0.93	42.5

calcination, the material was stored in sealed plastic containers until testing.

A composite cubic experimental design was used to select the compositions of the samples tested in two stages. The first one studied the influence of three parameters (maximum calcination temperature, limestone content and residence time) on the properties and pozzolanic reactivity of calcined clay. The range of the parameters was based on previous studies that have shown good results in terms of kaolinite dehydroxylation and pozzolanic reactivity [9, 11, 19], and the range of limestone impurities commonly encountered. The calcination temperature (X_1), limestone content (X_2) and residence time (X_3) were centered at 700 °C, 5% by mass and 40 min, respectively. A response surface methodology was used to explore the experimental region around this central point. Factor levels were defined using a central composite design (CCD) for 3 factors which produces second order response surface models [20]. Six replications of the central point allowed the experimental variance to be estimated. According to CCD each factor is applied in five levels: $-\alpha$, -1 , 0 , 1 , α , where $\alpha = (\sqrt[4]{2^k})$, where k is the number of factors) is 1.682 in this study to obtain a rotatable design [20]. The materials and factor levels considered for the 20 experimental points (coded as M-01 to M-14 plus centerpoints Ci) of the first stage (Table 2).

In light of the results obtained in the first stage, a second stage was carried out to better understand the effect of calcite impurities on the reactivity of calcined clay by comparison with the behaviour of the material without calcite, and to examine the behaviour of calcite-containing materials calcined at 700 °C compared to higher temperatures. The factor levels of the 12 additional experimental points (coded M-A to M-L) of the second stage (Table 2 bottom part).

In order to facilitate the identification of specific experimental points in the graphs in this paper, the symbol key in Fig. 2 is adopted. In the presentation of the results we are mainly interested in the calcite content and the calcination temperature, so the third factor (residence time) is represented by a “—”, “—”, “+” or “++” sign next to the experimental point.

2.2 Material characterization

X-ray diffraction (XRD) was used to assess the mineralogical composition of the calcined materials. Measurements were made on back loaded powder samples to reduce the effects of preferred orientation. The samples were measured in Bragg–Brentano mode using a X’Pert PANalytical diffractometer with CuK α source operated at 45 kV and 40 mA with a 1/2° soller slit. Samples were scanned from 7° to 70° 2 θ with a step size of 0.0167 2 θ using a X’Celerator detector, resulting in an equivalent time per step of 60 s. Commercial software (HighScore Plus version 4.6) coupled with the ICCD database were used for phase matching and Rietveld refinement.

Fourier transform infrared spectroscopy (FTIR) measurements were made for some of the calcined materials to complement the information obtained from XRD, using a 6700 Nicolet spectrometer by Thermo Fischer Sci. An attenuated total reflectance (ATR) accessory was used for the measurements, equipped with a diamond crystal and a potassium bromide (KBr) beam splitter. A total of 32 background and sample scans were taken each time, with a resolution of 4.0 cm⁻¹.

The specific surface area (SSA) of the materials was determined by gas adsorption using the Brunauer–Emmett–Teller (BET) method, with a Micromeritics TriStar II analyser. Nitrogen (N₂) was used as analysis adsorptive gas. Samples of approximately 1 g of powder material were introduced in analysis tubes and

Table 2 Experimental design and factor levels considered in both experimental stages of the study

Material		Factor levels					
ID	Exp block	Coded			Experimental		
		X ₁ : m_temp	X ₂ : cal_cont	X ₃ : r_time	X ₁ : m_temp (°C)	X ₂ : cal_cont (%)	X ₃ : r_time (min)
First stage							
M-01	I	− 1	− 1	− 1	600	2	20
M-02	II	1	− 1	− 1	800	2	20
M-03	II	− 1	1	− 1	600	8	20
M-04	I	1	1	− 1	800	8	20
M-05	II	− 1	− 1	1	600	2	60
M-06	I	1	− 1	1	800	2	60
M-07	I	− 1	1	1	600	8	60
M-08	II	1	1	1	800	8	60
M-09	III	− 1.682	0	0	532	5	40
M-10	III	1.682	0	0	868	5	40
M-11	III	0	− 1.682	0	700	0	40
M-12	III	0	1.682	0	700	10	40
M-13	III	0	0	− 1.682	700	5	6
M-14	III	0	0	1.682	700	5	74
Ci	I–II–III	0	0	0	700	5	40
Second stage							
M–A	–	1	− 1.682	− 1	800	0	20
M–B	–	1	− 1.682	0	800	0	40
M–C	–	1	− 1.682	1	800	0	60
M–D	–	− 1	− 1.682	− 1	600	0	20
M–E	–	− 1	− 1.682	1	600	0	60
M–F	–	0	− 1.682	− 1	700	0	20
M–G	–	0	− 1.682	0	700	0	40
M–H	–	0	− 1.682	1	700	0	60
M–I	–	0	− 1	− 1	700	2	20
M–J	–	0	− 1	1	700	2	60
M–K	–	0	1	− 1	700	8	20
M–L	–	0	1	1	700	8	60

