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Impact of calcination technology on properties of calcined clays

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Abstract

Calcined kaolinitic clays are known to be very reactive pozzolans, and combined with limestone can enable significant clinker substitution in cementitious systems. Thermal activation of kaolinitic clays takes place when the hydroxyl groups are removed, leading to formation of an amorphous reactive structure. There are several technologies for clay activation, but the most used at industrial scale are flash and stationary soak calcination. The objective of this paper is to investigate the impact of the calcination regime on the properties of the calcined product. It presents the results of an experimental program carried out with a kaolinitic clay calcined at a flash calciner and at a laboratory furnace. In both cases calcination brings about a drop in specific surface, and an increase of average diameter due to agglomeration, an effect more pronounced in stationary soak calcination. No major differences were found at the heat of hydration, CH consumption and phase assemblage for the fully dehydroxylated material. The flash calcined material had slightly better results mainly due to a finer PSD compared with the one soak calcined. No major difference was found in water demand and compressive strength for both regimes. In conclusion, for the experimental set and the clay used, calcination regime appears to have little influence on the properties of the calcined clay, except for the degree of agglomeration of the calcined material.

Keywords: Calcined clays; Calcination; Pozzolanic reactivity; Standard mortars

1 Introduction

A very popular approach for improving the sustainability of cement production is the use of clinker substitutes (Supplementary Cementitious Materials, SCM) such as fly ash, slag and natural pozzolans. The main problem associated with this approach is that SCMs are not widely available, or have a poor reactivity, thus, clinker current substitution ranges between 25-30% as an average. If carbon emissions around 600 kg CO_2/ton of cement are targeted, clinker content should be further reduced [1–3].

Calcined clays have been used as pozzolans for centuries, especially in regions where other SCMs are scarce. Most used calcined clay was Metakaolin ($Al_2Si_2O_7$) (MK), a highly reactive pozzolan made through the calcination of a clay rich in kaolin. It is produced from high quality crude clays using state of the art technologies to remove impurities and control particle size [4,5]. Recent studies have proven that low grade kaolinitic clays can be used to produce MK [6]. These results expand the opportunities of using calcined clays as SCMs, because of the broad geographic distribution of kaolinitic clays throughout the world [7]. The investigation of the synergy between calcined clays and limestone proved the possibility of further replacing up to 50% clinker with a 2:1 combination of calcined clay and limestone [8,9]. For very low clinker content in ternary systems clinker-calcined clay-limestone, the pozzolanic reactivity of the calcined clay plays a major role [10]. Thus, calcination parameters and technology are crucial in terms of achieving the maximum reactivity.

The kaolinitic clays become reactive through the removal of the hydroxyl groups in a process called “dehydroxylation”. OH^- groups are broken down between 400-700°C and are released as water vapor. This process can render a partially disordered structure characterized by major changes in Al and Si coordination within the crystal lattice of the calcined clay [11]. The structural disorder caused during dehydroxylation is associated with the loss of the lattice periodicity in the direction perpendicular to the structural layers. This enables the creation of a disordered metastable material, called metakaolin or metaclay [12].

Calcination parameters such as temperature and residence time are crucial in terms of guaranteeing a proper reactivity of the calcined material [6,12,13]. Several authors have discussed the influence of the calcination regime on the disorder, and consequently, the ability of the calcined

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material to react in cementitious systems [14]. Comparisons are made between the most frequently used processes: (i) Soak calcination and (ii) Flash calcination.

This paper aims at assessing the reactivity of a kaolinitic clay calcined in a flash calcination pilot unit, and compare it to a clay calcined at a lab furnace simulating the soak calcination conditions that take place at a rotary kiln.

2 Materials characterization

2.1 Clay

The clay deposit chosen was Pontezuela located at the center of Cuba. The chemical composition was determined using X-Ray Fluorescence (XRF) with a Bruker AXS S4 Explorer spectrophotometer operating at 1 kW and equipped with a Rh X-ray source. Qualitative mineralogical composition analysis was conducted via X-Ray Diffraction (XRD) on powder samples using a PAnalytical X' Pert Pro MPD diffractometer in a θ -θ configuration with a CuKα source (λ = 1.54 Å) and a fixed divergence slit size of 0.5°. Samples were scanned on a rotating stage between 4 and 65 [° 2θ] with an X' Celerator detector, utilizing a step size of 0.0167° 2θ and a time per step of 30 s.

Thermogravimetric Analysis (TGA) of the raw samples was carried out with a Mettler-Toledo TGA/SDTA 851 balance using a 10 °C/min ramp from 30 to 900 °C under a 30 ml/min flow of N_2. The kaolinite content was determined by analyzing the first derivative of the TGA curve (DTG) within the temperature range of 400 – 600 ºC and calculating mass changes in the TGA curve accordingly. The chemical composition is detailed in Table 1, while the mineralogical composition is provided in Table 2. Mineralogical analysis shows kaolinite as the main clay mineral, representing 48.5 wt.%, while a low or moderate contents of 2:1 clays could also be detected. Quartz and iron oxyhydroxides are the main associated minerals present. This clay is expected to have good potential to produce high quality pozzolans [15].

