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Materiales

Parametric analysis about the synthesis of metakaolin-based geopolymers

Análisis paramétrico para la síntesis de geopolímeros base metacaolín

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Abstract

Geopolymers are materials synthesized from aluminosilicates activated by an alkaline agent, which leads to their setting and hardening, providing a material with excellent ceramic properties. The chemical formula of the geopolymers: $M_n\{-(SiO_2)_z-AlO_2\}_n wH_2O$, where M is a cation, n is the polycondensation rate, z is the number of silicon units and w are water molecules present in the structure. The name of the material and its mechanical properties vary as a function of the number of silicon units. This research analyzes the effect of potassium hydroxide concentration and silicon units as variables in the application of the design of experiments (DoE) method, the mechanical properties of compressive strength and Young's modulus were analyzed as a process response. The results showed that the geopolymer presented better mechanical properties of Young's modulus and compressive strength, when z = 2, in addition, an increase in compressive strength values was observed when increasing the molar concentration of the geopolymer mixture for z = 1 and z = 2. Finally, it was found that the highest compressive strength value is 31.03 ± 0.31 MPa for z = 2 and 14 M values, additionally, FTIR and XRD analyses were carried out to obtain information about physiochemistry properties.
Keywords: polysialates, ceramics, alkaline activation, inorganic materials, alternative cement, geopolymer.

Resumen

Los geopolímeros son materiales sintetizados a partir de aluminosilicatos activados por un agente alcalino, lo que conduce a su fraguado y endurecimiento, proporcionando un material con excelentes propiedades cerámicas. La fórmula química de los geopolímeros: $M_n\{-(SiO_2)_z-AlO_2\}_n wH_2O$, donde M es un catión, n es la tasa de policondensación, z es el número de unidades de silicio y w son moléculas de agua. El nombre del material y sus propiedades mecánicas varían en función del número de unidades de silicio. Esta investigación analiza el efecto de la concentración de hidróxido de potasio y las unidades de silicio como variables en la aplicación del método de diseño de experimentos (DoE), se analizaron las propiedades mecánicas de resistencia a compresión y módulo de Young como respuesta del proceso. Los resultados mostraron que el geopolímero presentó mejores propiedades mecánicas cuando z = 2, además, se observó un aumento en los valores de resistencia a compresión al aumentar la concentración molar de la mezcla de geopolímero para z = 1 y z = 2. Finalmente, se encontró que el valor más alto de resistencia a compresión es 31.03 ± 0.31 MPa para valores de z = 2 y 14 M, adicionalmente se realizaron análisis FTIR y XRD para obtener información sobre las propiedades fisicoquímicas.
Palabras clave: Polisialatos, cerámicas, activación alcalina, materiales inorgánicos, cementos alternativos, geopolimero.

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1 Introduction

Portland cement is the most used material in the world, with approximately 150 ton/s. This material produces approximately 8% of carbon dioxide (CO_2) emissions worldwide (Nie *et al.*, 2022) since it is made of clinker, a material obtained by calcination at 1400 °C of limestone and clay, causing dust emissions (Alonso, et al., 2019); the use of large kilns with high energy consumption; and, finally high-water consumption (Nie *et al.*, 2022), which generates air pollution, environmental damage and global warming. Thus, alternatives to the use of Portland cement-based concrete have been sought. Geopolymers have high mechanical, thermal, and chemical resistance, and the advantage that for their production low amounts of greenhouse gases (CO_2) are emitted into the atmosphere, which allows their use in numerous high-value applications (Marín-López et al., 2009; Meshram and Kumar, 2021). It has been reported that the production of 1 ton of Portland cement emits approximately 1 ton of CO_2. In contrast, less than 0.2 ton of CO_2 is emitted to manufacture 1 ton of geopolymer (Ribeiro et al., 2019). These materials can act as a binder to manufacture concrete and polymer cement by bonding with an inert aggregate, are heat and fire-resistant and very durable (Nuruddin et al., 2016; Youssef et al., 2020; Ahmed *et al.*, 2021). In addition, they have a low thermal conductivity that allows their application as insulating materials for construction or cladding (Oviedo et al., 2019).

