Chemical and Mechanical Characterization of Ternary Cement Pastes Containing Calcined Clay and Nanosilica

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Abstract: Research regarding new SCMs (supplementary cementitious materials) is in constant progress, aiming to improve cement properties, reduce its operational costs and make it more sustainable. One such material is calcined clay, which reduces CO_2 emissions and overall cost when blended with cement. Nanosilica is also an SCM, highly reactive. While the benefits of both are well established, their combined effect in a ternary mixture with cement still demands more research. Therefore, the present work evaluates that mixture, aiming to contribute to the cement industry and environmental sustainability. Four cement pastes were studied: OPC (100% Portland cement), 2NS (2% substitution by nanosilica), 25CC (25% replacement by calcined clay produced in the laboratory) and 23CC2NS (replacement by 2% of nanosilica and 23% calcined clay). w/b (water/binder) ratio was fixed in 0.35 and superplasticizer admixtures were used to keep the same workability. fc (compressive strength), XRD (X-ray diffraction) and TGA (thermogravimetric analysis) were performed in the pastes. Results show that the calcination process of the raw clays was efficient, with conversion of kaolinite and that both binary and ternary pastes showed fc equal to or higher than the reference, demonstrating the viability of the calcined clay for clinker substitution at high contents.

Key words: Calcined clay, nanosilica, SCM, blended cements, sustainability, low CO_2 cements.

1. Introduction

Portland cement is a clinker-based product. Clinker is a mixture of carbonate rocks and clay, which are grinded, homogenized and submitted to calcination at high temperatures. This process results in high CO_2 emissions. The production of 1,000 kg cement generates approximately 600 kg of CO_2 and the worldwide production results in a total of 5%-8% of world carbon emissions [1]. Besides CO_2, other gases are released in cement production, such as sulfur dioxide, nitrogen dioxide, carbon monoxide and compounds contain lead, all of which are pollutant.

A viable solution for large scale applications is the use of SCMs' (supplementary cementitious materials) mixed with clinker. This is widely adopted since the

1990s, mainly with slag and fly ash [2]. However, the availability of those materials is limited, depending on other industrial processes. Thus, the application of other materials, such as calcined clays and limestone filler, which are vastly available worldwide, is a necessary step in sustainable production of cement. Overall, clinker replacement by SCMs reduces energy consumption in cement production, as well as reducing CO_2 emissions.

In Brazil, clinker/cement ratio was of 80% in 1990, decreased to 68% by 2014 and is expected to decrease even further by 2030 (59%), one of the lowest at a global scale. This represents a reduction in specific CO_2 ton/cement ton ratio from 0.56 to 0.48 [3]. While clinker substitution by SCMs is already established, there is still need to develop materials that are available worldwide, cheap and beneficial to performance, in order to supply the demands of the cement industry, such as calcined clay.

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The reduction of CO_2 emissions of cement is one of the strategies used to make construction more sustainable, but the process as a whole can be improved by other strategies. For instance, reducing the concrete volume used in buildings. Using high strength concretes can help achieve that goal, since it allows for pillars, beams and slabs with smaller dimensions. Highly reactive SCMs, such as silica fume and nanosilica can be blended with cement to achieve that purpose. In that regard, nanosilica has shown good results, improving hydration with mechanisms potentialized by its high surface area.

2. Theoretical References

The benefits of using calcined clay in blended cements are established in the literature. Many studies show that using this SCM increases fc (compressive strength) in mortars [4-7]. Chemical composition of the raw clay, calcination temperature, material fineness and substitution content in the blended cement are influential in the fc of materials using blended cements with calcined clays [8, 9]. Therefore, the ideal replacement content is dependent on the calcined clay used.

Raw clays, vastly available worldwide, need to be extracted, calcined and grinded in order to become a calcined clay. These processes are essential to transform the clays in a reactive material [10] Kaolinitic clays are the most suitable for calcined clay production, presenting the highest potential for pozzolanic activity [11]. Zampieri (1989) [12] studied clays with different kaolinite contents, demonstrating that even with impurities, these materials have potential reactivity.