Table 1. Chemical composition of the clay materials used for the experimental program.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Others	LOI
Ptz raw	54.63	27.33	12.60	1.73	0.93	0.70	0.30	1.57	0.80	0.67	10.17
MK	50.62	46.91	0.38	0.02	0.09	0.08	0.28	0.18	1.29	0.16	
OPC	19.86	4.64	3.52	63.67	1.11	2.89	0.14	0.63			2.13

Table 2. Mineralogical composition clay Pontezuela.

Clay 1:1	Clay 2:1	Associated phases	Equivalent kaolinite content, %
Kaolinite	Montmorillonite e illite	Quartz, Goethite	48,5

2.2 Ordinary Portland Cement, OPC

A Portland cement (CEM I) containing only trace amounts of limestone was used for the studies in pastes and mortars. Mineralogical composition of the cement, with 92% clinker, consists of 62.9% C_3S, 8.7% C_2S, 5.6% C_3A and 12.7% ferrite. Blaine specific surface of 5180 cm^2/g and alkalis content below 0.5%.

2.3 Other materials

A reference, highly purity kaolinite content Optipozz metakaolin (MK) produced by flash calcination by Burgess (USA) was used as a reference to a high reactivity MK. Table 1 presents the chemical composition of the materials used for the experimental program.

3 Experimental program

The raw clay was dried and ground in a ball mill for 2 hours. Table 4 and Figures 4 and 5 provide details on the particle Size Distribution, PSD, and other physical properties of the raw clay and the calcined products [16].

Calcination was carried out in two regimes: (i) flash calcination and (ii) stationary soak calcination. In both cases the raw clay feed had the same fineness. Flash calcination was conducted at a Clay Activation Unit, CAU at CUJAE, Havana, see Figure 1. The material was calcined at 750°C, 850°C and 900°C. Retention time in the flash calciner was less than 1 sec. The calcination temperature of the flash calciner was measured in four points along the calcination duct. Point T1 is immediately after feeding the material, point T2 is located within the duct where the gas flow carries the calcined product, point T3 is located at the cyclone where calcined material is collected and point T4 is at the bag filter. More details are published at [17]. Temperature at T1 was considered to best represent the calcination temperature.

The stationary soak calcination was carried out at a lab muffle furnace at 750°C, which is considered within the optimum calcination temperature range, and the material was kept for one hour in the furnace [11].

The degree of dehydroxylation was assessed aided by TGA, whereas weight losses in the interval 400-600°C are monitored. Further, XRD analysis was also used to evaluate the dehydroxylation process. Additionally, the calcined material was analyzed by quantitative XRD, including the estimation of amorphous content (Am) in the calcined product following the method proposed by O'Connor and Raven [18], using rutile as external standard.

A Micromeritics Accupyc 1330 V2 instrument was used for bulk density measurements, and a Micromeritics Gemini 2375 V4 instrument allowed the determination of a specific surface (BET).

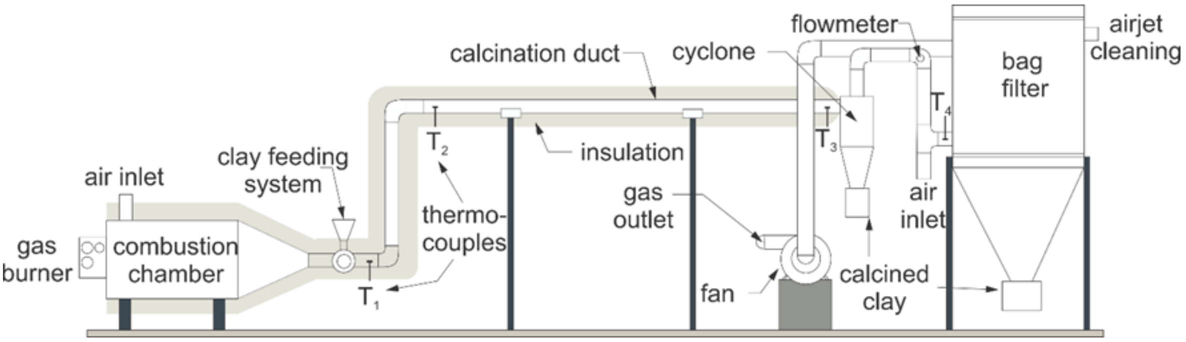

Figure 1. Diagram of the Clay Activation Unit.

Cement pastes with a water/binder ratio of 0.4 were made with a combination of 70% CEM I and 30% of the calcined material. An additional 2% of gypsum was added to avoid sulphation problems. Hydration of paste samples was stopped at 1d, 3d, 7d and 28d by immersion of 5 mm thick paste slices for 7 days or more in isopropanol and further vacuum drying during at least 3 days. After stopping hydration, TGA analysis were carried out on ~40 mg paste samples crushed in an agate mortar. TGA measurements were done with a Mettler-Toledo TGA/SDTA 851 balance using a 10 °C/min ramp from 30 °C to 900 °C under a 30 mL/min flow of N_2.