degassed for 2 h at 200 °C under N₂ flow. Subsequently, they were immersed in a liquid nitrogen bath (77.3 K) where the measurements were performed. Five measurements at different relative pressures were collected and used to calculate the specific surface area of the material.

The initial kaolinite content of the raw clay (kaolin) was determined by thermogravimetric analysis (TGA), considering the weight loss between 400 and 600 °C corresponding to the kaolinite dehydroxylation. A Mettler Toledo unit equipped with a rotary

autosampler was used, heating from 30 to 1000 °C at 10 °C/min heating rate under a N₂ 30 mL/min flow as protective atmosphere. As the dehydroxylation of kaolinite and the decomposition of limestone peaks overlap, the tangent method was selected to compute both weight losses [21].

TGA was also used to assess the amount of calcined kaolinite (equivalent to the metakaolinite content) in the calcined materials. This parameter is defined as the difference on kaolinite measured on the raw clay and

Fig. 2 Symbol key for identification of experimental points of CCD throughout this paper

the calcined clay (Eq. 1) to account for partial dehydroxylation.

$$\% \text{Calcined kaolinite} = \% \text{kaolinite}_{\text{rawclay}} - \% \text{kaolinite}_{\text{calcinedclay}} \quad (1)$$

To compare the efficiency of calcination of the kaolinite in the clay–limestone systems, the normalized calcined kaolinite content was computed according to Eq. (1), to account for the dilution due to the limestone additions.

$$\% \text{Normalized calcined kaolinite} = \frac{\% \text{kaolinite}_{\text{rawclay}} - \% \text{kaolinite}_{\text{calcinedclay}}}{\% \text{kaolinite}_{\text{rawclay}} \cdot (1 - \% \text{limestone})} \quad (2)$$

Isothermal calorimetry was used to assess the pozzolanic reactivity of calcined clays. For this purposes, the R^3 test proposed by Avet et al. [13] was selected due to its reliability and ease of interpretation. In this procedure, calcined clay is mixed with portlandite, calcium carbonate, potassium sulphate, potassium hydroxide and water at 40 °C, and put into glass ampoules inside the calorimeter at 40 °C. The total heat evolved after 24 h is taken as a measure of the reactivity of the clays and shows good correlation with compressive strength results obtained on blended cement–mortar bars. In this study, the heat evolved after 24 h and 72 h was analysed. Further details can be found in [13].

In order to observe morphological changes of clays after calcination with and without limestone impurities, scanning electron microscopy (SEM) observations were conducted. A FEI XL30 series microscope equipped with a field emission gun and an in-lens SE detector was used for high resolution imaging (HR-SEM). Clay samples were dispersed in a 0.01% sodium poly-acrylic acid (PAA) solution. A few droplets of the dispersed particles were subsequently dried on a glass plate. Afterwards, the particles were placed over carbon holders and coated with 4 nm osmium oxide (OsO_4).

Further insights into particle composition after calcination were gathered using transmission electron microscopy (TEM) analyses. A thin lamella was prepared from the calcined clay particles: the powder was first mixed with G2 resin (hard epoxy resin from Gatan®) with a high concentration of particles (approx. 50% by mass). This mix was then heated at 40 °C in order to increase fluidity, and centrifuged 15 min at 15,000 rpm. The polymerization of the resin was conducted at 80 °C during 12 h. A semi-disc of approx. 3 mm of diameter and 700 µm thick was cut from the bottom of the centrifuged cone, in order to maximize the concentration of particles. This semi-disc was then thinned down to less than 5 µm with a bevel to have a thin part at the front and a thicker part at the back, ensuring good mechanical behavior upon manipulation. The semi-disc of embedded particles was then glued on a TEM copper half-ring of 3 mm of diameter.

