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A Preliminary Insight into the Effects of Tailing Wastes Addition on Metakaolin-based Geopolymers

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Abstract **-** Geopolymers are inorganic binders made up by alkali activated aluminosilicates tetrahedrons. Given during the 1970s by Davidovits with reference to inorganic or mineral materials, geopolymers have good chemical properties, stability in alkaline or acidic media, high mechanical strength, and their synthesis is based on the polycondensation of aluminosilicate tetrahedrons. In the meantime, after the high failures rate of tailing dams the storage of mining wastes became difficult, leading to considering other storage destinations. Combining these two aspects, this study deals with the effects of the addition of some iron ore tailings in different binders of metakaolin-based geopolymers. The effects of iron tailing wastes addition, the composition in mass percentage, and the calcination time are independently evaluated in terms of compressive strength. Their mutual effects are also studied, highlighting the need for an in-depth control of the calcination conditions of metakaolin and the composition of the geopolymer samples to have the desired strength properties.

Keywords**:** tailings; geopolymers; kaolinite; compressive strength; calcination; metakaolin.

1. Introduction

The Iron ore Quadrangle of Minas Gerais produces about more than 60% of the Brazilian iron ore and represents an important product exported to many countries. The mining activity produces huge volume of wastes, usually stored within basins usually retained by step-by-step raised dams whose high rate of recent collapses (Fig. 1) poses serious social, economic and environmental threats ([1]-[2]-[3]-[4]). For these reasons the storage of tailings became difficult, leading to considering other storage destinations such as storage in piles and their use as raw materials for other manufacturing chains, such as backfill material, aggregate in road construction, or fine aggregate for cement and concrete paving as shown in the Fig. 2 ([5]-[6]-[7]).

Fig. 1: The collapse of Feijão tailing dam - Brazil – 2019 ([8]).

Fig. 2: Re-usage of tailings: civil structure made of iron tailings ([7]).

In the meantime, the interest in geopolymers is increasing both because of low CO2 emission in their manufacturing process if compared to Portland cement, and their good chemical and mechanical properties. Indeed, geopolymers are cementitious binders made up by different raw materials, among them mineral extraction wastes (tailings) and wastes from industrial activities. In the current research, geopolymers were prepared by mixing metakaolin (obtained from kaolinite calcined which represents a by-product of sand extraction), alkaline sodium silicate and sodium hydroxide solution. The aim of the experimental campaign carried out in this study is a better understanding of the effects on the mechanical strength of some iron tailings addition in different binders of metakaolin-based geopolymers in terms of heating rate, the calcination time, and composition in mass percentage.

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2. Material and Experimental Methods

2.1. Kaolinite characterization and metakaolin formation

Samples of kaolin were provided by GH Areias, a company of sand extraction placed in Minas Gerais (Brazil), as a by-product of their operations. Kaolin samples have different greyish colours increasing in intensity with depth. Kaolin samples were then oven dried at 120°C for 24 hours, so their particles were reduced by means jaw and planetary mills, and then rollers were used to disaggregated ASTM #16 sieves retained particles (Fig. 3). They were characterized as shown in Table 1 (Fig. 4, Fig. 5 and Fig. 6).

Fig. 3: Preparation method of kaolinite samples

Table 1. Characterizations performed on the tailing samples.

Property	Technique	Equipment
Particle density	Helium pycnometry	Quantachrome, model Ultrapycnometer
Particle size distribution, specific area	N_2 adsorption	Quantachrome, model NOVA 2000
Chemical analysis	Infrared spectroscopy (FTIR)	ABB Bomem, model MB102*
	X-rays fluorescence (XRF)	Shimadzu equipment EDX-720
Mineral composition	X-rays diffractometry (XRD)	D\Max Ultima Plus**
Mass loss and endothermic and exothermic events in metakaolin	Thermal analysis	Differential scanning calorimetry (DSC)***

*Performed on kaolinite samples before and after the calcination at 800°C (formation of metakaolin). ** XRD spectra collected with Cu-Kα radiation, power 40kV and current 30mA. *** performed at 120°C for 24 hours in air, heating rate at 10°C.min^{-1}, N_2 atmosphere in a STA 449 F3 Jupiter from Netzsch instrument.

