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INFLUENCE OF GRINDING OF CALCINED KAOLINITIC WASTE ON THE PROPERTIES OF CEMENT PASTES

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Abstract: The present work aims at investigating the influence of grinding the calcined kaolinitic waste (CKW) on hydration, pozzolanic activity and microstructure of cement pastes partially replaced by it. The hydration of the pastes was studied by isothermal calorimetry and thermogravimetry. The cured pastes had their microstructure evaluated by XRD and SEM and their compressive strength was determined. The results showed that the CKW accelerated the hydration reactions and changed the microstructure of the cured pastes. The results were more expressive for the ground waste. The mechanical strength increased at the ages studied for pastes with ground CKW.

Keywords: Kaolinitic waste, Metakaolin, Supplementary cementitious materials, Cement paste, Hydration, Calorimetry, Thermal analysis, Pozzolanic activity

INTRODUCTION

Cement production in Brazil in 2021 was approximately 65.8 million tons [1] with energy consumption of 3.50 GJ/t of clinker [2]. Besides the high energy consumption, the production of one ton of cement clinker generates approximately one ton of carbon dioxide [3]. Therefore, reducing CO_2 emissions is a major challenge for the cement industry and the main strategies to achieve this goal are: increasing thermal and electrical efficiency; using alternative fuels; replacing clinker and using innovative and emerging technologies [4].

One of the most effective and promising approaches is the use of solid waste as mineral additions in Portland cement to partially replace it. Previous studies have shown that cement with these materials shows improved hydration, good mechanical properties and increased durability [5–11]

The beneficiation of kaolin, which has as its main destination the paper industry, generates, of its gross production, 26% of a waste that is deposited in ponds, thus becoming a financial and environmental problem. This waste is rich in kaolinite and has low quartz content, and thus can be a raw material to produce highly reactive metakaolinite [12]. Metakaolinite ($Al_2O_3.2SiO_2$) (MK) is a material composed of SiO_2 and Al_2O_3 with a high degree of crystalline disorder, obtained through thermal processing of the kaolinite clay mineral. In the heating process, most of the octahedral alumina is converted into more active tetra-coordinate and penta-coordinate units [13–15]. This structural change gives MK pozzolanic activity, which consists in its reaction with calcium hydroxide, a product of Portland cement hydration, forming compounds with cementitious properties [16].

The particle size of the additives has an important role with respect to chemical reactivity and densification of the solid structure. The pozzolanic reaction occurs with one of the components in solid state, so increasing the contact surface with calcium hydroxide is determinant for a satisfactory reaction rate. In addition, ultrafine grinding increases the specific surface area of the mixture, thus increasing the effects of micro aggregation and nucleation in the cement matrix [7,17–19]. However, the materials obtained from the calcination process are not always in the ideal granulometry, so the objective of this study is to evaluate the influence of the grinding of calcined kaolinitic waste on hydration, pozzolanic activity and microstructure of cement pastes.

MATERIALS AND METHODS

The materials used in this study were: kaolinitic waste (KW) from a Brazilian company located in the state of Pará and Portland Cement type II F-32 (PC).

KW was calcined at 700°C, the final temperature was maintained for 90 min, conditions defined as ideal by [6]. The calcined kaolinitic waste (CKW) was then characterized, the density was obtained through a gas pycnometer (AccuPyc 1340, Micromeritics), the particle size distribution of PC and CKW particles was determined in a laser particle sizer (Mastersizer 2000, Malvern). The Blaine specific surface was obtained according to ABNT NBR 16372:2015 [20]. The specific surface area was determined by the multipoint Brunauer-Emmett-Teller (BET) method [21], using nitrogen as the sorbent gas performed on the ASAP 2020 equipment (Micromeritics).

After calcination, a study was conducted on the ideal grinding time to obtain the CKW in a particle size closer to that of commercially used MK. The grinding times were 5, 3, 2, and 1 minute. As will be shown in the results, with 3 minutes of grinding it was possible to obtain the CKW with the desired particle size. Therefore, half of the mass of CKW was ground for 3 minutes.

The ground calcined kaolinitic waste (GCKW) had its density and specific surface determined by the previously mentioned techniques.

The pastes were prepared with 10, 20 and 30% replacement of PC by CKW e GCKW and also the reference paste, with only water and cement. In all cases the water/solids mass ratio was maintained in 0.5.

The heat release during hydration evolution and the accumulated heat of the pastes was measured in an isothermal calorimeter TAM (TA Instruments) for 3 days at 27°C.

