RESISTANCE TO COMPRESSION AND ANALYSIS OF THE MICROSTRUCTURE OF METACAULINITE-BASED GEOPOLMERIC MORTAR

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Abstract

Geopolymer binders have been seen as an alternative material for reducing the use of Portland cement due to its excellent mechanical properties and low environmental impact. This article presents geopolymer mortars produced from metacaulinite, from kaolin calcination at 750 ° C for 6 hours. The developed geopolymers were synthesized with potassium hydroxide and potassium hydroxide silicate as activators mixed with metakaolin, cement and sand. The compressive strength tests were performed at the ages of 7, 14 and 28 days. The geopolymer microstructure was observed by scanning electron microscopy (SEM). Samples presented maximum performance of compressive strength of 58 Mpa, with a dense and homogeneous microstructure.

1. INTRODUCTION

The reduction of energy consumption and pollution generated during the production of cement became a concern in industrial processes of global manufacture. The search for alternative materials that could reduce energy demand and pollutants gases increased in recent years [1]. In this context, the development of geopolymers, formed through the activation of aluminosilicates in strongly alkaline environment, has great potential to replace conventional concrete [2]. The term "geopolymer" was created by J. Davidovits [3] to describe the chemical properties of inorganic polymers based on aluminosilicates.

Geopolymers have cementitious properties and can be composed from natural raw materials or residues from various sources, provided that these residues are rich in amorphous or semi-crystalline aluminosilicates, which through heat treatment become more reactive and alkaline [1]. Studies about the functions and behavior of raw materials involving kaolinite and other clays were initially used in 1974 and 1975. Davidovits [4] mainly used kaolin and calcined kaolin (metacaulinite) as the source of aluminosilicate oxides, in order to synthesize geopolymers. Many other researchers have also focused on the manufacture of geopolymeric products and their industrial applications using a kaolinite or metakaolinite as the main reactant [5-7].

Metacaulinite as base of the geopolymer may have mechanical properties comparable or superior to Portland cement [8]. In general, the product obtained depends on the chemical and mineralogical composition of metacaulinite, which may have a greater or lesser degree of fineness, a greater or lesser specific surface, and present a white, creamy or slightly pinkish color. In essence metacaulinite consists of alternating layers of silicate, aluminum and silicon [9].

Another important factor are the grains, which the finer the better the gel dissolution and formation rates favor. However, the larger the particle diameter, the greater the occurrence of pores and specific mass [10,11]. The combination of fine particles, less than 5μm, and better dissolution, similar results are obtained with lower amounts of precursor materials [12].

This new technology contributes greatly to the reduction of environmental impact, since there is an 80% reduction in the emission of carbon dioxide to the atmosphere [13]. Another relevant feature, although it is water-based, the reaction products are not calcium hydrates as in conventional cements. This results in the formation of an amorphous matrix, but chemically stable. Thus, it has excellent durability, not suffering the intense degradation processes that are observed in the structures realized with conventional cement. It has higher bending and tensile strength than conventional ones [14].

This study develops a geopolymer mortar containing metacaulinite as a precursor, characterizing properties of resistance, microstructure and other tests, in order to present new alternatives in civil construction.

2. MATERIALS AND METHODS

2.1 Materials

In this work, cement of type CPIII 40RS was used. The silica used in the blends is industrial. The river sand, with granulometry passed through the 0.979mm sieve. The alkaline activator was potassium hydroxide (KOH).

The kaolin in natura was macerated with the aid of a rod, in a porcelain bowl. After the procedure, was placed in a greenhouse of brand De Leo for a period of 24 hours at a temperature of 100 ° C to remove moisture. The material was calcined in a muffle furnace of the manufacturer GP Scientific at a temperature of 750 ° C for a period of 6 hours to obtain metakaolin. Finally, it was placed in a ball mill for a period of 6 hours and sifted in the 200 mesh sieve.

2.2 Geopolymer synthesis

The mixing ratio of geopolymer mortar was determined by attempting blends so that the mortar gets good mechanical properties, moderate hardening time and suitable rheology. Table 1 shows the proportion of the materials used to make the matrix.

Table 1. Dosing of the mortar

Material	Proporção
Metacaulinita	0,228
Cimento	0,134
Areia	0,142
Silica	0,128
NaOH	0,193
Àgua	0,172

According to Palomo and Glasser [15], the mixing order of the reactants is a critical point that can significantly affect the phase development of the final product. From the chemical and physical point of view, there are compelling reasons to justify a particular order of mixing the components. According to the same authors, it would be interesting in a first step to mix

and allow the soluble components to mature and then, in a later dispersed phase, add the products which are normally insoluble. Thus, the preparation of the mixtures was carried out in the following sequence:

- Production of potassium hydroxide silicate with the mixture of silica, water and potassium hydroxide;
- After 24 hours, mixing the powders: metacaulinite, cement and sand for 3 min manually;
- Addition in silicate mixer;
- Launch, little by little of powders;
- Mixing for 3 minutes;
- 1 minute stop for removal of material retained in the mortar;
- Mixing for 1 minute.