Standard mortars were cast with a combination of 70% CEM I and 30% of the calcined material, with a water/binder ratio of 0.5 with standard sand according to EN-197-1. An additional 2% of gypsum was added to avoid sulphation problems. Flowability was assessed following the shake table protocol. Compressive strength measurements were carried out on mortars at 1, 3, 7, and 28 days on 3 prisms of 120×40×40 mm and 6 prisms of 40×40 mm section respectively according to EN-197-1.

4 Discussion and results

4.1 Degree of dehydroxylation during calcination

To consider a practically complete dehydroxylation of the sample no weight losses should be registered between 400°C-600°C, while the main XRD peaks for the basal planes of kaolinite must also disappear. The DTG curves and the XRD pattern for the raw and the calcined material are presented in Figure 2 and Figure 3 respectively. The clay activated through flash calcination at 750°C and 850°C shows a degree of dehydroxylation of only 76.9% and 88.5%, respectively, thus indicating a not complete dehydroxylation of the clay minerals for both temperatures, a factor that prevents the calcined sample to reach its full potential as a pozzolan [19]. At 900°C flash calcination is close to a full dehydroxylation (degree of dehydroxylation 92.4%). In the material calcined at the lab oven it is considered that kaolinite is fully dehydroxylated, reaching a degree of dehydroxylation of 97.7%.

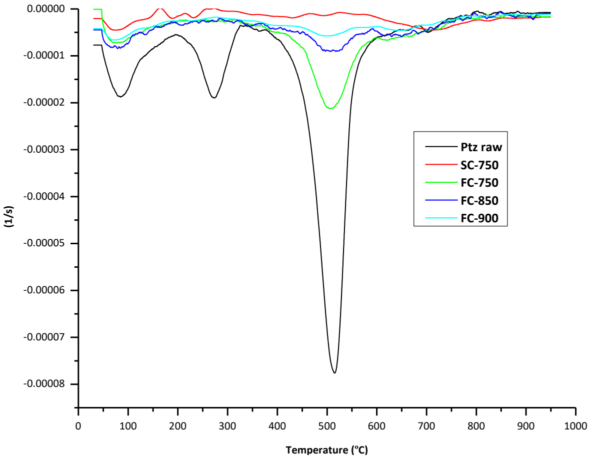

Figure 2. DTG of raw and calcined material.

The XRD patterns of both the raw and calcined clay samples are presented in Figure 3. In the case of soak calcination at 750°C (SC-750), it appears that there has been a complete transformation of kaolinite. During the flash calcination process at 750°C (FC-750), low-intensity peaks of kaolinite (with a content of 8.97% in Table 3) can still be observed. This suggests that, with this calcination process, a higher temperature is required to achieve complete dehydroxylation. As the calcination temperature increases beyond 850°C, the flash calcination process seems to lead to complete dehydroxylation of kaolinite. In this sample, all main peaks of kaolinite have disappeared, and its presence could no longer be quantified (Table 3). This observation aligns with previous studies on kaolinite-rich clays activated through flash calcination, which reports that at temperatures slightly above 900 °C [20], the clay undergoes complete dehydroxylation.

For both calcination technologies 2:1 clay minerals could still be detected at all temperatures, although their content gradually decreases while increasing calcination temperature (Table 3). However, the stationary soak calcination at 750°C (SC-750) seems to have minor effect on the 2:1 clay phases [21]. No spinel and mullite formation are observed in agreement with the findings reported for flash calcination between 700-900°C [20,22,23].

The quartz content slowly increases as the calcination temperature rises. In terms of amorphous phases, there is an observed increase during flash calcination. However, no significant differences can be observed between SC-750 and FC-850/FC-900. These results are consistent with the results obtained from the analysis of the TGA curves, as shown in Figure 2.

Table 3. Results of quantification using an external standard (wt.%).

Sample	Quartz	Goethite/ Hematite	Kaolinite	2:1 clay minerals	Am
Ptz raw	7.63	9.88	48.28	15.75	18.47
SC-750	23.78	10.10		11.98	54.13
FC-750	20.06	9.94	8.97	8.98	52.05
FC-850	22.98	13.26		7.89	55.87
FC-900	24.10	14.22		5.56	56.11

Table 4. Physical properties of the material calcined vs. raw clay.

Sample Name	BET (m^2/g)	He Picnometry (g/cm^3)	Dv10 (µm)	Dv50 (µm)	Dv90 (µm)
OPC			2.0	10	28.0
Ptz raw	43.1	3.0428	0.42	3.08	26.2
FC 900	35.1	2.9950	0.49	6.62	30.52
SC 750	33.0	3.1076	0.57	12.2	65.50

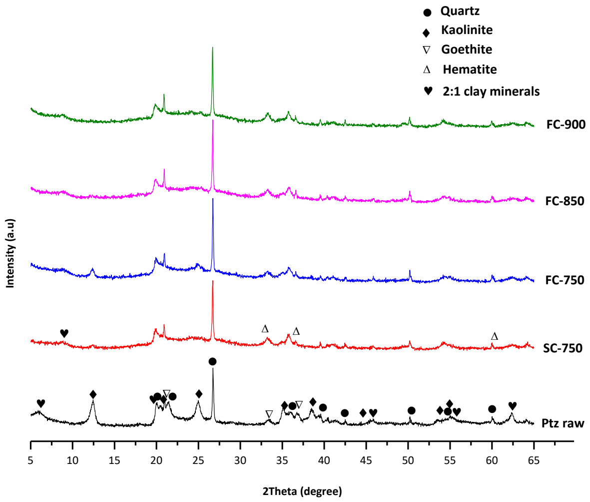

Figure 3. XRD of the calcined material.

