

Use of Sand Extraction Wastes in the Synthesis of Geopolymer

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Abstract: Environmental degradation is a matter that worries the world's population. Therefore, there is an incentive to search for alternative materials, which in addition to enabling the reuse of dispersed substances in the environment, can replace the polluting materials already in use. Around 1972, Davidovits discovered the Geopolymer, an inorganic polymeric material like zeolites, composed of alumina and silica that restructure by alkaline activation. With the innovation of the Geopolymers, it is sought the incorporation of tailings of the mining in its synthesis. For that reason, the present work aims to study the influence of three factors on the calcination of kaolinite in metakaolin for the response “compressive strength” of the obtained Geopolymer. GH Areias Company, Inhaúma, Brazil, which has sand as its main extraction product and the clay, the waste of the process, provided the kaolinite used in this study. The factors studied were calcination time, heating rate and composition in the mass percentage. Through the Variance Analysis, it was possible to verify that the geopolymer with the highest percentage of metakaolin, 8h of calcination time and heating rate of 10°C/min presented higher values of compressive strength an average of 53,187 MPa.

Key words: Geopolymer, calcination, mining, kaolinite

1. Introduction

Even with the social and technological development, it still has a significant growth in natural extraction. An example occurs in the mining section reach mainly the mining of the iron ore. According to Mesquita, Carvalho, and Ogando (2014) [1], Brazil is the second country with the highest iron ore reserves in the world, where the extraction is focused on the Iron Quadrangle, Minas Gerais, Brazil. A high quantity of co-products (materials with no commercial value) as sandy and clay (sludge) are generated due to the huge production of the iron. The non-using of both sum to the deposition on the environment, like the usage of tailing dam, due to the low cost of production and maintenance, generate high risk to the flora, fauna, and population who live close to these locations. The most recent

environment disasters was the collapse of the tailings dam of Fundão in Mariana–MG and Córrego do Feijão, in Brumadinho–MG, where also the population suffered an irreparable loss [2, 3].

According to Guimarães et al. (2018) and Gonçalves (2007) [4, 5], researches looking for alternatives to the use of this waste in production of materials, mainly on the civil construction sector, as roof, ceramic, concrete, structural blocks, and others. In accord to Barroso (2009) [6], a material with high potential is the geopolymer produced and named for Davidovits (2002) [7] in 1972. The geopolymers have a polymeric structure of SiO_4 and AlO_4 , developed from the reaction of substances rich in aluminosilicate, varying from metakaolin, flying ashes, blast furnace slag and until residual sludge, and alkali solution who restructure the polysilicate present [8]. Zeolites are substances compost by hydrated aluminosilicate, characterized by the presence of linear chains with

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tridimensional tetrahedral crystal lattice of SiO_4 and AlO_4 . Both substances are formed by tetrahedral structures who share the oxygen present in those compositions [9].

Because of the compact structure of the geopolymers and the components used in your confection, these solidify at room temperature and this process is known as polycondensation. There are several studies based on the cure time of geopolymers, oscillated between 1, 7 or 28 days in test of compressive strength [10-13]. The transformation of kaolinite to metakaolin occurs due to the loss of water content during the calcination. However, if the loss of water content is fast or the quantity of added water is low, the geopolymer structure cannot be completely formed originating a weak product. Water provide the oxygen to create polymeric chains and assists in the polymerization velocity, once it improves the activation by the reagents dissolution. On the other side, if in excess there is the formation of huge crystals in the structure bringing fragility to the product, reducing your resistance. Therefore, the quantity of water needs to be proportional to the others reagents [14].

Comparing the regular ceramic section of civil construction, the production of a geopolymer reduces the CO_2 emission in the atmosphere. In addition, the indices of mine exploration grow reducing raw material sources and bring Environmental concerns with the accumulation of wastes in the dams. The present paper proposes a study to analyze the influence of some factors in the synthesis of the geopolymer. These factors are calcination time of kaolinite, the heating rate during the process of the calcination and the composition in weight percent of the reagents. The kaolinite used in this work was provided by the GH Areias Company, Inhaúma, Minas Gerias, Brazil. The main activity of this Company is the sand extraction. The kaolinite is extracted before the sand during the process and stays stored in piles and it is considered a waste due to the difficulty of commercialization. Therefore, your use in the geopolymer synthesis has

the intent to increase add value.