Therefore, the reactivity of the calcined clays is mainly dependent on the crystalline structure of the raw clay. A kaolinite with disorganized structure, using the correct calcination process and grinding will have its pozzolanic potential fully utilized, thus allowing higher replacement content while maintaining the same overall performance [13].

Besides kaolinite content, calcination temperature is important in the reactivity. A low calcination temperature is insufficient to convert kaolinite into metakaolin and a high temperature will lead to new crystallization, both limiting the reactivity.

Many authors observed the benefits to fc in cementitious materials generated by SCM replacement, due to the pozzolanic reaction of the material, which consumes CH to produce additional C-S-H, the main component responsible for fc [4].

Nanosilica is a highly reactive SCM, which promotes reduction in porosity and permeability, improves the interstitial transition zone, increasing the cementitious matrix density and finally improving fc, especially in the early ages [14].

SiO_2 nano particles have high reactive potential, consuming CH to form additional C-S-H by the pozzolanic reaction [15]. The high surface area due to nano-scale of the particles changes cement hydration kinetics, accelerating the reaction [16]. Both these effects result in an increase in fc at the early ages [17]. Furthermore, using nanosilica affects the interaction between cement and other components, such as superplasticizer admixture, thus influencing the rheological behavior of cementitious materials [18, 19].

The combination of two SCMs with cement, creating a ternary mixture, can be used to promote benefits from both materials the mix. Depending on the materials, a synergistic effect can also occur, improving the mix even further. Nanosilica has already been used in ternary mixtures with silica fume and metakaolin nanossílica [20-22], yielding promising results. The combination with metakaolin was found to promote a synergistic effect, improving the microstructure of C-S-H, decreasing porosity and increasing fc. Considering the similarities between metakaolin and calcined clay and the growing interest in the latter due to sustainability concerns, it is important to study this combination, evaluating the viability of the mix between calcined clay and

nanosilica.

3. Materials and Methods

3.1 Materials

The following materials were used in this work:

• OPC (100% Portland cement): Portland cement CPI 40, produced with only clinker and gypsum and acquired in 50 kg bags, commercially sold by Cimentos Poty, from Votorantim;

• NS: colloidal nanosilica dispersed in water with 30% solid content, produced by AkzoNobel Brasil;

• CC: calcined clay produced in the laboratory;

• Superplasticizer admixture Viscocrete 6900, provided by SIKA.

The calcined clay was produced using raw clays from a deposit located at Distrito Federal. This raw clay was calcined at 850 °C for 2 h in a muffle furnace. The calcination temperature was chosen based on the literature [23]. After calcination, the clay was cooled at room temperature, until the material reached approximately 25 °C [24]. This material was then grinded, using a Los Angeles abrasion equipment. The Los Angeles equipment consists of a steel cylinder, closed at both ends, with inside diameter of 710 ± 5 mm and an inside length of 508 ± 5 mm. The cylinder rotates at 30-33 rpm. Grinding was performed until the calcined clay presented a granulometry similar to that of cement. The grinding load consisted of 15 steel spheres 47 mm wide, weighing approximately 420 g each. Grinding time was 4 h. Granulometry parameters, obtained by laser granulometry, are shown in Table 1.

Material characterization test results are shown in Tables 1 and 2. Chemical composition was obtained with X-Ray Fluorescence, performed on a WDS Bruker S8 Tiger spectrometer, equipped with Rh tube. Specific mass was determined with a Penta-pycnometer. Particle size distribution was determined by laser granulometry, using a Cilas Particle Size 1180, with accuracy between 0.04 and 2.500 μm and with alcohol (99.8%) as a dispersing medium. Specific surface area was calculated by the BET method, using the Nova Station A equipment. Nitrogen flow was used, temperature was maintained at 77.350 K and the analysis lasted 33 min.