Flash calcination, although with a shorter residence time, needs a higher temperature (>850°C) to reach a practically complete degree of dehydroxylation. Soak calcination, on the contrary, is completed at 750°C for one hour residence time. From this point on the study will further work only with the fully dehydroxylated material, so for further studies only samples SC-750 and FC-900 will be considered.

5 Imapact of calcination on the shape of particles

Table 4 presents the physical properties of the raw clay and the calcined material under different regimes. It includes BET specific surface, density, and D_{v10}, D_{v50} and D_{v90} for all materials subject of study. Figure 4 presents the PSD for the raw and the calcined material.

The PSD at the raw clay (Figure 4 and Figure 5) is bimodal. The first peak, around 0.8 µm, presumably corresponds to some inert particles present in the material. This peak remains unchanged after calcination, consistent with the fact that inert materials such as quartz do not undergo any transformation at the temperature used for calcination. The second peak, however, corresponding to sizes around 3-70 µm, moves to coarser fractions as calcination is carried out. It indicates the presence of agglomeration, probably caused by partial superficial sintering. [12]

Calcination brings about a drop in specific surface, thus affecting the pozzolanic reactivity [6]. SC-750 is a coarser material and still has a similar specific surface compared to FC-900. This could be attributed to the agglomeration that takes place in both calcination regimes, since BET measures the total specific surface, including internal surface in the agglomerates.

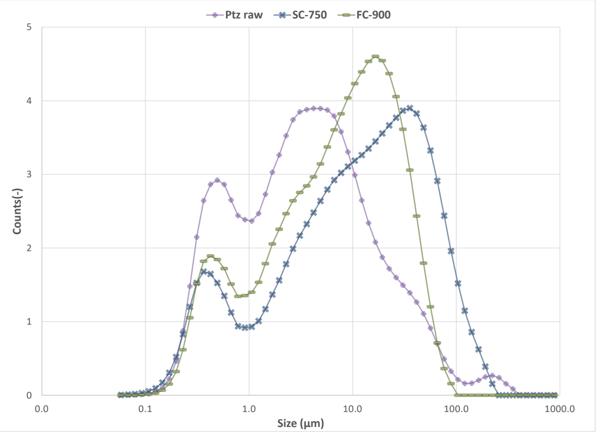

Figure 4. Particle size distribution of the calcined material vs. raw clay.

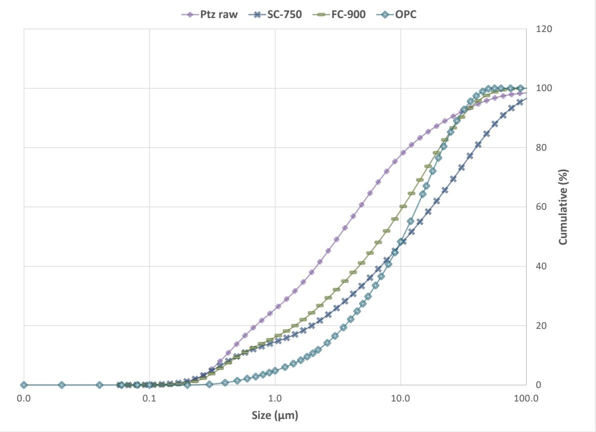

Figure 5. PSD of the different materials.

6 Pozzolanic reactivity

Figure 6 shows the early age isothermal calorimetry results for the blends, normalized with respect to the content of Portland cement. Proper sulphation of the system is assessed by measuring the time where the aluminate peak resulting from the reaction between limestone present as cement component and C_3A from the cement react [24]. If the peak falls within the first 24 hours the system is properly sulphated. Marginal difference in sulphation can be seen between cement pastes made with SC-750 and FC-900, probably indicating a slight over-sulphation in the paste made with SC-750, most likely caused by the lower specific surface [25]. This could eventually impact early age properties of the cement. As expected, the most reactive material appears to be the MK reference.

Figure 7 presents the cumulative heat of hydration for all cement pastes up to 2 days. The maximum total cumulated heat is achieved by the MK paste, due to its high reactivity. SC-750 is following, slightly below MK, and then FC-900. There are no significant differences between cumulated heat at SC-750 and FC-900, thus indicating that the combination of a filler effect enhancing the hydration of cement and the pozzolanic reaction of the calcined clays is similar in both cases [26].