2. Material and Methods

Firstly, the samples of kaolinite were dried at 120°C for 24 hours before comminution performed in jaw and planetary mills to reduce the particle size as much as possible. After sieving in 16 # sieves, the retained portion was disaggregated with the use of rollers. The calcination of the kaolinite was performed in muffle kiln NA-2312. During the calcination process, the kaolinite reorganizes and becomes metakaolin with coloration change from gray to orange and pink. The calcination processes was performed at 800°C oscillating the calcination time and heating rate.

The samples were identified according to the code GH1-04-10-1, where GH1 represents the origin of the material which no changed in this study. The second term represents the calcination time (CT) oscillated from 8 h, 4 h, 2.8 h and 1 h as shown in Table 1. The third term represents the heating rate (HR) ranging from $10^\circ\text{C}/\text{min}$ to $1^\circ\text{C}/\text{min}$. The last one term represents the composition (C) of each reagent used in the geopolymers synthesis (metakaolin MK, sodium silicate SS and 10M sodium hydroxide solution). Seven compositions were made based on the stoichiometric composition (45 wt% of MK, 33 wt% of SS and 22 wt% of NaOH solution). However, the two compositions that presented the best workability, best solidified product with lower porosity and no efflorescence were chosen. These compositions were referred to as C1 and C5 and were shown in Table 2.

The geopolymer samples were synthesized by mixing metakaolin with alkaline sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio = 2.22) and 10 M sodium hydroxide solution. A paste was obtained which was placed in polyethylene cylindrical molds (5 cm diameter and 5 cm height) and subjected to stirring on an orbital shaker (IKA – KS 130 Control S1) at 350 rpm for 10 minutes to remove air bubbles. After 24 hours at room temperature, the hardened samples were desmolded. The geopolymer samples were

characterized for compressive strength based on the Brazilian Standard NBR 5739 [15] and NBR 7215 [16], after 28 days of curing at room temperature, in a

273 kN press at a loading rate of 30 MPa/min (press EMIC 22762).

Table 1 Code of samples in accord to HR, CT and C.

HR (°C/min)	CT (h)			
	1	2.8	4	8
1	GH1-1-1-1	GH1-2.8-1-1	GH1-04-1-1	GH1-08-1-1
	GH1-1-1-5	GH1-2.8-1-5	GH1-04-1-5	GH1-08-1-5
10	GH1-1-10-1	GH1-2.8-10-1	GH1-04-10-1	GH1-08-10-1
	GH1-1-10-5	GH1-2.8-10-5	GH1-04-10-5	GH1-08-10-5

Table 2 Compositions of the matrices 1 and 5.

Matrices	Metakaolin (wt%)	Sodium Silicate (wt%)	NaOH solution (wt%)
C1	55	25	20
C5	50	35	15

3. Results and Discussion

3.1 Compressive Strength

Tables 3 and 4 are shown the results of the compressive strength to geopolymeric matrices C1 and C5, respectively.

The results were interpreted according to Analysis of Variance (ANOVA), with 95% confidence level. Therefore, it was verified the influence of the factors

HR and CT in the response “compressive strength CS” in both compositions and matrices studied. The calculation of the effects of the factors and their interactions was done with the aid of Minitab software 19. The results are shown in Tables 5 and 6. Two 2³ factorial designs was performed separately each with two pairs of CT for better interpretation of data from ANOVA.

Table 3 Compressive strength results of geopolymeric matrix 1.