For TGA, Scanning electron microscopy (SEM) and Nitrogen adsorption analysis, Freeze-Drying process was used to stop hydration, because this method is the most effective with regard to preserving the microstructure due to the softening of the effects of capillary stress generated by water vapor during drying and leads to more realistic porosity results [22,23]

TGA analyses of the pastes were performed in paste samples cured for 4 h, 8 h, 1, 3, 7, 28 and 120 days in a simultaneous TG/DTA/DSC equipment, model SDTQ600 (TA Instruments). The samples were heated at a heating rate of 1°C/min up to 35°C, remaining for 1h at this temperature to eliminate free water. Afterwards the temperature was raised to 1000°C at a heating rate of 10°C/min. To compare the results between pastes of different compositions, mass losses and other calculated parameters were obtained from TG / DTG curves based on the initial cement mass [24] as detailed in [6]

TM-1000 Hitachi SEM was conducted to investigate the micro–morphological structure of the paste samples cured for 3 and 28 days. Nitrogen adsorption analysis (ASAP 2020 equipment Micromeritics) served as pore size distribution measurement of hardened pastes with 28 days of hydration. Surface area was calculated by the Brunauer-Emmett-Teller (BET) [21] and Barret, Joyner and Halenda (BJH) [25] methods. The pore size distribution was determined by the BJH method.

X-ray diffraction (XRD) analyzes of pastes with 3 and 28 days of hydration were performed using a diffractometer model D8 Focus (Bruker), with Cu – Kα radiation ($\lambda = 1.5406$ Å) operating at 35 kV and 40 mA.

Compressive strength tests were conducted at a test rate of 0.03mm/min in an electronic hydraulic testing machine (Wykeham Farrance) with a capacity of 200 kN. For the compressive strength test, cylindrical specimens of 2.5 cm in diameter and 5 cm in height were molded and cured for 3 and 28 days.

RESULTS AND DISCUSSION

RAW MATERIAL CHARACTERIZATION

Table 1 shows the results of characterization tests of type II Portland cement (PC) and calcined kaolinitic waste (CKW):

Physics and chemical properties	GCKW
Density (g/cm^3)	2.58
D10 (µm)	1.18
D50 (µm)	3.84
D90 (µm)	46.39
Blaine specific surface area (m^2/kg)	2273
BET specific surface area (m^2/kg)	23280

Table 1 – Chemical and physical properties of PC and CKW

It was observed that during calcination there was an agglomeration of particles, as there was a significant increase in D_{50} in relation to that of KW, which was 3 µm, as determined by [6], this agglomeration also occurred with Lima [26] and Huang [27]. Therefore, a study of the grinding was made and the time required to obtain a material with a smaller size was determined, as shown in Figure 1 and Figure 2.

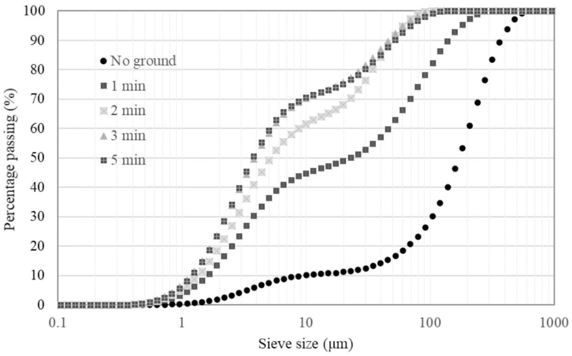

Figure 1 - Particle size curve of CKW after gridding

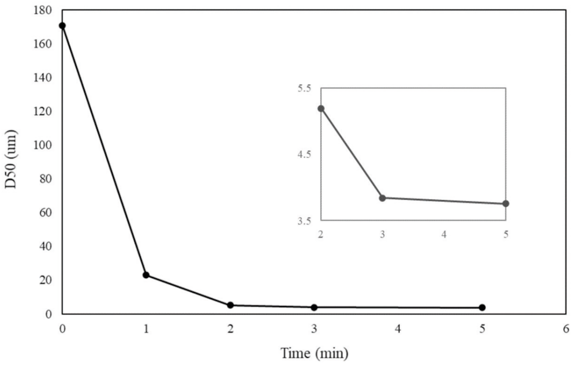

Figure 2 – Particle size versus gridding time

As can be seen from Figure 2, with 3 minutes of grinding the minimum D_{50} was reached, 3.8 µm, a typical value for the use of metakaolinite in engineering[28], so it was decided to work with this grinding time. After grinding the waste was also characterized in its density and specific surface area, the results are shown in Table 2:

Physics and chemical properties	GCKW
Density (g/cm^3)	2.58
D10 (µm)	1.18
D50 (µm)	3.84
D90 (µm)	46.39
Blaine specific surface área (m2/kg)	2273
B.E.T. specific surface área (m2/kg)	23280

Table 2 - Physical properties of GCKW

The density practically did not vary, but the specific surface area by both Blaine and BET methods increased significantly. Thus, with a short gridding time, ultrafine metakaolinite was obtained with a specific surface area greater than 20000 m^2/kg. As the pozzolanic activity is related to the particle size, it is practical to grind the CKW so that it can play a better role in cementitious based materials.

ISOTHERMAL CALORIMETRY ANALYSIS

Figure 3 shows isothermal calorimetry curves of pastes with CKW (a) and paste with GCKW: (b):

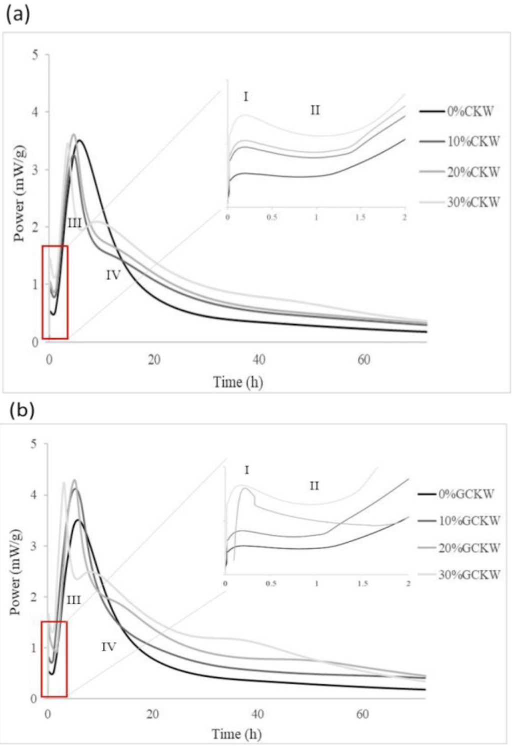

Figure 3 - Isothermal calorimetry curves. (a) Pastes with CKW. (b) Pastes with GCKW

From the pre induction and induction periods (I and II), it can be observed that as the addition of calcined kaolinitic waste in the pastes increased the minimum heat flow released by the pastes also increased, reaching 2.7 times higher than that of the reference paste.

The addition of calcined waste promoted a higher reaction rate in the acceleration period (III). For the replacement of 30% of cement by CKW there was an increase of about 28% in the reaction rate compared to the reference paste and with 30% of CKW, 97%. The maximum heat flow suffered little influence from the addition of CKW but was altered by up to 18% in the pastes with GCKW.

In the deceleration period (IV), in the pastes with 20% and 30% of CKW and GCKW, at approximately 12 h, it is possible to see the third peak, that can associate with the hydration of the ferrite phase or the conversion of the ettringite phase into monosulfate [29].

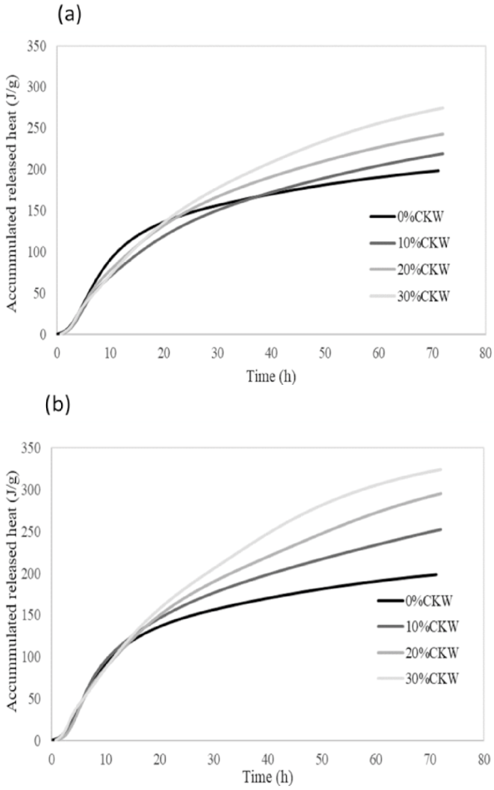

Figure 4 - Accumulated heat curves of (a) Pastes with CKW. (b) Pastes with GCKW

The amount of heat accumulated in 72 hours of hydration increased with the addition of calcined waste (Figure 4). This increase is due to the additional exothermic reactions caused by MK, its high specific surface area and the amount added [29].