The sample was thinned to approx. 100–150 nm using a Gatan® Precision Ion Polishing System (PIPS, model 691), with decreasing voltages of the Argon guns from 1.5 to 0.4 kV. The TEM transparency is achieved when equal thickness fringes can be seen on the edge of the sample by optical microscopy.

The thinned lamella was then transferred into a FEI Tecnai Osiris TEM, where a voltage of 80 kV and a small spot size (8, corresponding to a current of 0.15 nA) were used in order to minimize the beam damage on the sample. TEM was operating in scanning-TEM (STEM) mode and the high angular annular dark field (HAADF) detector was used. For the EDS acquisition, a set of 2 windowless FEI Super-X SDD detectors were used simultaneously and the lamella was tilted 20° to face the detectors. A defocus of 200 nm was applied to minimize sample damage.

3 Results and discussion

3.1 Effect of limestone on specific surface area, calcined kaolinite content and calcined clay reactivity

The specific surface area (SSA) results, measured using nitrogen adsorption and computed using the BET model, are shown in Fig. 3. The repetitions of the central point give an estimation of the experimental variability. As the calcination temperature increases, the SSA is reduced. This is in agreement with previous studies [9, 12, 17]. Limestone additions lead to lower SSA at all temperatures. As the limestone is less fine than the clay (SSA of clay = $9.30 \text{ m}^2/\text{g}$ and SSA of limestone = $2.08 \text{ m}^2/\text{g}$) there will be some reduction of surface area just due to the incorporation of the less fine material. This can explain the reduction of SSA measured between the materials with residence times of up to 20 min. However, the reductions seen for the 8% limestone materials calcined for 60 min indicate another mechanism decreasing the specific surface for longer residence times.

XRD patterns for experimental points corresponding to the core of the experimental program (M-1 to M-8) are shown in Fig. 4a (2% calcite materials) and Fig. 4b (8% calcite materials). Calcination at 600°C

Fig. 3 BET specific surface area versus calcination temperature for materials considered in the CCD experimental design. Contour plots of response surface for 2 and 8% materials calcined for 60 min are included

does not completely dehydroxylate kaolinite, even at high residence times (60 min), as seen by the persistence of the main kaolinite reflection at $12.36^\circ 2\theta$. Furthermore, there is no change in the calcite content at this temperature. For 8% initial calcite content materials, the amount of remaining calcite after calcination at 600°C was 7.92 and 7.85% by mass for 20 and 60 min residence time respectively, as determined by TGA (see Fig. 13 in “Appendix”).

At 800°C a higher level of dehydroxylation is measured for low residence time (20 min) materials and kaolinite became undetectable in materials calcined for 60 min (see Fig. 4a, b). On the other hand, a reduction in the intensity of the main reflection of calcite ($29.40^\circ 2\theta$) is detected for the materials calcined for 20 min and, more significantly, for the material calcined for 60 min. The amount of remaining calcite determined by TGA in the material calcined for 60 min is 0.65% and 2.23% by mass for 2% and 8% initial calcite content, respectively. However, there was no evidence of crystalline free lime (CaO) in the 2% calcite sample and only traces in the 8% one, as seen by the lack of the main reflection at $37.30^\circ 2\theta$. Therefore, there is a question of where the calcium from the calcite has gone, as XRD does not indicate any other crystalline phases containing calcium. The amount of free lime estimated from Rietveld refinement for the 8% calcite 60 min residence time clay (0.43% by mass) only accounts for a small amount of the decomposed calcite.

Figure 5 shows the normalized kaolinite content for blended materials with 0, 2 and 8% initial limestone contents calcined for 20 (Fig. 5a) and 60 (Fig. 5b) min versus calcination temperature. For 20 min residence time materials, the effect of limestone on the amount of calcined kaolinite content is detected at 700°C and 800°C , in comparison to the behaviour of the 0% limestone clay. Extending the residence time to 60 min leads to an increased amount of calcined kaolinite. 700°C and 800°C for 60 min calcination conditions shows complete dehydroxylation of kaolinite.