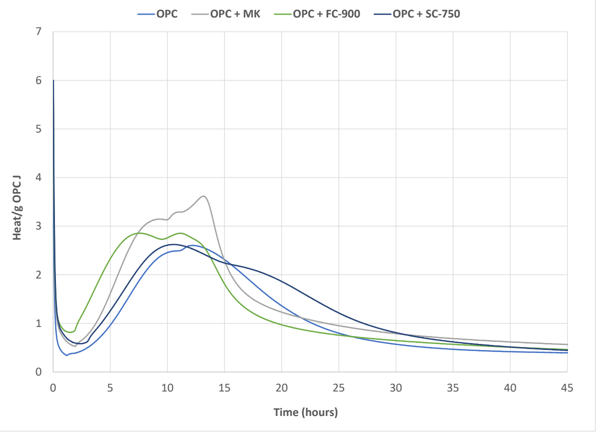

Figure 6. Heat of hydration cement pastes.

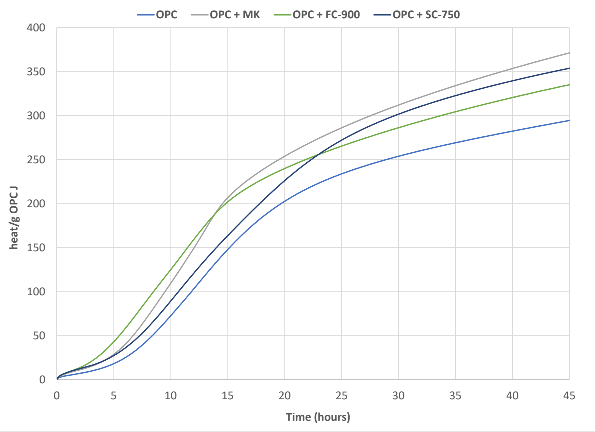

Figure 7. Cumulative heat of hydration cement pastes.

Figure 8 shows the evolution of calcium hydroxide content over time for the different cement/calcined clay pastes at 1d, 3d, 7d and 28d. The incorporation of reactive mineral admixtures such as calcined clays enhance the hydration of cement [11] with the so-called filler effect. The pozzolanic activity can be assessed by monitoring the Calcium Hydroxide (CH) consumption, usually by measuring the weight losses at the temperature interval where CH is decomposed [27].

At one day and three days the highest CH consumption is observed for the MK and FC cement paste; the MK remains with the highest CH consumption until 28 days, thus confirming its higher pozzolanic reactivity. FC-900 shows a higher CH consumption than SC-750, especially up to 3 days. The differences between FC 900 and SC 750 decrease from 7 days on and at 28 days they have both similar values of CH consumption. This test tends to indicate that there is a marginal increase in pozzolanic activity in the paste FC-900, but it could also be explained by a coarser material with SC-750, thus leading to a less completed hydration (Figure 6).

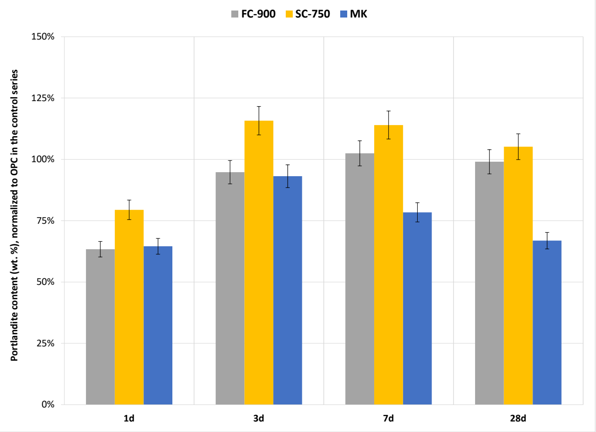

Figure 8. CH consumption on cement pastes.

XRD results of pastes may help to provide a better insight on the hydration behavior of blended cements containing calcined clays. The ratio between C_3S reaction and portlandite content are depicted in Figure 9. For a better comparison between the different series, for each given series the results at 1, 3, 7 and 28 days are normalized to the C_3S and portlandite content at 1 day. Similarly, the correlation between C_3A consumption and the formation of ettringite

(Aft) and hemicarboaluminates and monocarboaluminates (AFm) - like hydration phases is given in Figure 10.

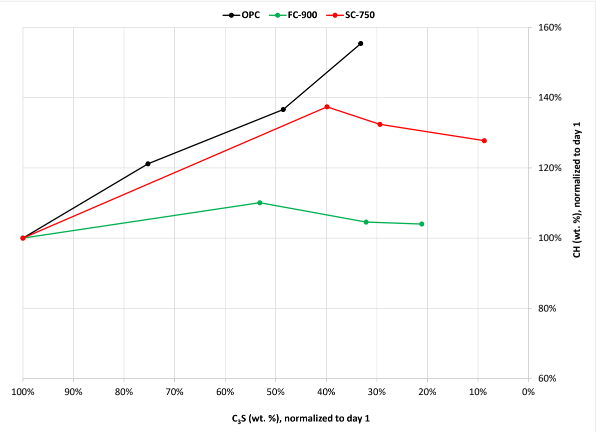

Figure 9. C_3S and portlandite content at 1, 3, 7 and 28 days, normalized by its respective content at 1 day.