Pastes with GCKW had more significant changes in hydration, showing higher values of heat flow, reaction rate and accumulated released heat. The cement hydration mechanism is accelerated due to the incorporation of GCKW, this occurs mainly because of the fine GCKW particles that promote nucleation formation, and consume free CH, and form secondary hydration products, which greatly shorten hydration during the induction period [30]. And also because when GCKW is added to the cement, $H_2SiO_4^{2-}$ is formed and reacts with available Ca^{2+}, which generates additional C-S-H, spreading in the water between the cement particles and serve to form the denser C-S-H phase; the formation of the C-S-H phase is not only limited on the surface of the particles, as in pure C3S phase, but also occurs in the pores [13].

THERMOGRAVIMETRIC ANALYSIS

Sample	4h	8h	1d	3d	7d	28d	120d
REF	1.80	2.65	4.43	8.29	9.90	12.70	13.04
10% CKW	2.25	4.74	8.66	10.56	15.47	16.49	16.52
20% CKW	2.97	4.74	9.60	11.39	17.79	19.93	20.59
30% CKW	3.43	3.73	6.81	10.22	17.26	19.83	21.00
10% GCKW	4.04	4.68	8.42	12.64	15.33	16.54	16.58
20% GCKW	2.02	4.46	7.46	10.75	17.22	17.69	17.82
30% GCKW	2.96	3.68	5.88	11.96	18.15	20.00	21.83

Table 3 – Combined water without CH content at different ages

Table 3 presents the combined water values discounting the CH content obtained in the thermogravimetric analysis. As can be observed, there is a quantitative increase in the combined water content without CH over time and with the increase in the level of substitution. In general, the values were higher for the pastes with the GCKW, this is due to the more intense pozzolanic activity of the ground calcined kaolinitic waste, which produces more C-S-H.

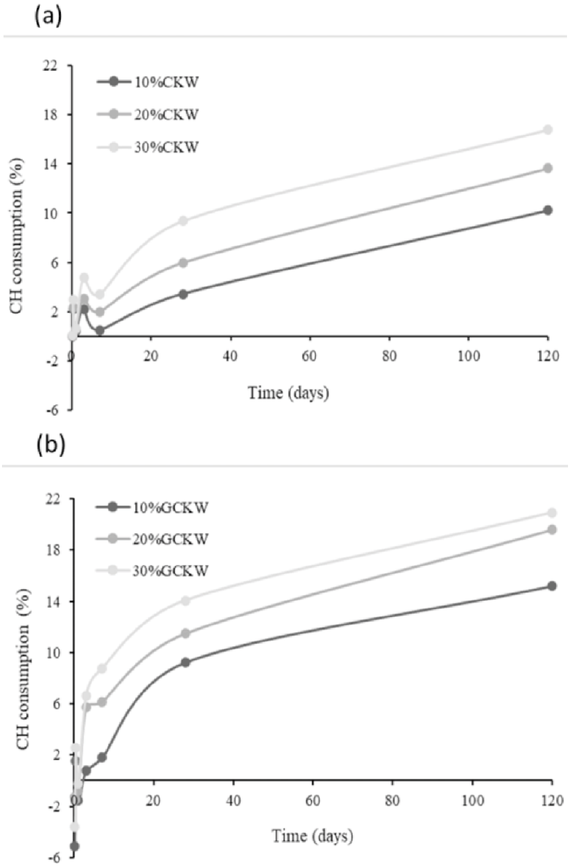

Figure 5 – CH consumption content of (a) Pastes with CKW. (b) Pastes with GCKW

The increase in the degree of substitution of cement causes a greater cumulative consumption of calcium hydroxide by metakaolinite and, therefore, lower is the remaining calcium hydroxide in the paste according to data in Figure 5. From the results obtained this effect is more pronounced the higher the degree of substitution and the longer the hydration time [31,32]. The consumption of CH was also higher in pastes with GCKW, this is because a smaller particle size leads to a greater surface area, dissolution rate, presence of precipitation nuclei and extension of pozzolanic activity [18,33].