The term geopolymer is used to refer to materials formed by inorganic synthetic polymers of aluminosilicates (Tchadjié and Ekolu, 2017), activated by an alkaline agent (Ilcan *et al.*, 2024), forming covalent chemical bonds, through a chemical process developed in several separate but interrelated stages called geopolymerization (Nuruddin *et al.*, 2016). The geopolymerization process is carried out in three steps: 1) alumosilicate dissolution, 2) gelation and reorganization of the structure, and 3) polymerization and hardening (You *et al.*, 2019). Geopolymers can be made from metakaolin, natural pozzolan, ground granulated blast furnace slag, red mud, or fly ash (Ahmed *et al.*, 2021). Studies have shown that materials rich in silicon oxide (SiO_2) generate geopolymers with excellent mechanical properties; moreover, this material is more environmentally friendly than ordinary Portland cement (Torres-Ochoa et al., 2018). This research focuses on using metakaolin as a raw material to obtain geopolymers. Metakaolin ($2SiO_2 \cdot Al_2O_3$) is a pozzolanic material, produced from the controlled thermal treatment of kaolinite ($Al_2Si_2O_5(OH)_4$) within the temperature range of approximately 600–900 °C, according to equation 1 (Agredo and De Gutiérrez, 2007; De Belie *et al.*, 2018).

$$Al_2Si_2O_5(OH)_4 \rightarrow 2SiO_2 \cdot Al_2O_3 + H_2O \quad (1)$$

Geopolymers are also designated by the term sialate, which is an abbreviation for silicon oxo-aluminate because they are formed by a sialate network consisting of the intertwining of silicate (SiO_4) and aluminate (AlO_4) tetrahedrons (Davidovits and Orlinski, 2000). The basic polymeric units are poly(sialate) (– Si – O – Al – O), poly(sialate-siloxo) (– Si – O – Al – O – Si – O), and poly(sialate-disiloxo) (– Si – O – Al – O – Si – O – Si – O) (Cioffi *et al.*, 2003), these polymeric units depend on the silicon/aluminum (Si/Al) molar ratio, which is closely linked with its properties and applications (Davidovits, 1994).

Geopolymer properties can be affected by factors such as molar ratios, temperature and setting time, precursor materials, alkaline activators, etc. (Ilcan *et al.*, 2024). Recent studies have focused on developing the optimal composition of geopolymer paste to provide properties such as strength, fire resistance, and electrical or thermal insulation (Le *et al.*, 2023). Oliveira and Lameiras (2022) mentioned that processing, concentration, and raw material characteristics can cause incomplete settings, resulting in unreacted materials with cracks or fluorescence. Meftah et al. (2016), studied the behavior between hydrated and dehydrated geopolymers at different Si/Al ratios, by FTIR analysis they found that O-H bonds are present, which after oven drying at 80 °C are replaced due to evaporation of the water molecule. In addition, they mention a possible direct relationship between silica content and mechanical strength, because the Si-O-Si bonds are stronger than the Si-O-Al and Al-O-Al bonds, which causes that by increasing the amount of silica, Si-O-Si bonds increase and therefore the mechanical resistance of the geopolymer (Meftah *et al.*, 2016).

Zainal *et al.* (2020) analyzed the effect of sodium hydroxide and sodium silicate solution concentration in a range of 8M to 12M, finding that 8M concentration is the concentration that provides the highest result of compressive strength with 0.992 MPa and this decreases as the molarity increased, furthermore, they found that the two variables that affect the resistance and durability of the geopolymers are the NaOH concentration and the curing regime (temperature). Jaya *et al.* (J 2018), carried out a study on how molarity affects the physical and mechanical properties of geopolymers, in a range from 6 to 14 M, finding that for compressive strength the optimal molarity was 10 M and the lowest recorded value was 6 M.

In the present work, the influence on the polymerization process and mechanical properties of compression stress and Young's modulus of the concentration of potassium hydroxide and z in metakaolin-based geopolymers has been studied.