The total heat release per gram of solids obtained from the R^3 test for the samples in the first stage are shown in Fig. 6a, b for 24 and 72 h heat release, respectively. Contour plots obtained from the regression of the experimental results are also included, corresponding to 2 and 8% limestone content clays calcined for 60 min. At 24 h (Fig. 6a), materials

Fig. 4 XRD patterns of **a** 2% and **b** 8% initial calcite content clays. Symbol key: K = kaolinite; Q = quartz; A = anatase; C = calcite; L = lime

calcined at 800 °C exhibit similar reactivity compared to those calcined at 700 °C. At 72 h (Fig. 6b), there is a bigger difference between 2 and 8% limestone materials at 800 °C, as also shown by the contour plots of the response surface. These indicate that at 72 h, the heat release in the R^3 test of the high limestone content

(8%) clays is slightly lower than that for the low limestone content (2%).

According to the CCD, Table 3 shows the regression coefficients for the effect of the different factors on kaolinite content, specific surface area and heat output, along with their respective p values.

Fig. 5 Normalized calcined kaolinite content versus calcination temperature **a** materials calcined for 20 min and **b** materials calcined for 60 min

Fig. 6 Total heat released at **a** 24 h and **b** 72 h, per gram of solids versus calcination temperature for materials considered in the CCD experimental design

p Values < 0.05 are statistically significant at a 95% confidence level and are indicated in bold. The maximum calcination temperature (X_1) is the dominating factor for all characteristics. Limestone content has a significant effect on specific surface area and heat release at 72 h (Figs. 3, 6b), but not on the

normalized calcined kaolinite content. Residence time also appears to be a relevant factor for the kaolinite content and the heat release, but not specific surface area. The coefficients presented in Table 3 allow the reconstruction of the response surface for any given

Table 3 Regression coefficients and *p* values for the experimental responses analysed

Factor	N. Cal. Kaolinite		SSA		Heat 24 h		Heat 72 h	
	Effect (%)	<i>p</i> Value	Effect (m ² /g)	<i>p</i> Value	Effect (J/g)	<i>p</i> Value	Effect (J/g)	<i>p</i> Value
X_0 : constant	70.08	0.0000	8.56	0.0000	78.33	0.0000	116.84	0.0000
<i>First order</i>								
X_1 : m_temp	30.28	0.0000	− 0.42	0.0000	18.05	0.0000	31.42	0.0000
X_2 : ls_cont	− 3.48	0.1139	− 0.15	0.0194	− 1.80	0.1129	− 5.37	0.0253
X_3 : r_time	14.15	0.0000	− 0.09	0.1093	7.58	0.0000	12.73	0.0000
<i>Interactions</i>								
$X_1 \cdot X_2$	− 1.35	0.5829	0.04	0.5873	0.28	0.8267	− 1.94	0.4561
$X_1 \cdot X_3$	− 1.16	0.7004	0.00	0.9990	− 3.11	0.0550	− 3.29	0.3071
$X_2 \cdot X_3$	2.86	0.1805	− 0.12	0.0993	0.33	0.7577	1.18	0.5965
<i>Second order</i>								
$X_1 \cdot X_1$	− 11.28	0.0001	− 0.19	0.0043	− 7.73	0.0000	− 14.87	0.0000
$X_2 \cdot X_2$	3.66	0.0728	− 0.15	0.0155	1.75	0.0944	2.35	0.2648
$X_3 \cdot X_3$	− 8.63	0.0027	− 0.04	0.4261	− 6.47	0.0000	− 11.36	0.0004

Significant effects (*p* value < 0.05) are shown in bold

set of factor levels within the explored experimental region.

3.2 Interaction of calcite and kaolinite during calcination

As previously shown, the amount of calcium in the crystalline phases detected by XRD does not balance the initial calcium content from limestone addition. However, calcium could be included in an amorphous phase that is not detected by XRD. As the formation of metakaolinite dominates the characteristic amorphous hump of the calcined clay patterns, it is not possible to observe the possible appearance of minor amounts of other amorphous phases.

An amorphous form of calcium carbonate has been reported in the literature [22]. To explore the possibility that such phase is forming when the calcite decomposes, FTIR measurements were made of the raw materials and some calcined clays with CaO unaccounted for after calcination. These are shown in Fig. 7. Calcite gives two peaks at 710 and 870 cm^{−1}, corresponding to symmetric in-plane bending and asymmetric out of plane bending of CO₃ groups, respectively. The broad band at 1395 cm^{−1} is assigned to the asymmetric stretching of CO₃, while the small peak at 1795 cm^{−1} is attributed to symmetric CO₃ deformation and stretching [23]. In the raw clay