For the reference OPC series, as expected, there is an almost linear correlation between the consumption of C_3S by the hydration reactions and the increase of the content of portlandite in the paste. Similar trend is observed for the series containing the soak calcined clay (SC-750) from 1 to 3 days. However, both the relative degree of reaction of C_3S and the consequent relative release of portlandite within this period seems to be much higher as compared with the control series, which could be associated with the well-known filler effect. From 3 days on, the portlandite content starts to decrease, probably associated with the onset of the pozzolanic reactions. For the series containing flash calcined clays the relative degree of reaction of C_3S at all ages is lower as compared with the paste containing soaked calcined clay but still higher when compared to the control series. On the other hand, the lower relative content of portlandite may indicate an earlier onset of the pozzolanic reaction for these systems.

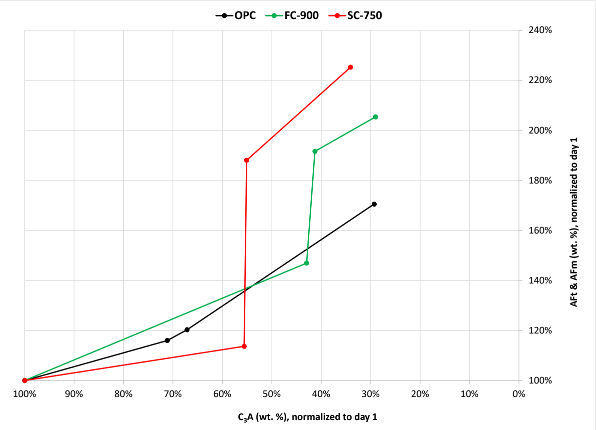

Figure 10. Aft, AFm and C_3A content at 1, 3, 7 and 28 days, normalized by its respective content at 1 day.

In Figure 10 the relative consumption of C_3A is depicted in association to the relative increase of Al-rich hydration products (AFm and Aft) from 1 day on. From 1 to 3 days, the series containing the flash calcined clay shows the higher relative increase of Aft and AFm phases in correspondence with the relative degree of reaction of C_3A, which may again indicate an earlier onset of the pozzolanic reaction of the Al-rich flash calcined kaolinitic clays. For the two series containing calcined clays there is a sudden increase in the relative content of Al-rich hydration products from 3 to 7 days, not associated with the relative degree of reaction of C_3A phases, suggesting a strong development of the pozzolanic reaction for this period. The highest relative increase of hydration products potentially associated to the pozzolanic reaction corresponds to the series containing the clay calcined under a soak regime at 750°C. At 28 days the relative increase of AFm and Aft phases from 1 day on was higher for the SC-750 series in comparison with the series containing flash calcined clays while the relative increase on the degree of reaction of C_3A was similar for all series at 28 days.

7 Impact of calcination on water demand

The presence of calcined clay in a cementitious system is reported to increase water demand compared to ordinary cementitious systems, due to the high specific surface of the calcined material. This effect is more evident at the level of mortar or concrete [28]. For this paper mortars with the fully dehydroxylated material are used to prepared mortars with a binder composition 70% CEM I + 30% calcined clay.

Figure 11 presents the results of the spread in fresh mortars. All three mortars are within the same range of flow, all with similar flow to the OPC series. In terms of water demand the soak calcination seems to be slightly better than flash, but the differences are marginal.

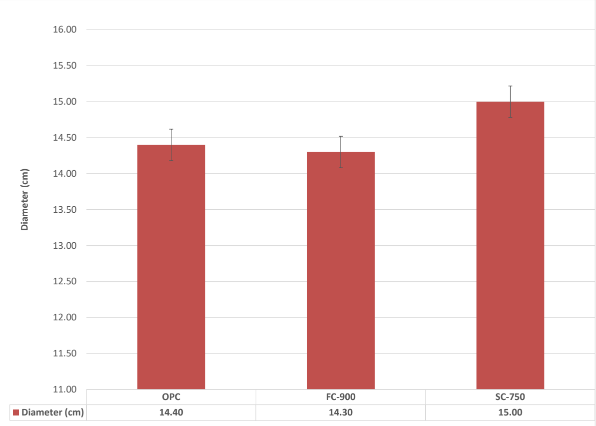

Figure 11. Spread in standard mortars.

8 Impact of calcination on mechanical strength

Mechanical properties are the ultimate confirmation of the pozzolanic reactivity of the material under study. Figure 12 presents the results of measuring compressive strength in standard mortars made with a combination of 70% CEM I + 30% calcined clay, following the procedure of EN 197-1 at 1, 3, 7 and 28 days. Compressive strength is comparable at all ages in the series SC-750 and FC-900, thus indicating a similar behavior in both systems. The relatively large difference with results from OPC series can be explained by the very high strength of the cement used and the dilution effect of replacing 30% with calcined clay.