It can be observed that even after 28 days the pozzolanic reaction continued to take place, as there was an increase in hydroxide consumption at 120 days.

To evaluate the consumption of CH at early ages, the curves for ages up to 7 days were plotted (Figure 6). As can be seen, before 3 days, the formation of CH was predominant in relation to the pozzolanic reaction, and therefore a negative consumption. However, after 3 days the pozzolanic activity became more significant, even in relation to the unground CKW.

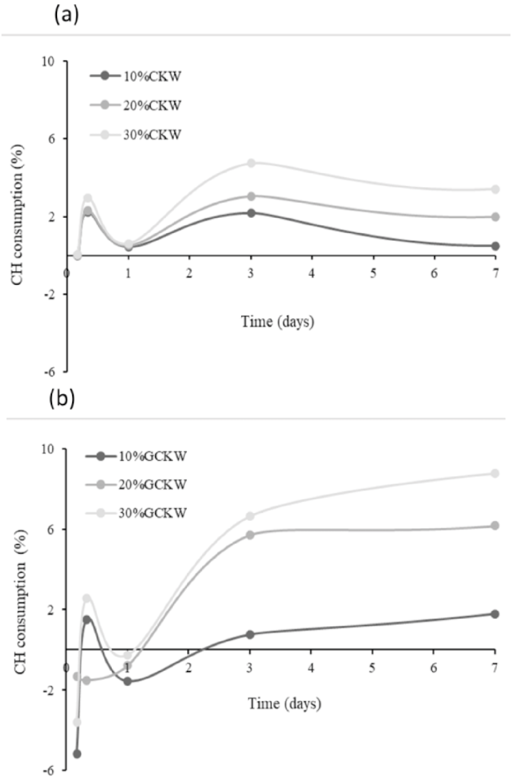

Figure 6 - CH consumption content at early ages of (a) Pastes with CKW. (b) Pastes with GCKW

XRD ANALYSIS

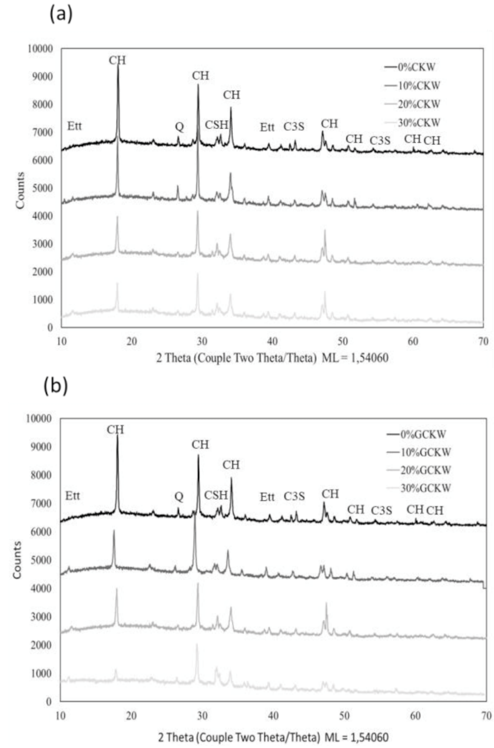

Figure 7 – XRD patterns at 3 days of (a) Pastes with CKW. (b) Pastes with GCKW

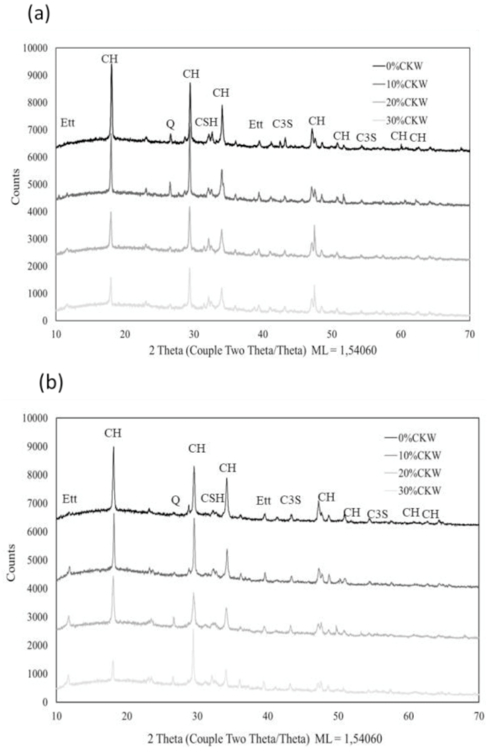

Figure 8 - XRD patterns at 28 days of (a) Pastes with CKW. (b) Pastes with GCKW

The figures 7 and 8 show the diffractograms of the pastes at 3 and 28 days, respectively. In them one can find hydration products such as portlandite, calcium silicate hydrate, ettringite, and non-hydrated minerals in the hardened pastes. It can be observed that the amount of CH in the cement paste with the CKW and GCKW was lower than in the reference paste. The results are in qualitative agreement with those of [19,34,35] in which reduced calcium hydroxide (CH) diffraction peaks were reported for cement mixtures with MK.