spectra, peaks at 750 and 790 cm^{−1} are attributed to kaolinite lattice vibration, which disappear upon dehydroxylation [12, 24]. The band around 910 cm^{−1} is assigned to OH[−] bending vibrations, while the peak at 1000 cm^{−1} is attributed to Si–O stretching vibrations of kaolinite, which broadens as the structure is distorted upon dehydroxylation [12, 25]. The peak at 1115 cm^{−1} is assigned to vibration of O^{2−} atoms perpendicular to the kaolinite layers, and is also affected by stacking defects that may be introduced upon calcination of the clay [26]. The peak at 3615 cm^{−1} is assigned to inner hydroxyl groups situated at the interface of Si tetrahedral and Al octahedral layers, while the ones at 3650 and 3680 cm^{−1} are related to OH[−] stretching vibrations of hydroxyl groups situated at the basal surface of the Al layer of kaolinite [12]. The latter peaks are expected to disappear when dehydroxylation is complete, as they are related to the water molecules in kaolinite.

The spectra of 0% calcite material calcined at 800 °C for 60 min is included to give a reference for the signals from a fully dehydroxylated uncontaminated clay. The band at 1000 cm^{−1} associated to Si–O stretching vibrations of kaolinite broadens significantly as expected, and shifts to higher wavenumbers. The peaks associated with hydroxyl stretching at 3615, 3650 and 3680 cm^{−1} completely disappear. For the

Fig. 7 FTIR spectra of raw materials and calcined clays calcined at 800 °C with different amounts of calcite (LS)

clay with 8% calcite addition, calcined at 800 °C for 20 min, the signals associated with hydroxyl stretching are still visible, indicating an incomplete dehydroxylation in this case. The asymmetric stretching of CO_3 peak at 1395 cm^{-1} is visible, suggesting the presence of remaining calcite in the calcined clay, in agreement with XRD results. Similarly, materials with 2 and 8% initial limestone contents calcined at 800 °C for 60 min appear both to be completely dehydroxylated. In these materials, the peak associated with calcite is barely visible. However, the characteristic peak associated with free lime around 3650 cm^{-1} is not detected in these materials, further supporting the hypothesis of the formation of a different phase upon calcination. Nevertheless, this phase does not correspond to amorphous calcium carbonate, as the peak at 870 cm^{-1} should remain visible in this case [22].

Figure 8a shows a micrograph of clay mineral particles (kaolinite) contained in the raw clay. They exhibit a layered structure, with single layer thickness ranging from 30 to 50 nm.

Figure 8b shows a micrograph of a metakaolinite particle in calcined clay with no initial calcite addition, calcined at 800 °C for 60 min. TGA

measurements confirmed complete dehydroxylation of this clay. Interestingly, the layered structure of kaolinite is persistent after complete dehydroxylation and transition into metakaolinite. The thickness of the layers remains in the same range as the ones measured for the raw clay, between 30 and 50 nm.

Figure 9a shows a metakaolinite particle in the material with 8% initial calcite addition and calcined at 800 °C for 60 min. While the layered structure of metakaolinite is still visible to some extent, part of the surface is covered with a granular deposit not observed in the raw materials. It consists of particles around 50 to 100 nm in size, which is a completely different size as compared to the original limestone (Fig. 1). To study the possibility of an artefact due to sample preparation (artificial blending of raw clay and limestone powders before calcination), a raw clay naturally intermixed with calcite from the field with approximately 10% calcite (as measured by TGA) was calcined in the same conditions described above and prepared for high resolution SEM observation (Fig. 9b). As the same morphological features were observed, the mechanism seems to be representative of

Fig. 8 High resolution SEM micrographs of kaolinite in raw clay (a) and metakaolinite in calcined clay (b) mounted on carbon film and coated with 4 nm OsO₄

Fig. 9 High resolution SEM micrographs of a metakaolinite particle in the material with 8% calcite addition (a) and metakaolinite particle from raw clay with approximately 10% calcite (b)

the case of raw clays with limestone impurities found in quarries.

The size of the granular deposits partially covering clay particles makes EDS analysis in the SEM unsuitable for a detailed assessment due to effects of interaction volume. Therefore, a sample of the 8% calcite material calcined for 60 min was prepared for TEM observation.

Figure 10a shows a HAADF image of a group of metakaolinite particles in the prepared lamella, Fig. 10b shows the EDS map distribution of Al, Si and Ca over the same area. The calcium rich areas (1, 2 and 3 in Fig. 10a) were analysed by EDS as well as a reference metakaolinite particle (Al/Si ratio of 1.0, corresponding to section 4 in Fig. 10a). A summary of

the values measured for Ca, Si and Al as well as computed Al/Si and Ca/Si ratios for measuring sections 1 to 4 shown in Fig. 10 are presented in Table 4.