Sample	Compression Strength (MPa)					
GH-1-1-1-800	28.646	41.077	39.648	20.796	12.791	
GH-2.8-1-1-800	22.429	29.412	17.836	20.106	19.711	
GH1-4-1-1-800	29.392	34.743	31.494	23.259	4.264	
GH1-8-1-1-800	36.257	41.496	25.914	40.812	29.826	
GH-1-10-1-800	21.486	12.988	19.412	26.294	37.638	
GH-2.8-10-1-800	22.160	25.628	14.026	1.873	16.650	
GH1-4-10-1-800	44.773	47.057	42.009	38.836	41.165	
GH1-8-10-1-800	48.261	48.814	63.141	44.774	47.990	

Table 4 Compressive strength results of geopolymeric matrix 1.

Sample	Compression Strength (MPa)					
GH-1-1-5-800	14.116	10.275	20.360	22.962	12.219	
GH-2.8-1-5-800	20.088	20.909	21.147	17.562	21.352	
GH1-4-1-5-800	35.485	30.840	32.802	42.927	32.827	
GH1-8-1-5-800	28.251	30.377	28.240	23.489	29.675	
GH-1-10-5-800	14.357	14.243	16.857	12.877	16.158	
GH-2.8-10-5-800	21.482	29.624	15.555	15.495	31.934	
GH1-4-10-5-800	25.711	27.049	24.919	25.786	28.349	
GH1-8-10-5-800	38.697	39.972	41.393	41.823	47.059	

Table 5 Results from ANOVA to the CT of 1 and 2.8 hours.

Term	Effect	Coef	EP of Coef	Valor-P
Constant		20.50		0.000
C	-4.05	-2.03		0.090
HR	-2.34	-1.17		0.321
CT	-0.51	-0.26		0.827
C*HR	3.09	1.55	1.16	0.191
C*CT	6.58	3.29		0.008
HR*CT	0.72	0.36		0.757
C*HR*CT	1.12	0.56		0.631

Table 6 Results from ANOVA to the CT of 4 and 8 hours.

Term	Effect	Coef	EP of Coef	Valor-P
Constant		35.499		0.000
C	-5.430	-2.715		0.008
HR	9.760	4.880		0.000
CT	6.629	3.314		0.002
C*HR	-7.176	-3.588	0.964	0.001
C*CT	-2.401	-1.200		0.222
HR*CT	4.998	2.499		0.014
C*HR*CT	6.199	3.100		0.003

From the results of ANOVA was possible to verify that all the factors were significant for the CS (MPa), except for interaction C*CT. Concerning to the CT, the CS at 8h was 6.629 MPa higher than the CS at 4h. For the HR, the CS in the 10 °C/min is on average 9.760 MPa higher than the lower heating rate and for the composition, the matrix 1 the CS is on average 5.430 MPa higher than the matrix 5. Comparing the CT in the HR at 10°C/min, the CS at 8h is on average 11.627 MPa higher than at 4h. For HR at 1°C/min, the CS at 8h was higher on average 1.630 MPa than at 4h. Comparing HR and C, the CS of the matrix 1 at HR of 10°C/min was 16.936 MPa higher than the matrix 5, and for the HR at 1°C/min, the CR was closer to the matrix 1, with CS 2.584 MPa higher than the matrix 5. Notice that the geopolymer composition and kaolinite calcination conditions influence the compressive strength. There is a complexity of the geopolymeric reactions when different conditions of calcination are evaluated. Overall, the highest compressive strength (48.2 MPa) was obtained for composition 1 with kaolinite calcined at 10°C/min for 8 hours, while the

lowest compressive strength (26.7 MPa) was obtained with the sample of composition 5, with kaolinite calcined at 10°C/min for 4 hours.

Concerning to calcination time at 1 and 2.8 hours, the CS results was not significant from the statistical point of view, except for the interaction between CT and C. That is mean there was determined CT for the CS to be higher and this difference was positive. For example, for the CT at 2.8 h, the matrix 5 presented CS on average 2.5316 MPa higher than the matrix 1. At counterpart, for the CT at 1 h, the matrix 1 presented the CS on average 10.635 MPa higher than the matrix 5.