The intensity of the CH peaks decreased with increasing substitution level. Comparison between the diffractograms of the cement pastes reveals that the addition of 30% GCKW to the cement paste leads to a reduction in the intensity count of the maximum calcium hydroxide peak from 2764 to 442 at 3 days and from 2217 to 235 at 28 days.

In the pastes with 3 days of hydration, it is already possible to observe the consumption of CH by MK. The results were more significant for pastes with GCKW.

It can be observed that the content of C-S-H of pastes with the calcined kaolinitic waste is higher than without, although the difference in content of C-S-H between pastes containing MK is small. MK reacts with CH to generate C-S-H-containing compounds, which results in a strong decrease in CH and an increase in C-S-H [36].

SCANNING ELECTRON MICROGRAPHS

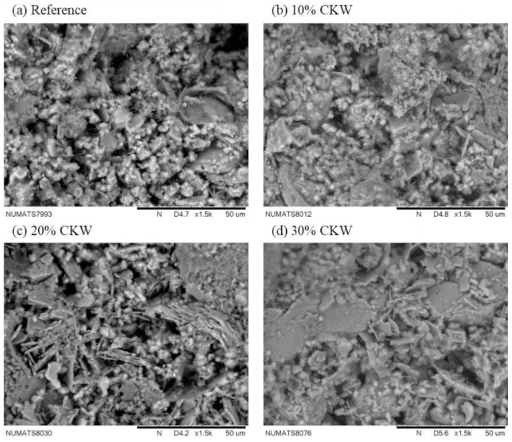

Figure 9 - SEM photograph of cement pastes with CKW at 3 days

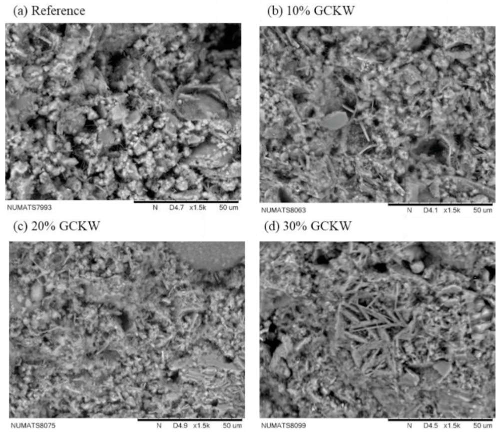

Figure 10 -SEM photograph of cement pastes with GCKW at 3 days

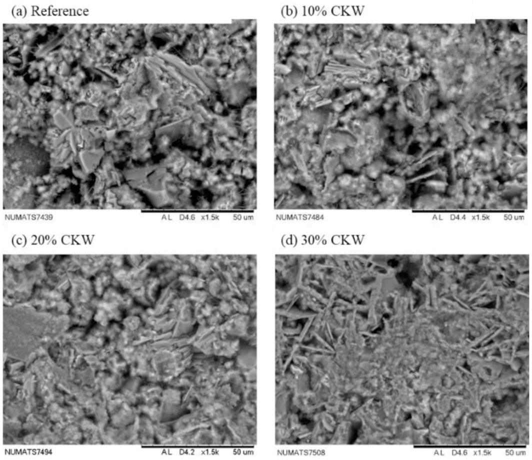

Figure 11 - SEM photograph of cement pastes with CKW at 28 days

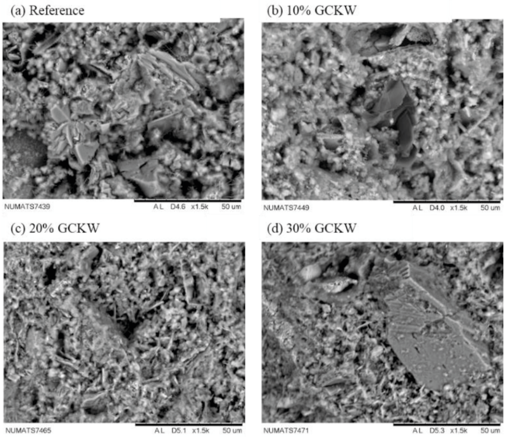

Figure 12 - SEM photograph of cement pastes with GCKW at 28 days

As can be seen in the micrographs (Figures 10, 11 and 12), the initial products of the reference paste were ettringite crystals, CH crystals and C-S-H and the pore structures are improved with the increase of curing time, this is due to the progress of hydration.