2 Materials and methods

2.1 Materials

The materials used in this study to prepare the geopolymer were: Metakaolin from the BASF corporation, metamax. The chemical composition in weight percentage of metakaolin was: 51.550% SiO_2, 1.610% TiO_2, 44.780% Al_2O_3, 0.480 Fe_2O_3, 0.004% MnO, 0.125% MgO, 0.155% K_2O. Potassium hydroxide pellets from J. T. Baker Chemical Analytical Grade. Fumed silica, with a standard GB/T 20020-2013 from Chinese Standard and Distilled water.

2.2 Methods

The initial synthesis of the polymer paste was carried out by mixing different stoichiometric amounts of metakaolin, nano-silica, potassium hydroxide, and distilled water. During the formation process of the geopolymers, a mixed factorial design was carried out using the Statgraphics software to identify the factors with the greatest impact, as well as the interaction effects of the factors on the compressive strength and Young's modulus with a 95% confidence (p-value <0.05). The design is shown in Table 1. The conditions to develop this study were the following: z: 1, 2, 3 and molarity (M): 6, 8, 10, 12, 14 M. Samples were formulated with molar oxide ratios shown in Table 2. Samples were tested in triplicate and the average values were used in the analysis.

The geopolymer paste was transferred to cylindrical molds (1 in inside diameter and 2 in height) covered with a film to prevent moisture loss, and finally, heat treated at 60 °C for 24 h in an internal convection oven. Subsequently, the samples were de-molded and stored at room temperature for 28 days. Muñiz-Villarreal *et al.* (2011) mentioned that when a paste was synthesized at 60 °C it provided the optimum compressive strength after 28 days. Compressive strength and Young's modulus were measured according to standard ASTM C 773, using an Instrom 3345 universal testing machine. Additionally, the samples were analyzed by Fourier transform infrared (FTIR), where the functional groups in the 4000–400 cm^{-1} region are shown. To study the structure and crystalline phases samples were analyzed by XRD in a 2θ angle range of 10-80°. The phases in XRD were determined using X'pert HighScorePlus software.

Table 1: Mixed factorial design.

Sample	Variables		The response variable, average	
	z	M	Compressive strength, MPa	Young's modulus, MPa
1	1	6	-	-
2	1	8	8.49 ± 0.48	2898 ± 0.52
3	1	10	9.21 ± 0.26	5404 ± 0.49
4	1	12	9.41 ± 0.50	4878 ± 0.63
5	1	14	13.14 ± 0.34	4473 ± 0.24
6	2	6	-	-
7	2	8	20.40 ± 0.51	15361 ± 0.32
8	2	10	29.23 ± 0.25	17429 ± 0.43
9	2	12	29.70 ± 0.57	16972 ± 0.12
10	2	14	31.03 ± 0.31	19737 ± 0.40
11	3	6	-	-
12	3	8	1.53 ± 0.29	98 ± 0.05
13	3	10	1.43 ± 0.46	104 ± 0.06
14	3	12	1.11 ± 0.38	95 ± 0.02
15	3	14	1.01 ± 0.36	102 ± 0.04

Table 2: Molar oxide ratios for geopolymer mixtures.

Molar ratios	z = 1 8 M	z = 1 10 M	z = 1 12 M	z = 1 14 M	z = 2 8 M	z = 2 10 M	z = 2 12 M	z = 2 14 M	z = 3 8 M	z = 3 10 M	z = 3 12 M	z = 3 14 M
SiO_2/Al_2O_3	2.00	2.00	2.00	2.00	4.00	4.00	4.00	4.00	12.00	12.00	12.00	12.00
K_2O/SiO_2	0.47	0.59	0.71	0.82	0.24	0.29	0.35	0.41	0.24	0.29	0.35	0.41
K_2O/Al_2O_3	0.94	1.18	1.41	1.65	0.94	1.18	1.41	1.65	2.83	3.53	4.24	4.95
H_2O/K_2O	13.87	11.10	9.25	7.93	13.87	11.10	9.25	7.93	13.87	11.10	9.25	7.93

3 Results and discussion

It should be noted that the samples corresponding to 6 M were not taken into account in the design of experiments because the low molarity of the mixture did not allow the correct activation of the nano-silica, causing low workability of the geopolymer mixture and incorrect formation of the geopolymer. Le *et al*. (2023) indicate that workability is the ability of the geopolymer mixture to form a homogeneous mass and allow the correct filling of a mold using a specific compaction method.