Figure 1 illustrates the molding process, in figure 1 (a) the mold is filled and Figure 1 (b) shows the compaction of the mortar. The demolding occurred 24 hours later, the specimens were placed in bags for complete cure, in order to avoid the appearance of microcracks.

Figure 1. Molding of specimens

2.3 FRX

To obtain a chemical measure of the materials an X-ray dispersive energy spectrometer (EDS), model EDX-720 from Shimadzu was used. An important mass was determined in a helium gas pycnometer, Micromeritics, model AccuPyc 1340. In order to determine the chemical composition of the materials, a ray dispersive energy spectrometer X (EDS), model EDX-720 Shimadzu. The specific mass was determined in a helium gas pycnometer, Micromeritics, model AccuPyc 1340. For the performance of the test, the sample was oven dried at 60 ° C for 24 hours.

Table 2. Chemical composition of materials

Composition	Metacaulinite	Cement CP-IV	Silica
Al2O3	42,1973%	8,348%	2,371%
SiO2	53,9093%	21,504%	85,449%

K2O	0,3353%	0,843%	2,479%
CaO	0,0833%	61,879%	0,755%
MnO	0,0020%	0,224%	0,112%
Fe2O3	1,3417%	2,621%	3,673%
TiO2	1,6093%	0,451%	
SO3		3,992%	2,439%
SrO		0,120%	0,007%
ZnO		0,019%	0,554%
MgO			2,021%
Especific mass	3,0522	3,1264	2,4679

2.4 MEV

The interface was observed by microscopy, the samples were removed from the test specimens after the compression test, where cubes with a maximum dimension of 1cm were extracted from sections that had undergone the most influence and rupture during the test. To prepare the sample, it was necessary to dip the cube in resin and let it dry for 24 hours. The analysis was performed using a scanning microscope, Hitachi, tm 3000.

2.5 Compressive strength testing

The compression test was performed on an Emic universal test machine, with a load capacity of 300 kN, at the ages of 7, 14 and 28 days. For each age, three cylindrical specimens of 50 mm diameter and 100 mm height were molded. The assay was performed at a rate of 0.2 mm / min.

3. RESULTS AND DISCUSSION

3.1 Compressive strength testing

In Fig. 2 shows the compression graph of the geopolymer matrix at the ages of 7, 14 and 28 days.

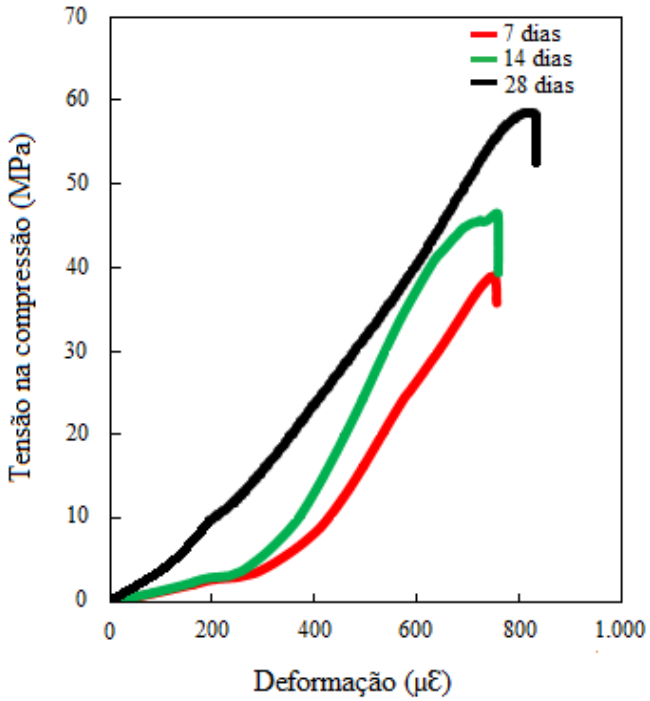

Figure 2. Stress curve in compression x deformation

From Stress x Strain curves, average values of maximum compression stress ($^{\delta}$max) and axial strain of maximum stress ($^{\varepsilon}$máx).The results are presented in table 3.