Calcium (white) is located in some of the areas containing metakaolinite particles, in general agreement with the SEM observations, where the metakaolinite particles were observed as not fully covered by the deposit (Fig. 9). The advantage of STEM-EDS analysis is that the volume of interaction effect is restricted to the beam size and the thickness of the lamella (100–150 nm). The results show that while different amounts of calcium were detected in the different areas (between 20 and 30 at%), the Al/Si ratio is different from 1.0 (value expected and

Fig. 10 HAADF TEM micrographs of calcined clay particles with 8% calcite addition (a) and EDS map showing the distribution of silicon (green), aluminium (red) and calcium (blue) (b). (Color figure online)

Table 4 Summary of values measured by STEM-EDS over the observed Ca-rich phase and a clear metakaolinite particle

Section no.	1	2	3	4
	Ca-rich phase over MK particles			MK particle
Ca (at%)	30.842 ± 1.932	23.393 ± 1.626	21.432 ± 1.526	0.167 ± 0.004
Si (at%)	18.644 ± 0.402	17.951 ± 0.489	25.055 ± 0.807	30.091 ± 0.182
Al (at%)	16.413 ± 1.091	13.422 ± 1.005	18.775 ± 1.400	31.965 ± 1.966
Al/Si	0.88	0.75	0.74	1.06
Ca/Si	1.65	1.30	0.86	< 0.01

measured for pure metakaolinite in section 4), ranging from 0.74 to 0.88 in sections 1 to 3. If the areas were solely an intermix of a free lime deposit and metakaolinite, the Al/Si should have remained equal to 1. However, results suggest that a new phase is

forming, probably as an amorphous transition state between the free lime and metakaolinite and the crystalline phases expected at higher temperatures such as wollastonite, anorthite and gehlenite. The Ca/Si ratio measured ranged from 0.86 to 1.65.

The TEM and FTIR results show that the calcium oxide from the calcite decomposition interacts with kaolinite forming a calcium-rich phase which covers metakaolinite particles as a granular shaped deposit. This compound covers the metakaolinite particles reducing the specific surface area, but without major influence on the normalized kaolinite content of the calcined clay.

4 Conclusions

This study explored the effect of calcite impurities in kaolinitic clays on reactivity after calcination. Based on the results presented in this study, the following conclusions can be drawn:

1. Calcite impurities reduce the specific surface area of calcined clay as compared to clays without calcite, which explains most of the measured reduction in reactivity in the samples with calcite impurities. The decrease in specific surface area is beyond the expected reduction by the blending of limestone and the raw clay. This effect is amplified with the increase of calcination temperature, residence time and initial calcite content.
2. At calcination temperatures beyond the decarbonation threshold of calcite, a reduction in the calcite content in the calcined clay is seen compared to the uncalcined material, but this reduction does not correspond to the formation of crystalline free lime or amorphous calcium carbonate. High resolution SEM images showed a granular deposit partially covering the surface of metakaolinite particles. EDS analysis suggests that this deposit is composed of a calcium rich phase. TEM analysis showed that this deposit corresponds to a new phase formed from the interaction between calcite and kaolinite particles. This phase forms below the recrystallization temperature required to form the phases previously reported in the calcite–kaolinite system.
3. Reducing the maximum temperature to 700 °C and increasing the residence time to at least

60 min allows a significant reduction of the influence of calcite on specific surface area, while allowing a virtually complete dehydroxylation of kaolinite for the studied clay. The reduction on reactivity is minor if the dilution effect is accounted for.

Therefore, and within the experimental limits of this study, clays with calcite content up to 10% are suitable for use as SCM in cement-based materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Appendix

See Figs. 11, 12 and 13.

Fig. 11 TGA curves of raw kaolinitic clay used in this study and calcined clay at 800 °C for 60 min. Weight loss associated to dehydroxylation of kaolinite is indicated

Fig. 12 TGA curves of blended kaolinitic clay + calcite. Weight loss associated to decarbonation of calcite is indicated

Fig. 13 TGA curves calcined clays with 8% calcite, calcined at 600 °C for 20 and 60 min. Weight loss associated to dehydroxylation of kaolinite and decarbonation of calcite are indicated

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