3.1 Compressive strength

The compressive strength test for the geopolymer samples obtained after 28 days is presented in Fig. 1. In this figure, it was shown that molarity can be directly related to the compressive strength of geopolymers when z = 1 and z = 2 was used, but inversely proportional at z = 3 value. Furthermore, a significant improvement can be observed in the compressive strength test when a z = 2 value was used and a significant decrease when it was used a z = 3 value. In this case, it is inferred that by increasing the proportion of water to achieve the workability of the geopolymer paste in the samples corresponding to the z = 3 value, the porosity increases and therefore the compressive strength of the materials decreases. Even so, there are unusual cases in which the relationship is different from the one found in this work as reported by Kang, *et al*., (2010) and Perera *et al*., (2008).

The results strengthen what was reported by You *et al*. (2019), who concluded that when the pH decreases, the dissolution of aluminosilicate particles is negatively affected and, therefore, the action of hydroxide ions with dissolved aluminate and silicate, causing an incomplete activation of the geopolymer mixture and consequently a decrease in compressive strength.

It is important to mention that the highest compressive strength is obtained with a molarity of 14 M and z = 2. However, this does not vary significantly concerning the samples corresponding to 10 M, z = 2 and 12 M, z = 2, which could represent savings in manufacturing costs.

The statistical analysis presented in Table 3 shows the results of the ANOVA test to determine the main effects and the interactions on the compressive strength of geopolymers. The p-value was used to determine the significance level of each term. It is common to label the term as insignificant if the p-value is greater than 0.05. The effect values in Table 3 show that z had the most significant main effect on compressive strength, followed by molarity and finally, the interaction between both factors had a small significant effect.

The regression equation for compressive strength is expressed as:

$$Cs = -79.150 + 3.602M + 87.700z - 0.094M^2 - 0.400Mz - 21.923z^2 \quad (2)$$

Where Cs is the compressive strength, M is the molarity, and z is the silicon units. with an R^2 value of 97.13 %.

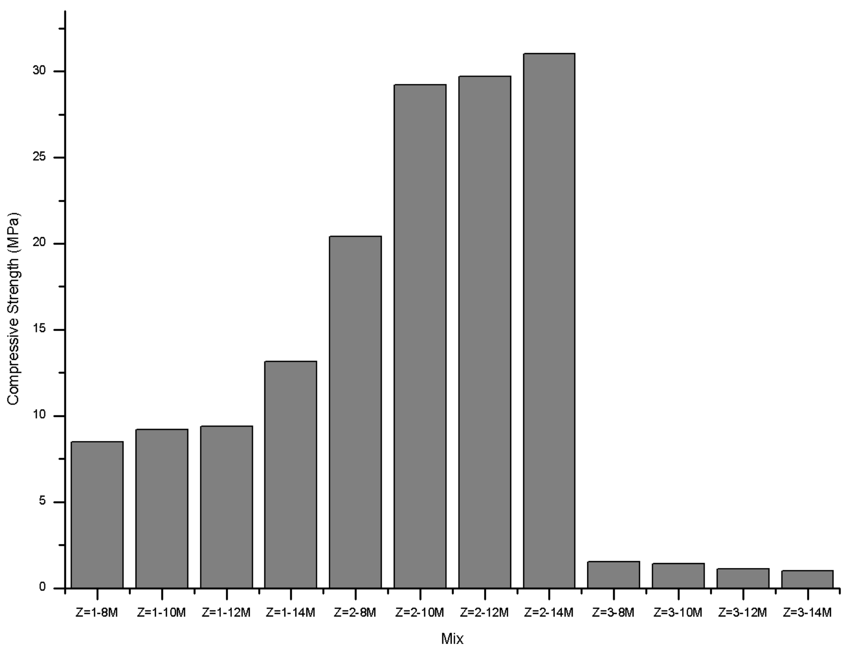

Fig. 1: Compressive strength of the geopolymer samples.