3.2 SEM Analysis

According to Silva (2002) [17], the determination of geopolymers structures formed are realized using the scanning electron microscope (SEM). The structure of the surface of samples is observed through electron beam bombing the material, as shown in Fig. 1. In both samples was observed the low index of crystallization on the images showing the amorphous character of the

geopolymer and low presence of water in the material after cure, mainly at sample 1, showing the good quality from it. In addition, is observed presence of bubbles at the surface of the sample. According to Hartmann (2016) [18], bubbles/pores are one of the

points responsible for the low resistance of geopolymers. These are formed from the presence of solid particles present in the paste that do not adhere to the matrix. Therefore, the pores are formed when the samples are submitted to leaching process [19].

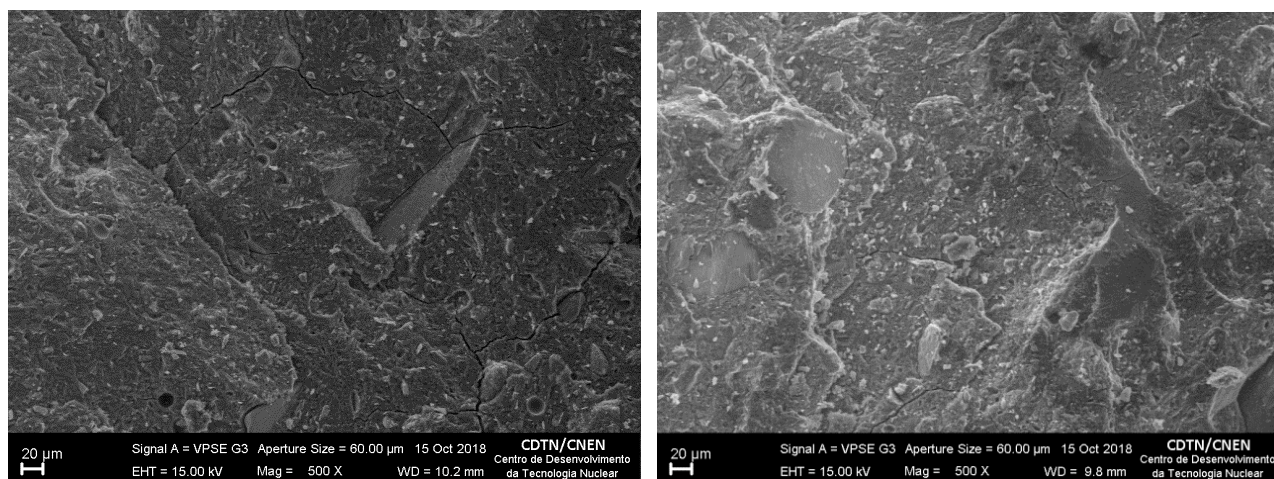


Fig. 1 Images from SEM, at left sample 1 – GH-08-10-1, at right sample 2 – GH-04-10-1.

Source: Center of Development of Nuclear Technology (CDTN), 2018.

4. Conclusion

The geopolymer samples were synthesized with different proportions of metakaolin, alkaline sodium silicate and sodium hydroxide solution. A strong influence of the composition of the geopolymer samples, calcination temperature, kiln heating rate, and calcination time on the compressive strength was observed, as well as synergistic and antagonistic interactions between two, three, and four factors indicating the complexity of the geopolymeric reactions. All calcinations conditions interfered in the transformation of kaolinite at 4 and 8 hours. There was a reduction in compressive strength in lower calcination times. At calcination time of 1h, the matrix 1 composition presented average on compressive strength of 12.02 MPa higher than the matrix 5. The calcination conditions of the sample GH-08-10-1 (matrix 1, 8 hours of calcination time and 10°C/min of heating rate) presented the best result with average on resistance of 50.596 MPa. Therefore, it is concluded that a rigid control over calcinations conditions need to

be considered when different raw materials were used to the synthesis of geopolymers.

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