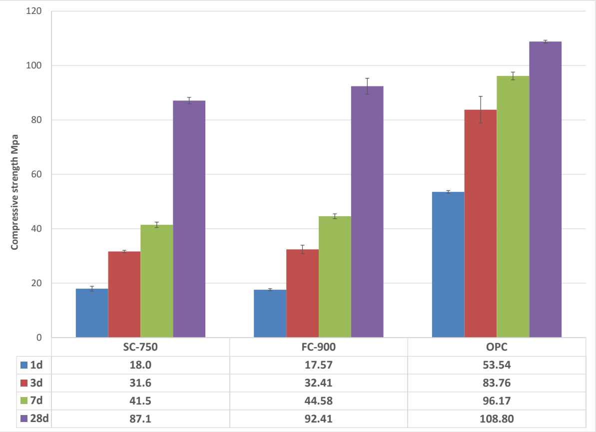

Figure 12. Compressive strength in standard mortars

9 Conclusions

The investigation presented in this paper yields relevant information for comparing flash and soak calcination, based on a lab experimental set, and using only one type of clay, as to respond to the question regarding the influence of the calcination regime on the properties of the calcined product, especially the reactivity.

The clay subject of study was ground to a fixed fineness and was calcined at a pilot industrial flash calciner, and also calcined at a lab furnace simulating soak conditions. A raw clay ground at the same fineness was fed to an experimental flash calciner and a laboratory furnace to carry out flash and soak calcination. To get a full dehydroxylation a much higher temperature was needed with flash calcination (900°C) compared to soak (750°C). The series with similar degree of dehydroxylation (FC-900 and SC-750) show a similar amount of amorphous content. The presence of agglomeration was assessed in both regimes. It took place only for the clayey fraction, while quartz remained in its original size. Flash calcination, with a shorter residence time, caused much less agglomeration than soak calcination, with a much longer residence time.

Pozzolanic activity assessed by measuring the cumulative heat of hydration and CH consumption in OPC-Calcined clay pastes properly sulphated yielded similar results for the series with flash calcined material compared to the soak calcined material, thus indicating that the combination of a filler effect enhancing the hydration of cement and the pozzolanic reaction of the calcined clays is similar in both cases. Phase assemblage figures also confirm that the hydration process is taking place in a similar way on both systems.

During preparation of standard mortars, both series shows a similar water demand. Compressive strength is very similar at all ages in the series SC-750 and FC-900, thus indicating a similar reactivity in both systems.

The evidence experimental results presented in this paper indicates that for the experimental set and the clay used, calcination regime appears to have little influence on the properties of the calcined clay, except for the agglomeration.

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Authorship statement (CRediT)

Fernando Martirena-Hernández: Conceptualisation, Writing – original draft, Visualization, Supervision. **Mathieu Antoni:** Formal analysis, Investigation, Supervision, Writing – review and editing. **Yanisleidy Oquendo-Machado:** Investigation, Data curation, Formal analysis. **Ruben Borrajo-Perez:** Formal analysis, Investigation, Resources, Writing – review and editing. **Adrian Alujas-Diaz:** Formal analysis, Investigation, Supervision, Writing – review and editing. **Roger Almenares-Reyes**: Formal analysis, Data curation, Supervision, Writing – review and editing, Visualization.

References

[1] K.L. Scrivener, V.M. John, E.M. Gartner, U.N. Environment, K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient cements : Potential economically viable solutions for a low-CO 2 cement-based materials industry, Cem Concr Res (2018). https://doi.org/10.1016/j.cemconres.2018.03.015

[2] M. Schneider, M. Romer, M. Tschudin, H. Bolio, Sustainable cement production-present and future, Cem Concr Res 41 (2011) 642-650. https://doi.org/10.1016/j.cemconres.2011.03.019

[3] E. Gartner, H. Hirao, A review of alternative approaches to the reduction of CO2 emissions associated with the manufacture of the binder phase in concrete, Cem Concr Res 78 (2015). https://doi.org/10.1016/j.cemconres.2015.04.012

[4] B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: A review, Cem Concr Compos 23 (2001) 441-454. https://doi.org/10.1016/S0958-9465(00)00092-5

[5] R. Siddique, J. Klaus, Influence of metakaolin on the properties of mortar and concrete : A review, Appl Clay Sci 43 (2009) 392-400. https://doi.org/10.1016/j.clay.2008.11.007

[6] A. Alujas, R. Fernández, R. Quintana, K.L. Scrivener, F. Martirena, Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration, Appl Clay Sci 108 (2015) 94-101. https://doi.org/10.1016/j.clay.2015.01.028

[7] A. Ito, R. Wagai, Global distribution of clay-size minerals on land surface for biogeochemical and climatological studies, Sci Data 4 (2017) 1-11. https://doi.org/10.1038/sdata.2017.1031

[8] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cem Concr Res 42 (2012) 1579-1589. https://doi.org/10.1016/j.cemconres.2012.09.006

[9] F. Zunino, F. Martirena, K. Scrivener, Limestone calcined clay cements (lc3), ACI Mater J 118 (2021) 49-60. https://doi.org/10.14359/51730422

[10] F. Zunino, K.L. Scrivener, Lowering the Clinker Factor of Limestone Calcined Clay Cements (LC3) below 50%: a Comparison with Natural Pozzolans, American Concrete Institute, ACI Special Publication SP-355 (2022) 81-88. https://doi.org/10.14359/51736014

[11] R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite, Cem Concr Res 41 (2011) 113-122. https://doi.org/10.1016/j.cemconres.2010.09.013