Fig. 4: Quantachrome apparatus for the specific area evaluation.

Fig. 5: XRD diffractometer.

Fig. 6: FTIR spectrometer.

According to previous work ([9]-[10]), the metakaolin was obtained by calcination of the kaolinite in a muffle kiln at 800°C for different calcination time (4 hours and 8 hours) and heating rate of 10°C.min^{-1} (Fig. 7).

a)

b)

Fig. 7: Preparation of the metakaolin sample. a) Muffle kiln, b) comparison of the sample before (kaolin) and after the calcination (metakaolin).

2.2. Geopolymer Matrix

Seven geopolymer compositions were created by mixing different amount of metakaolin (MK) with alkaline sodium silicate SiO_2/Na_2O molar ratio = 2.22 (SS), and 10 M sodium hydroxide solution (NaOH), as shown in Fig. 8 and Table 2. A paste was obtained which, placed in cylindrical polyethylene moulds (5.0 cm diameter, 5.0 cm height) and air bubbles were removed by means of stirring into an orbital shaker (350 rpm for 10 minutes). After 24 hours at room temperature, the hardened geopolymer samples were demoulded. The two compositions that gave the best workability, best-solidified product with the lower porosity and no efflorescence were chosen:

- composition “1” (55 wt% MK, 25 wt% SS and 20 wt% NaOH);
- composition “5” (50 wt% MK, 35 wt% SS and 15 wt% NaOH).

Fig. 8: Geopolymer paste.

Table 2. Seven initial compositions of geopolymer based on the stoichiometric composition.

Composition	MK (wt%)	SS (wt%)	NaOH (wt%)
1	55.0	25.0	20.0
2	60.0	25.0	15.0
3	55.0	30.0	15.0
4	45.0	33.0	22.0
5	50.0	35.0	15.0
6	50.0	30.0	20.0
7	50.0	25.0	25.0

The geopolymer samples of "compositions 1" and "compositions 5", obtained by metakaolin calcined at 4 hours and 8 hours, were added with iron tailing wastes (-TW), respectively 50% and 60%. The compressive strength tests were conducted on geopolymer samples after 28 days of ageing. Five samples were tested for each mechanical test (Fig. 9): compressive strength tests (CS) were performed on an EMIC, model PCI 150 testing machine shown in Fig. 10 (load: 273 kN, loading rate: 30 MPa/min), according to the Brazilian Standard NBR 5739:2007 (ABNT, 2007 [11]). Despite the standard refers to cemented products, it was used also to geopolymer samples because there is no standardisation about compressive tests for it. The 2^3 Factorial Design of Experiments is presented in Table 3. Three main factors were investigated in the current research:

- composition (-C), respectively 1 and 5;
- calcination time (-CT), respectively 4 and 8 hours;
- tailing wastes addition (-TW), respectively 50% and 60%.

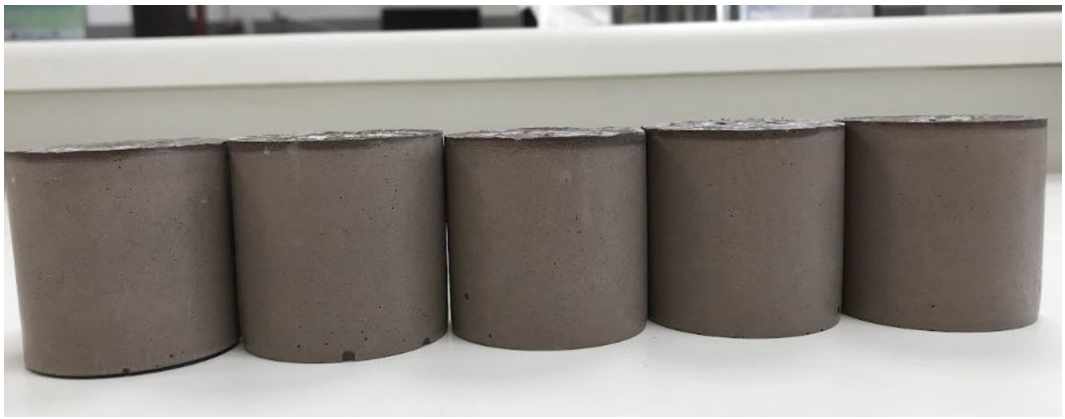

Fig. 9: Geopolymer samples.