At 3 days, more needle-shaped ettringite crystals are observed in all pastes and in pastes with the addition of the calcined kaolinitic waste more CH crystals, due to the still low pozzolanic action and a less dense structure. At 28 days, it can be observed that the amount of ettringite drops notably, probably having been converted to monosulfate, as well as that of CH in the pastes with CKW. The microstructure of the cement paste was significantly altered due to the incorporation of MK. Firstly, the pore structure was refined due to the introduction of MK, leading to a denser microstructure and the pozzolanic reaction between MK and CH which leads to the formation of fibrous C-S-H. Consequently, the microstructure is transformed into a matrix associated with higher densification and low porosity [33]. Similar results were found by [19,27,35,37].

SPECIFIC SURFACE AND PORES ANALYSIS

Analyzing the adsorption isotherms (Figure 13), pore distribution curves (Figure 14) and calculated area (Table 4), it can be concluded that the pastes with the addition of calcined kaolinitic waste showed lower values of adsorbed volume, surface area and pore size, this is due to the presence of MK, which refines the porous structure of the paste and makes the matrix denser.

The best results were for the paste with 10%GCKW. This result is consistent with those found by [17,36] who found that ultrafine MK substantially improved the porous structure of concrete and reduced the presence of large detrimental pores, which substantially improves durability.

MK acts in physical and chemical ways to bring about these effects: the ultrafine particles fill the voids in the cement, which makes the microstructure of the matrix denser. The chemical effect is the reaction of MK with hydrated cement products. The C-S-H formed transforms the coarser pores into finer pores. Due to the net reduction of the CH content in the hydrated matrix due to the pozzolanic reaction, the volume of the continuous capillary pores is proportionally reduced; the higher the CH content in the hydrated matrix, the larger the volume of the continuous pores [36].

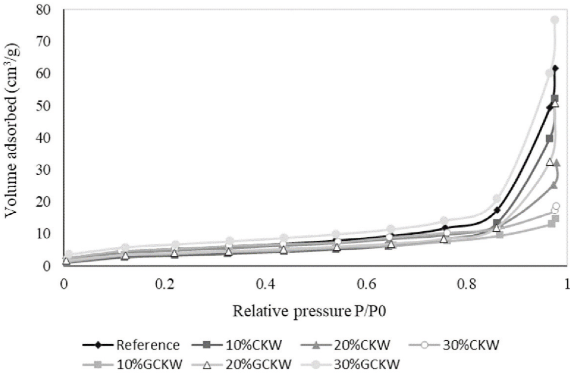

Figure 13 - Nitrogen adsorption isotherms

Formulação	Área superficial	
	BET	BJH
REF	18.43	17.10
10%CKW	18.10	16.68
20%CKW	16.79	16.07
30%CKW	15.89	15.36
10%GCKW	11.84	11.14
20%GCKW	13.86	13.98
30%GCKW	23.45	24.77