[12] T. Hanein, K.-C. Thienel, F. Zunino, A.T.M. Marsh, M. Maier, B. Wang, M. Canut, M.C.G. Juenger, M. Ben Haha, F. Avet, A. Parashar, L.A. Al-Jaberi, R.S. Almenares-Reyes, A. Alujas-Diaz, K.L. Scrivener, S.A. Bernal, J.L. Provis, T. Sui, S. Bishnoi, F. Martirena-Hernández, Clay calcination technology: state-of-the-art review by the RILEM TC 282-CCL, Mater Struct 55 (2022). https://doi.org/10.1617/s11527-021-01807-6

[13] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem Concr Compos 37 (2013) 319-327. https://doi.org/10.1016/j.cemconcomp.2013.01.002

[14] S. Salvador, Pozzolanic properties of flash-calcined kaolinite: A comparative study with soak-calcined products, Cem Concr Res 25 (1995) 102-112. https://doi.org/10.1016/0008-8846(94)00118-I

[15] R.S. Almenares, L.M. Vizcaíno, S. Damas, A. Mathieu, A. Alujas, F. Martirena, Industrial calcination of kaolinitic clays to make reactive pozzolans, Case Studies in Construction Materials 6 (2017) 225-232. https://doi.org/10.1016/j.cscm.2017.03.005

[16] E.C. Arvaniti, M.C.G. Juenger, S.A. Bernal, J. Duchesne, L. Courard, S. Leroy, J.L. Provis, A. Klemm, N. De Belie, Physical characterization methods for supplementary cementitious materials, Mater Struct 48 (2015). https://doi.org/10.1617/s11527-014-0430-4

[17] R. Borrajo-Pérez, J.J. Gonzalez-Bayon, A. Sanchez-Rodriguez, Modelling of the flash calcination process during clay activation, Ingenieria Mecanica 15 (2012).

[18] B.B.H.O. Connor, M.D. Raven, Application of the Rietveld Refinement Procedure in Assaying Powdered Mixtures, Powder Diffr 3 (1988) 1-6. https://doi.org/10.1017/S0885715600013026

[19] F. Avet, X. Li, K. Scrivener, Determination of the amount of reacted metakaolin in calcined clay blends, Cem Concr Res 106 (2018) 40-48. https://doi.org/10.1016/j.cemconres.2018.01.009

[20] A. Teklay, C. Yin, L. Rosendahl, L.L. Køhler, Experimental and modeling study of flash calcination of kaolinite rich clay particles in a gas suspension calciner, Appl Clay Sci 103 (2015). https://doi.org/10.1016/j.clay.2014.11.003

[21] C.J. MCconville, W.E. Lee, Microstructural Development on Firing Illite and Smectite Clays Compared with that in Kaolinite, Journal of the American Ceramic Society 88 (2005) 2267-2276. https://doi.org/10.1111/j.1551-2916.2005.00390.x

[22] A. Teklay, C. Yin, L. Rosendahl, Flash calcination of kaolinite rich clay and impact of process conditions on the quality of the calcines: A way to reduce CO2 footprint from cement industry, Appl Energy (2015). https://doi.org/10.1016/j.apenergy.2015.04.127

[23] R.H. Meinhold, P.H. Atakul, T.W. Daviesb, R.C.T. Slade, Flash Calcines of Kaolinite: Kinetics of Isothermal Dehydroxylation of Partially Dehydroxylated Flash Calcines and of Flash Calcination Itself, J. Mater. Chem 2 (1992) 913-921. https://doi.org/10.1007/BF01105062

[24] F. Zunino, K. Scrivener, The influence of sulfate addition on hydration kinetics and C-S-H morphology of C3S and C3S/C3A systems, Cem Concr Res 160 (2022) 106930. https://doi.org/10.1016/j.cemconres.2022.106930

[25] F. Zunino, K. Scrivener, Insights on the role of alumina content and the filler effect on the sulfate requirement of PC and blended cements Cement and Concrete Research Insights on the role of alumina content and the filler effect on the sulfate requirement of PC and blended ceme, Cem Concr Res 160 (2022) 106929. https://doi.org/10.1016/j.cemconres.2022.106929

[26] P. Suraneni, J. Weiss, Examining the pozzolanicity of supplementary cementitious materials using isothermal calorimetry and thermogravimetric analysis, Cem Concr Compos 83 (2017) 273-278. https://doi.org/10.1016/j.cemconcomp.2017.07.009

[27] P. Suraneni, J. Weiss, Examining the pozzolanicity of supplementary cementitious materials using isothermal calorimetry and thermogravimetric analysis, Cem Concr Compos 83 (2017) 273-278. https://doi.org/10.1016/j.cemconcomp.2017.07.009

[28] Y. Dhandapani, S. Joseph, D.A. Geddes, Z. Zhao, P. Boustingorry, S. Bishnoi, M. Vieira, F. Martirena, A. Castel, F. Kanavaris, K.A. Riding, Fresh properties of concrete containing calcined clays: a review by RILEM TC-282 CCL, Mater Struct 55 (2022) 151. https://doi.org/10.1617/s11527-022-01971-3