Fig. 10: Testing device used for the evaluation of the compressive strength of tailings-added geopolymer samples.

Table 3. 2^3 Design of experiments: calcination Time - CT, composition – C and tailing wastes addition - TW.

Factors	-CT (hours)	-C (-)	-TW (wt%)
Levels	4 - 8	1 - 5	50 - 60

3. Experimental Results and Discussion

Mineral constituents of kaolin samples were quantified carrying out X-rays diffractometry, revealing kaolinite as the major phase and quartz as a minor phase. The mean particle size of kaolin samples varied be-tween 7.75 µm and 11.05 µm, while chemical composition was investigated by means of X-rays fluorescence. X-ray fluorescence analysis showed similarity between the samples, except for the Cr and Mn ([9], and the results of XRF analysis for light grey sample used to synthetize of the geopolymer presented 51.02% of SiO_2 and 29.20% of Al_2O_3. The density of the kaolin samples ranged between 2.54 g/cm^3 and 2.62 g/cm^3, probably because the presence of quartz and organic matter contents. Thermal analysis of the kaolin samples reveals the dehydroxylation of kaolinite (Fig. 11) because of the presence of an endothermic peak around 500°C. A peak can be observed at 250°C and it is probably related to the burning of organic matter, while another small related to the transition from alpha-quartz to beta-quartz can be observed at 580°C. Finally, an exothermic peak, due the mullite formation can be observed at 980°C. The FTIR spectra of kaolin samples before (kaolinite) and after the calcination at 800°C (metakaolin) is provided in Fig. 12. Typical bands of kaolinite (range of 3697-3621 cm^{-1}) related to OH stretching disappear after the formation of metakaolin, so bands for wavenumbers smaller than 1500 cm^{-1} become indefinite, showing the presence of amorphous material. Indeed, the loss of crystallinity after formation of metakaolin could be observed by X-ray diffraction, except for the presence of quartz that, as stated before, was already present as a minor phase in kaolin samples.

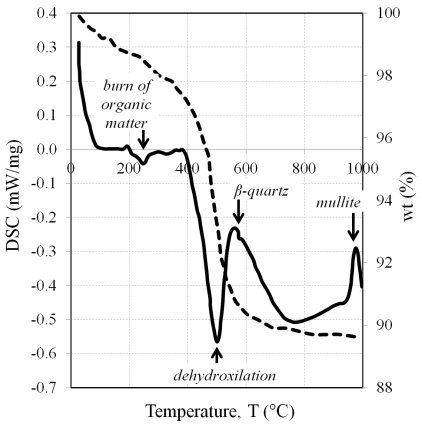

Fig. 11: Thermal analysis results for kaolinite samples after drying at 120°C for 24 hours in air, heating rate: 10°C/min, N_2 atmosphere.

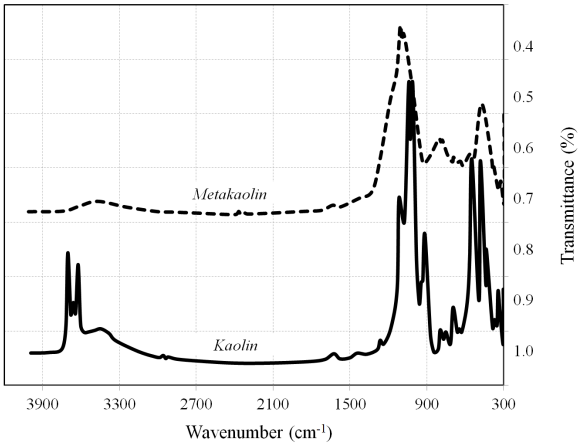

Fig. 12: Fourier transform infrared spectra (FTIR) of the kaolin and the metakaolin samples.