The mineralogy of raw clay before calcination and

Table 1　Chemical composition of raw clay, CC and OPC.

Analyzed oxides	Raw clay	CC	OPC
SiO_2	62.62	67.74	19.82
TiO_2	1.64	1.84	0.24
Al_2O_3	23.60	26.69	4.78
Fe_2O_3	1.69	1.64	3.13
MnO	<LQ	<LQ (below the limit of quantification)	<LQ
MgO	<LQ	<LQ	5.58
CaO	0.30	0.17	61.47
Na_2O	<LQ	<LQ	0.11
K_2O	0.26	0.24	0.33
P_2O_5	<LQ	<LQ	0.16
SO_3	<LQ	<LQ	2.75
Loss on ignition (%)	9.46	0.73	1.47

Table 2　Granulometry and specific surface area of OPC and CC.

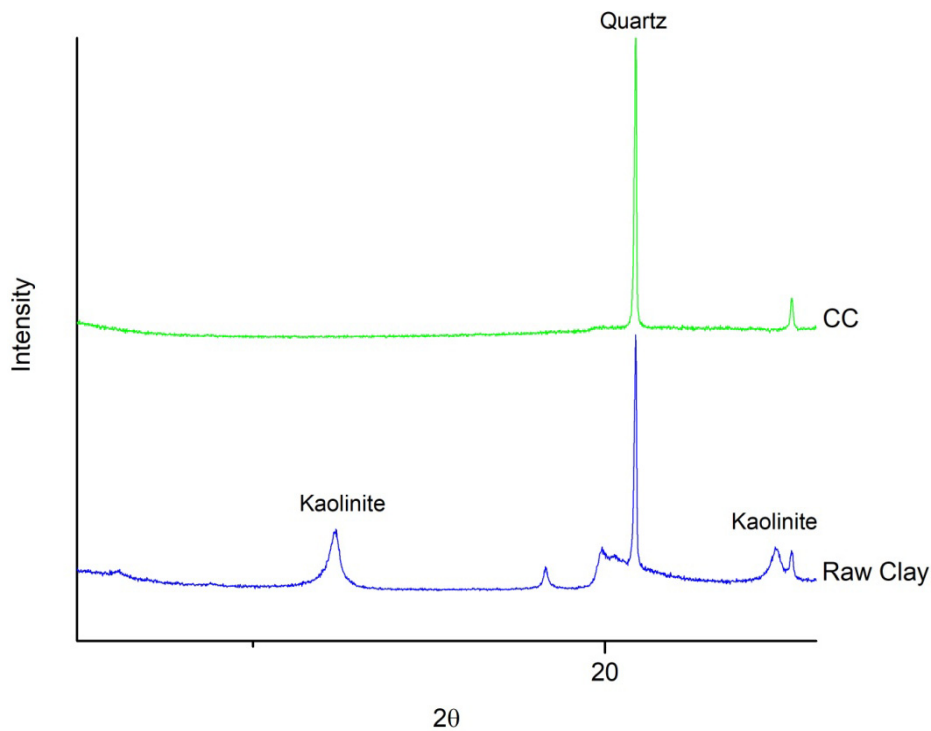| Material	Grinding (h)	Specific mass (g/cm³)	Average diameter (μm)	D10	D50	D90	Specific surface (m²/g)
OPC	-	3.11	21.65	2.19	20.17	42.60	2.86
Calcined clay	4 h	2.66	23.13	2.14	17.74	53.00	26.905

Fig. 1   XRD (X-ray diffraction) patterns of raw clay, CC.

Table 3   Paste composition in mass.