Table 4 – Surface area by BET and BJH methods

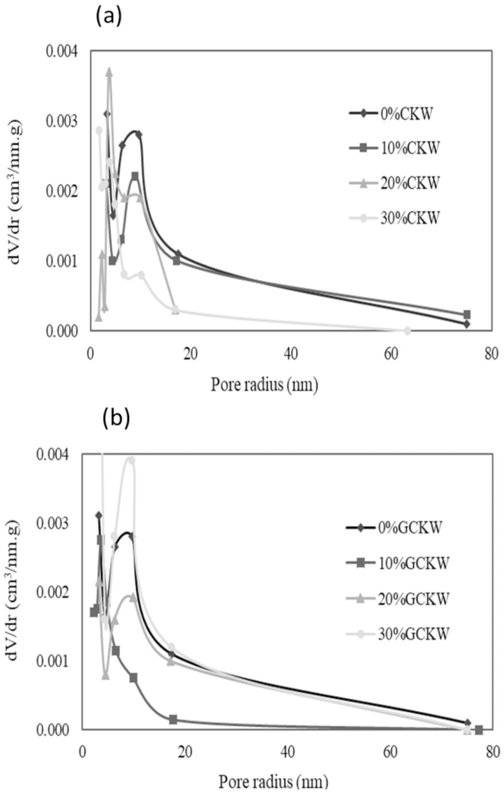

Figure 14 - Pore size distributions of (a) Pastes with CKW. (b) Pastes with GCKW

MECHANICAL STRENGTH

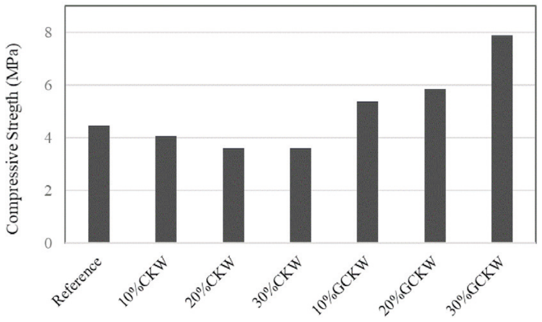

Figure 15 - 3 days compressive strength of cement–calcined kaolinitic waste mixtures

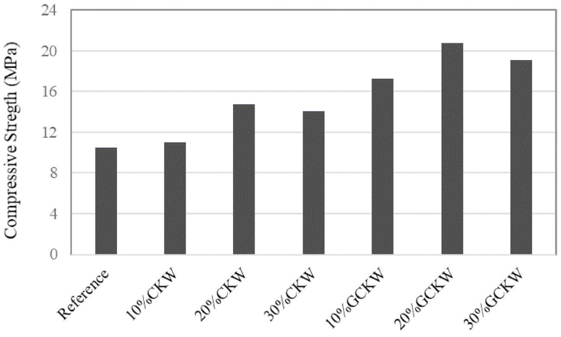

Figure 16 - 28 days compressive strength of cement–calcined kaolinitic waste mixtures

At 3 days, the pastes with cement replacement by unground calcined waste showed a decrease in compressive strength compared to the reference (Figure 15). The pastes with GCKW increased the tensile strength even after 3 days of curing. These results show that the GCKW starts its pozzolanic activity before 3 days and at this age it is already possible to see its action, which overcomes the decrease in the amount of cement. As for CKW, with 3 days of curing the pozzolanic activity is not yet effective to compensate for the decrease in the amount of cementing material. These data agree with those found by thermogravimetry, in which a greater consumption of CH was seen at 3 days in the pastes with GCKW.

It can be observed that all pastes with additions showed higher compressive strengths than the reference paste at the age of 28 days (Figure 16). The increase in mechanical strength of the pastes replaced by the calcined kaolinitic waste is due to the pozzolanic activity, which results in the formation of new hydration products and the formation of a less porous internal structure [36,38]. This result corresponds in principle to the increase in C-S-H content, seen in the TG and DRX results The use of ultrafine materials increases the compressive strength even more expressively, because it increases the extent of pozzolanic activity and pore refinement [17,18,33,39,40], which was seen in micrographs and in the results of surface area and pore analysis.

CONCLUSIONS

The grinding of the CKW produced a material with particle size similar to the commercial MK, with greater surface area, this made the changes in hydration kinetics more pronounced.

The pozzolanic activity of the calcined kaolinitic waste was greater the higher the degree of cement replacement and the longer the hydration time. It was also more extensive with the replacement by GCKW.

The intensity of the XRD peaks of the pastes corresponding to CH decreased with increasing substitution level and corresponding to C-S-H increased. From the micrographs obtained in the SEM, it was observed that the microstructure of the cement paste replaced by the calcined kaolinitic waste was transformed into a matrix associated with higher densification and less porosity. This was also observed by the results of surface area and pore size analysis, because the pastes with the addition of waste showed lower values of adsorbed volume, surface area and pore size, which is due to the presence of MK, which refines the porous structure of the paste and makes the matrix denser.

Regarding compressive strength, after 28 days, all substitutions showed an increase in compressive strength, the highest values were found for ground waste. This is due to the pozzolanic activity of the material studied, which resulted in the formation of new hydration products, and also to the lower porosity of the hardened paste.

Grinding is a simple and practical process, in the case of CKW with a very short time it was possible to produce an ultrafine material, with high surface area and that led to better properties of the pastes. But despite the improvement in properties after grinding, even without grinding the waste already showed excellent results.

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