Table 3. Mean values of compressive strength, strain at tensile and modulus of elasticity

Age	Tensão máxima (MPa)	$^{\varepsilon}$máx (μ^{ε})
7	38,99 MPa	754,53
14	46,51MPa	758,05
28	58,29 MPa	832,00

From the obtained data, it is verified that the compressive strength increased according to curing time. At the 28th day it presented maximum tension of 58.29 MPa, and when compared with Arioz and Kockar's results [16], on what it obtained in its samples 33.07 MPa and 34.7 MPa at 7 and 28 days respectively, we noticed that the use of potassium hydroxide increases the resistance. Rodrigues [17] found very similar values for the 28 day trial, presenting the maximum value of 57 MPa. In the study of Demie, Nuruddin and Shafiq [18], obtained a compressive strength of 53.8 MPa, while Soutsos [19] obtained a maximum value of compression resistance of 60.9 MPa, this is due to the fact its precursor has high iron value, once in the conventional cement iron contributes to the high resistance according to the curing time, it is believed that the same can happen with the geopolymer, but there are no studies analyzing this influence.

The experimental results were close to those obtained by other authors. However, there are several activators and different precursors that can be used in the synthesis of geopolymers, so there will be in the literature divergent values of resistance to compression due to the different geopolymer types studied. It was necessary to analyze the matrix to determine the ideal time to test the plates. It was observed that on 14th day it supported 46.51 MPa, thus, it was chosen to carry out the tensile and flexion tests at 14 days, once the matrix showed a good resistance.

4.3 MEV

In most cementitious materials the weakest point is the appearance of microcracks [20]. When making the geopolymer numerous microcracks appeared, in order to eliminate them the sand was added to the mixture. This made the matrix a denser structure, as shown in Fig. 3, besides increasing the strength and durability of the geopolymer paste. We can emphasize the role of the soluble silica for the alkaline activation, it was responsible for developing the microstructure of the material.

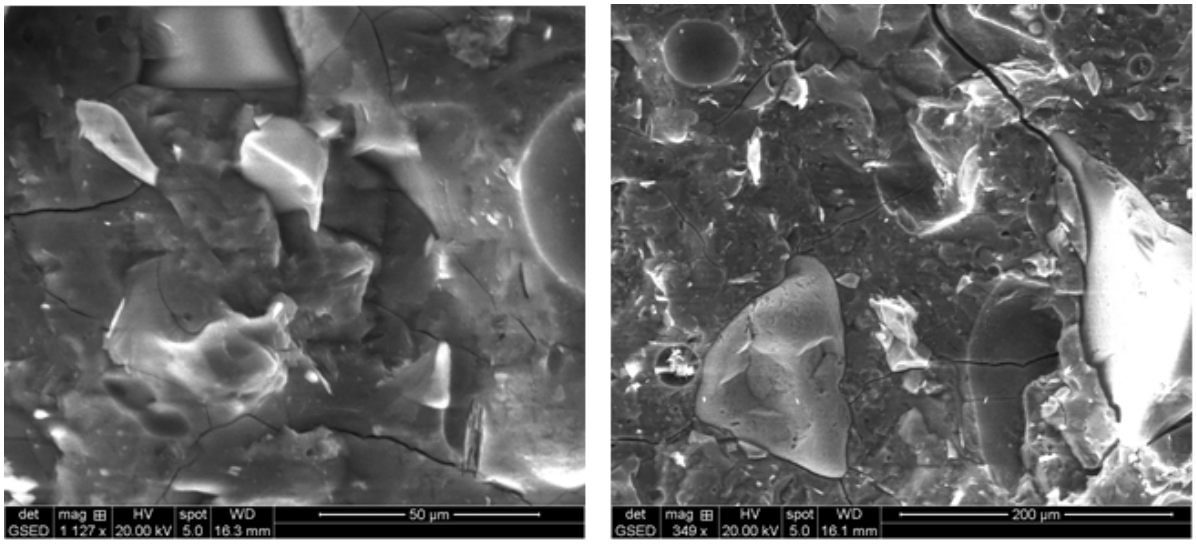

Figure 3. (a) Micrograph of the geopolymer matrix at 14 days (b) approximation of the sample

The use of metacaulinite as a source of aluminosilicate may alleviate this problem by providing a less impure starting material easier to characterize, facilitate the understanding of the microstructure that can be obtained by the analysis of the final products. Geopolymers based on metakaolinite are considered a model, without the complexities introduced by the use of fly ash, slag and other alternative raw materials due to the various amorphous and difficult characterization phases. Fly ash, for example, is not derived from a well-defined material, and consists of several crystalline phases [21]. Silva e Sagoe-Crenstil [22] reported that calcium-free metakaolinite-based geopolymers with higher compressive strengths were formed by a dense and homogeneous microstructure, according to SEM analyzes (figure 3).