Mix	OPC (g)	CC (g)	NS (solid nanosilica)	Water (g)	SP (g)	Mini-slump diameter (mm)
OPC	1,200	-	-	479.64	1.2	90
2NS	1,176	-	80 (24)	421.12	9.6	92
25CC	900	300	-		3.6	93
23CC2NS	900	276	80 (24)	419.77	14.1	95

2NS: 2% substitution by nanosilica;

25CC: 25% replacement by calcined clay produced in the laboratory;

23CC2NS: replacement by 2% of nanosilica and 23% calcined clay.

of calcined clay was evaluated with XRD patterns, shown in Fig. 1. A quartz peak can be detected in both and kaolinite peaks are found in the raw clay. After calcination, these kaolinite peaks are not found, evidencing that the previous material lost its crystalline structure, thus no longer being detected by XRD. The conversion of kaolinite in amorphous form (metakaolin) is beneficial for reactivity, therefore this result shows that the calcination process adopted was effective [23]

3.2 Paste Composition and Preparation

In the present work, four cement pastes were produced with different blended cements. An OPC paste was used as a frame of reference. Binary pastes with 25% calcined clay and 2% nanosilica were used to evaluate their individual effects. Finally, a ternary paste with 23% CC and 2%NS was used to study their combined effect. Mass composition of the pastes is shown in Table 3.

Mixing was performed in a planetary mixer, according to the Brazilian standard [25] with adaptations to mix pastes. w/b (water/binder) ratio was fixed in 0.40 for all pastes and the workability, measured by the mini-slump test [26], was fixed at 94 ± 5 mm, considered ideal for molding. In order to

achieve the desired workability, superplasticizer admixture was used. In order to maintain w/b ration at 0.40, water content of colloidal nanosilica and superplasticizer admixture were subtracted from the water added to the mix.

During molding, the water content present in nanosilica and superplasticizer admixture was subtracted from the water content added directly to the mix, in order to keep the same w/b ratio. Mixing procedure occurred as follows: water, superplasticizer and nanosilica were first added to the recipient, followed by cement (already blended). The materials were then mixed for 60 s at slow rotation, rested for 90 s and mixed at the fast rotation for 90 s. The paste was then placed at 5×10 cm cylindrical test specimens, demolded after 24 h and then cured by immersion in lime-saturated water until testing age.

3.3 Test Methods

fc was performed at 1, 3, 7 and 28 days of hydration, following the procedures prescribed by ABNT NBR 7215:2019, but using 3 test specimens for each age. Final fc was taken as the average between the 3 results.

XRD and TGA (thermogravimetric analysis) were performed in cement paste samples, at 1, 3, 7 and 28 days of hydration. The samples were obtained from the test specimens ruptured in the fc. Hydration was stopped by immersion in isopropanol for 24 h and drying at 40 °C for 6 h. This procedure was an adaptation based in the methodology described by Scrivener et al. (2016) [27]. Close to testing age, the cement paste fragments were grinded using a pan mill and agate mortar and pestle.

XRD was performed using a Bruker D8 Discover diffractometer, with monochromatic radiation from a tube with copper anode and using a Johansson monochromator for Kα1, operating at 40 kV and 40 mA, Bragg-Brentano θ-2θ configuration using a Lynxeye unidimensional detector. Measurements were made between 5° and 25° 2θ, with 0.01° steps and 15 rpm rotation during measurement.

TGA was performed using a Shimadzu DTG-60H, between 25 and 600 °C, with heating ramp of 20 °C/min, nitrogen flow of 10 mL/min, using aluminum crucibles of 70 μL. Sample mass was approximately 15 mg.

4. Results and Discussion

4.1 fc Data

fc values were found for all pastes, at 1, 3, 7 and 28 days of hydration. The results are shown in Fig. 2 A performance index, comparing the fc results of the pastes with the OPC at each age was also calculated and is presented with the mean fc in Table 4. At all ages, paste 2NS had the highest fc, followed by paste 23CC2NS, which displayed a similar strength grow trend. Both pastes had nanosilica, which accelerated strength development up to 7 days of hydration. This effect is expected due to the nucleation effect of nanosilica, which provides extra sites for hydrate formation, and is well established in the literature [15, 28, 29]. It is worth noting, however, that at 28 days the pastes without nanosilica reach strength values closer to pastes 2NS and 23CC2NS.