The compressive strength results of the 40 runs performed on the geopolymers tailings-added samples with (TW=50% or 60%, curing: 28 days) are given in the table below. The code GH-CT-C-TW refers to Fig. 13.

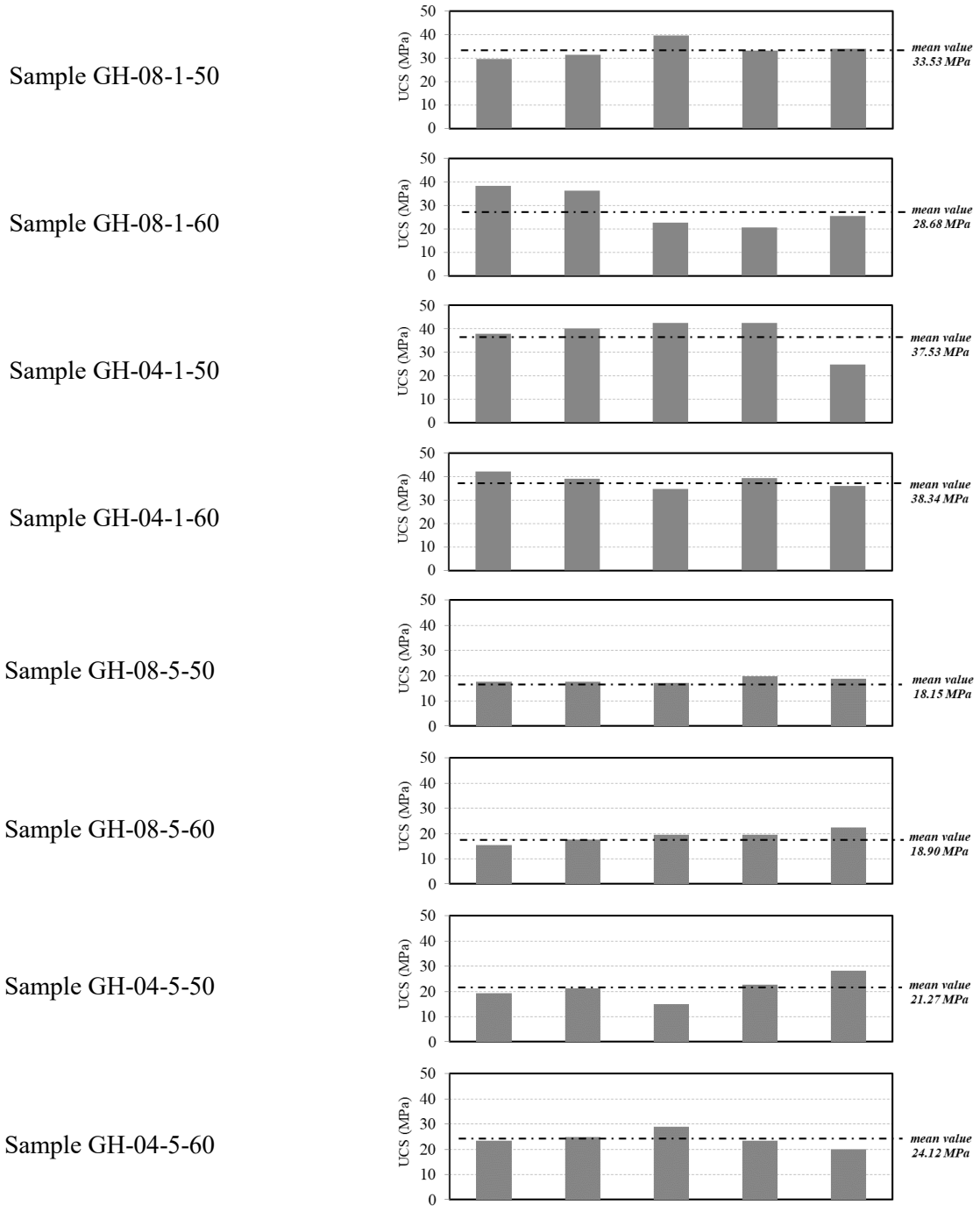

Fig. 13. Compressive strength (CS) on geopolymer tailings-added samples.