5. CONCLUSIONS

It was observed the appearance of micro-cracks in the production of the specimens, and to eliminate them, sand was added to the mixture. This procedure provided a better grain spreading and increased mechanical properties. The tensile strength in the compression of the geopolymer mortar was found a value of 58.29 Mpa at the 28th day. This result was obtained by curing at room temperature.

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REFERENCES

[1] ZHANG, Hai Yan et al. Development of metakaolin–fly ash based geopolymers for fire resistance applications. Construction and Building Materials, v. 55, p. 38-45, 2014.

[2] SANTA, Rozineide A. Antunes Boca et al. Geopolymer synthetized from bottom coal ash and calcined paper sludge. Journal of Cleaner Production, v. 57, p. 302-307, 2013.

[3] DAVIDOVITS, Joseph. Synthesis of new high temperature geo-polymers for reinforced plastics/composites. SPE PACTEC, v. 79, p. 151-154, 1979.
[4] DAVIDOVITS, Joseph. Synthetic mineral polymer compound of the silicoaluminates family and preparation process. U.S. Patent n. 4,472,199, 18 set. 1984.
[5] XU, H.; DEVENTER, J. S. V. Geopolymerisation of multiple minerals. Minerals Engineering, Elsevier, v. 15, n. 12, p. 1131–1139, 2002.
[6] BARBOSA, V. F.; MACKENZIE, K. J. Synthesis and thermal behaviour of potassium sialate geopolymers. Materials Letters, Elsevier, v. 57, n. 9, p. 1477–1482, 2003.
[7] ANDINI, S.; CIOFFI, R.; COLANGELO, F.; GRIECO, T.; MONTAGNARO, F.; SANTORO, L. Coal fly ash as raw material for the manufacture of geopolymer-based products. Waste management, Elsevier, v. 28, n. 2, p. 416–423, 2008.
[8] DAVIDOVITS, J. Properties of geopolymer cements. In: First international conference on alkaline cements and concretes. [S.l.: s.n.], 1994. v. 1, p. 131–149.
[9] DAVIDOVITS, J. Geopolymer Chemistry and Applications. Institut Géopolymère (Geopolymer Institute): Saint-Quentin, France, 2008. [S.l.], 2008.
[10] HARDJITO, D.; SUMAJOUW, D. M.; WALLAH, S.; RANGAN, B. et al. Fly ash-based geopolymer concrete. Australian Journal of Structural Engineering, v. 6, n. 1, p. 77, 2005.
[11] JAARSVELD, J. V.; DEVENTER, J. V.; LORENZEN, L. The potential use of geopolymeric materials to immobilise toxic metals: Part i. theory and applications. Minerals Engineering, Elsevier, v. 10, n. 7, p. 659–669, 1997.
[12] XU, H.; DEVENTER, J. V. The geopolymerisation of alumino-silicate minerals. International Journal of Mineral Processing, Elsevier, v. 59, n. 3, p. 247–266, 2000.
[13] Wang Y, Qinghua Z, Yong G. Trajectory and driving factors for GHG emissions in the Chinese cement industry. J Clean Prod 2013;53:252–60.
[14] GEOPOLYMER. Out. 2015. http://www.geopolymer.com.br. Julho 22, 2015. Disponível em: <http://www.geopolymere.com.br>.
[15] PALOMO, A.; GLASSER, F. Chemically-bonded cementitious materials based on metakaolin. British ceramic. Transactions and journal, Institute of Materials, v. 91, n. 4, p. 107–112,1992.
[16] ARIOZ, O.; KOCKAR, O. M. An experimental study on the mechanical and microstructural properties of geopolymers. Procedia Engineering, Elsevier, v. 42, p. 100–105, 2012.
[17] RODRIGUES, T. M. C. G. Argamassas e betões geopoliméricos: estado da arte e potencial de industrialização em Portugal. Tese (Doutorado) — INSTITUTO SUPERIOR DE ENGENHARIA DE LISBOA, 2014.
[18] DEMIE, S.; NURUDDIN, M. F.; SHAFIQ, N. Effects of micro-structure characteristics of interfacial transition zone on the compressive strength of self-compacting geopolymer concrete. Construction and Building Materials, Elsevier, v. 41, p. 91–98, 2013.
[19] SOUTSOS, M.; BOYLE, A. P.; VINAI, R.; HADJIERAKLEOUS, A.; BARNETT, S. J. Factors influencing the compressive strength of fly ash based geopolymers. Construction and Building Materials, 2015.
[20] MONTEIRO, P. Concrete: Microstructure, Properties, and Materials. [S.l.]: McGraw-Hill Publishing, 2006.
[21] DUXSON, P.; PROVIS, J. L.; LUKEY, G. C.; MALLICOAT, S.W.; KRIVEN,W. M.; DEVENTER, J. S. V. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, Elsevier, v. 269, n. 1, p. 47–58, 2005.