Pastes with calcined clay (25CC and 23CC2NS) had mechanical performance similar to their counterparts (OPC and 2NS) after 1 day of hydration. The relative difference between them at those ages was always lower than 5%. This result shows that even with high replacement content, this calcined clay promoted strength gain sufficient to compensate the lower clinker content, as a result of the pozzolanic reaction [30]. At 1 day, since pozzolanic reaction does not occur with significant frequency in calcined clays, the difference between pastes with and without calcined clay is higher.

Finally, regarding the ternary mixture, it can be observed that no significant synergistic effect occurs.
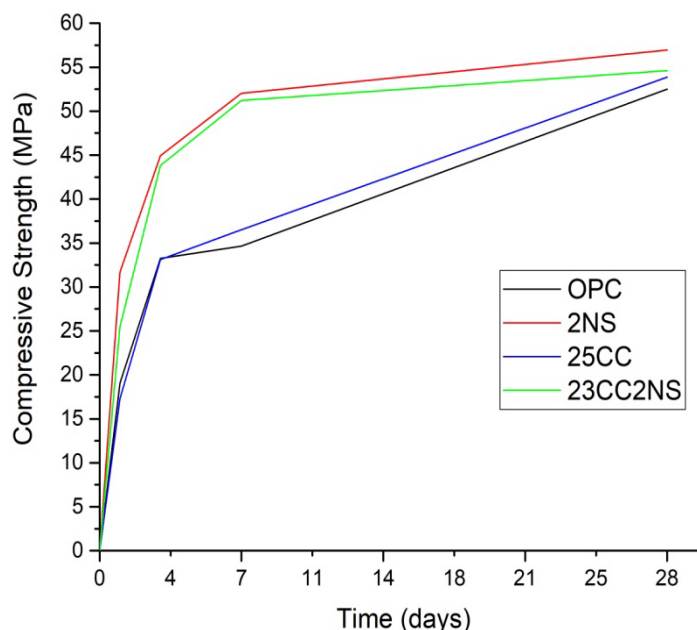
Fig. 2   Compressive strenght gain over time.

Table 4   Mean fc and performance index of the pastes at 1, 3, 7 and 28 days of hydration.

Time (days)	OPC		2NS		25CC		23CC2NS	
	fc (MPa)	Performance index (%)	fc (MPa)	Performance index (%)	fc (MPa)	Performance index (%)	fc (MPa)	Performance index (%)
1	19.06	100	31.69	166	17.28	91	25.49	134
3	33.24	100	44.93	135	33.12	100	43.81	132
7	34.63	100	52.04	150	36.50	105	51.21	148
28	52.50	100	56.94	108	53.87	103	54.60	104

Comparing paste 2NS with paste OPC, there is an increase in strength of 66%, 35%, 50% and 8% for 1, 3, 7 and 28 days of hydration, respectively. On the other hand, making the same comparison between pastes 23CC2NS and 25CC, the differences at those ages are 48%, 32%, 40% and 1%. Therefore, it is noted that the inclusion of 2% nanosilica benefited the ordinary cement to a greater extent than the binary mixture with calcined clay. In studies using metakaolin and nanossílica [20, 31], the synergistic effect was observed.. The current results indicate that clay reactivity and composition may be influential in the occurrence of this effect.

4.2 XRD Data

XRD was performed to identify crystalline phases in the hydrated pastes. Results are shown by age in Fig. 3. Portlandite (CH), quartz, calcite, alite, belite and periclase were detected. Quartz was detected in pastes with calcined clay, as expected since the material was present in the calcined clay, as shown in Fig. 3. Alite and Belite showed more distinguished peaks at the early ages, when their degree of hydration was still low. Finally, portlandite was detected in all pastes, with different peak intensities. Overall, it can be observed that blended pastes had lower peak intensities, indicating the occurrence of the pozzolanic reaction.