The effect of each factor -C, -TW, -CT and their mutual interaction (taken by two, or by three) on the compressive strength of tailings-added geopolymer samples, are calculated with Minitab® (Table 4).

Table 4. Compressive strength (CS): Analysis of the Variance.

Main factor	p- value	Effects
Calcination time -CT (hours)	0.002	-5.391
Composition -C (-)	0.000	-14.140
Tailing waste -TW (wt%)	0.478	1.157
Two factors interaction	0.805	-
Calcination time -CT * Composition -C	0.474	1.168
Calcination time -CT * Tailing waste addition -TW	0.620	0.807
Composition -C * Tailing waste addition -TW	0.873	-0.261
Three factors interaction	0.727	-
Calcination time -CT * Composition -C * Tailing wastes addition -TW	0.727	0.569

Results shown in Table 4 suggest the only significant terms in the compressive strength are –C and CT (-p values less than 0.05). Furthermore, the composition factor (effect: -14.140) has a major impact than the calcination time (effect: -5.391) or tailing wastes addition (effect: +1.157). Moreover, composition "1" gave high compressive strength than composition "5" (Fig. 13), while the calcination time of 4 hours gives high compressive strength than 8 hours. If two factors interaction are quantified (Table 4), only -CT and -C are the most relevant for the compressive strength (effect: 1.168), if compared with -CT and -TW (effect: 0.807) or compared with -C and -TW (effect: -0.261). The equation of the non-hierarchical empirical model predicting the compressive strength (CS) including only the significant interactions is given in Eq. (1) and the cube plot for the compressive strength is given in Fig. 14. According to the case under investigation, it can be observed that the combination of -C ("1" or "5"), -CT (4/8 hours) and -TW (50/60%) results in geopolymers with different value of compressive strength.

$$CS\ (MPa) = 42.6 - 3.57CT - 16.8C - 0.126TW + \\ +1.86CT \cdot C + 0.0404CT \cdot TW + \\ +0.145C \cdot TW - 0.0284CT \cdot C \cdot TW \quad (1)$$

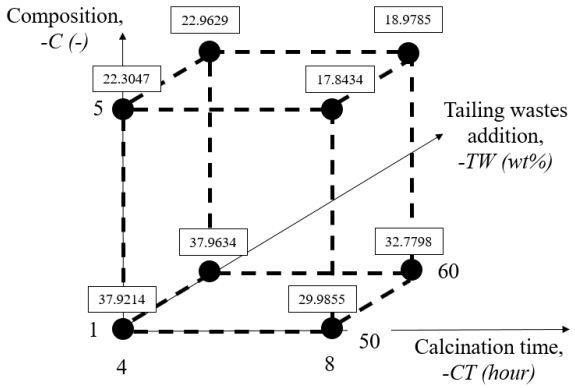

Fig. 14: Representation of the cube for the CS based on Eq. (1) (modified from [12]).

According to Eq. (1) evaluated with the response optimizer of Minitab® code, the maximum compression strength is 37.9 MPa (confidence level of 95%) obtained for -C = 1, -CT = 4 hours and TW = 50% and 60%, in good agreement with the experimental results.

4. Conclusion

Metakaolin was obtained by calcining kaolin at different temperatures, times and heating rates of the kiln. The geopolymer samples were synthesized with several proportions of metakaolin, alkaline sodium silicate, sodium hydroxide solution and added with tailings in different contents. The influence of composition, iron ore tailing waste addition, calcination time and their interaction on the compressive strength of geopolymer samples has been investigated. A relevant influence of the composition on the compressive strength of the tailings-added geopolymer samples was observed, followed by the calcination time. The compressive strengths observed may range from 18 MPa to 38 MPa in good accordance with to the empirical model calculated from a 2^3 factorial design, leading the need for a rigid control over these factors to get geopolymer samples having the desired mechanical properties. Further analysis could be carried out over a wider range of calcination time, composition and iron ore tailing waste addition, or by considering different ore tailings.

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