4.3 TGA Data

TGA was used to determine CH content in the hydrated pastes, in order to better understand the pozzolanic behavior. In order to do that, the weight loss due to decomposition of CH was identified and measured. Fig. 4 shows TG and DTG curves for paste

OPC at 1 day, displaying weight loss interval (410-460 °C), which was similar for all pastes. With the weight loss values, CH content in the samples was calculated using stoichiometry. Moreover, a CH index was calculated in order to compare all the samples with the OPC mix. The results are shown in Table 5.
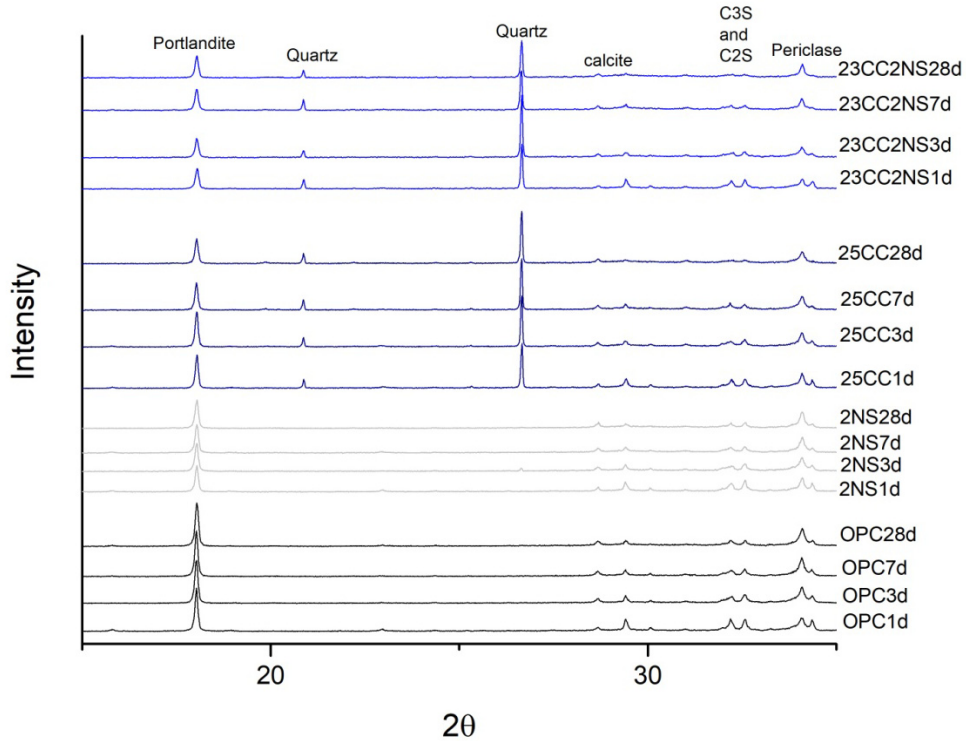

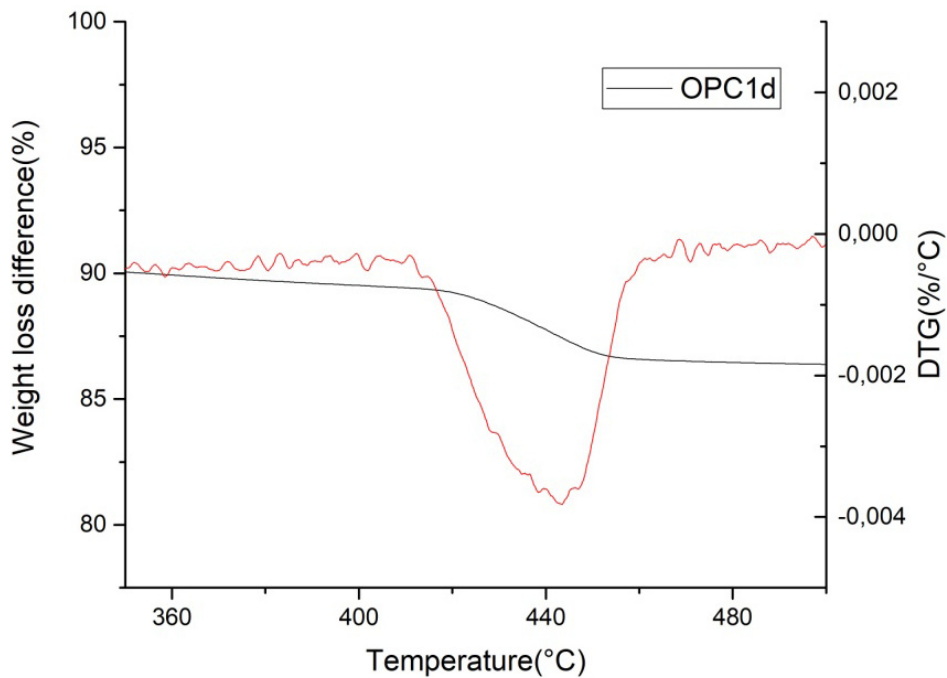**Fig. 3   XRD patterns for pastes at 1, 3, 7 and 28 days.**

Fig. 4   TG and DTG curves for paste OPC at 1 day of hydration.

Table 5 TGA test data.

Age	Mix	Weight loss (%)	CH content (%)	CH index
1 day	OPC	2.73	11.20	100%
	2NS	2.08	8.56	76%
	25CC	1.91	7.86	70%
	23CC2NS	1.54	6.34	57%
3 days	OPC	3.47	14.26	100%
	2NS	2.93	12.05	84%
	25CC	2.27	9.33	65%
	23CC2NS	1.61	6.61	46%
7 days	OPC	3.79	15.60	100%
	2NS	3.32	13.65	87%
	25CC	2.60	10.68	68%
	23CC2NS	1.79	7.34	47%
28 days	OPC	4.04	16.60	100%
	2NS	3.62	14.90	90%
	25CC	2.49	10.21	62%
	23CC2NS	1.83	7.53	45%

As expected, at all ages, CH content was higher for OPC pastes, steadily increasing as hydration progressed. In the blended pastes, lower clinker content and pozzolanic reaction are responsible for decreasing the overall CH content. In paste 25CC, CH index follows a decreasing trend, showing the progression of the pozzolanic reaction with time. On the other hand, paste 2NS shows CH index increasing over time. This shows that the deficit in CH content when compared to the OPC paste decreases, indicating that the pozzolanic reaction is more prominent at the early ages with this material. The ternary mix always showed the lowest CH content, due to a combination of low clinker content and high pozzolanic activity at both early and later age [20, 31].

5. Conclusions

The following conclusions can be drawn from the experimental results:

• The calcination process eliminated crystalline peaks relative to kaolinite presence in the XRD pattern of calcined clay, indicating that the process was successful in producing metakaolin;

• The binary paste with nanosilica showed CH consumption by the pozzolanic reaction since 1 day of hydration and accelerated clinker hydration, increasing fc by 50% at 7 days. Furthermore, it showed the highest fc result at 28 days;

• The binary paste with calcined clay showed CH consumption by the pozzolanic reaction, more prominently at the later ages. fc results were able to surpass that of OPC after 3 days, demonstrating that it is a viable option for high replacement content of clinker (25%);

• In the ternary paste, although CH consumption was increased, indicating that the pozzolanic reaction occurs more frequently in this mix, fc results did not indicate a synergistic effect.

6. Acknowledgements

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