Table 3: Analysis of Variance for Compressive Strength.

Source	Sum of Squares	*Gl*	Mean Square	F- Value	P- Value	Remarks
A: Molarity	99.59	1	99.59	21.31	0.0001	Significant
B: z	463.73	1	463.73	99.23	0.0000	Significant
AA	5.04	1	5.04	1.08	0.3079	Negligible
AB	19.22	1	19.22	4.11	0.0522	Significant
BB	3845.08	1	3845.08	822.78	0.0000	Significant
Total error	130.85	28	4.67			
Total (corr.)	4564.63	35				

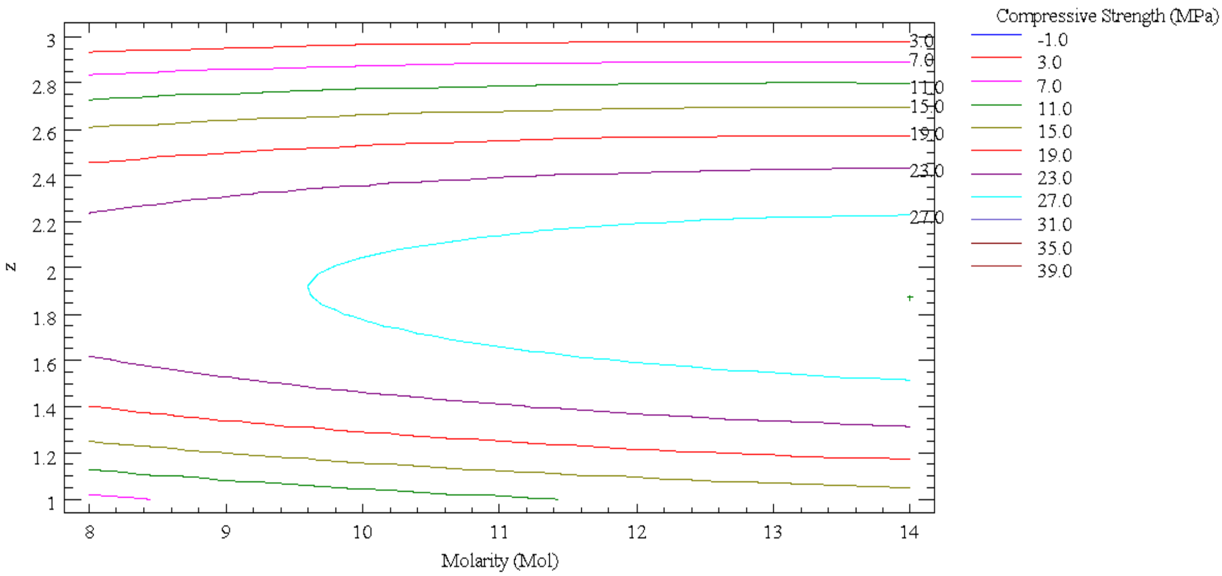

Fig. 2: Contour plot of compressive strength versus molarity and z.

The compressive strength function is shown in Figure 2 as a contour plot of equation 2. A certain curvature can be observed both in the sense of molarity and of z, which indicates that both factors are significant in the analysis, but since the curvature given by z is more marked, it indicates that the compressive strength depends more on this factor. Additionally, this graph can be used to estimate the compressive stress at any molarity and z within the regime of this experiment.

According to the experiment design described above, it is obtained that the minimum response value was 1.01 MPa with z = 3 and 14 M, and the best response was 31.03 MPa with z = 2 and 14 M. In addition, it is possible to determine that all the samples corresponding to z = 2 can be used as cement and concretes since they meet the minimum compressive strength requirements of 20 MPa for ordinary Portland cement (N-CMT-2-02-001/02).

3.2 Young's modulus

Fig. 3 shows the results of Young's modulus, in which it can be seen that the materials corresponding to z = 3 value present greater toughness, while the corresponding samples z = 2 value present greater rigidity. This parameter is important because it indicates the level of ductility of the material. Recent studies have focused on increasing the ductility of geopolymers, either by modifying a parameter in the composition of the geopolymer paste or by adding some reinforcing material to decrease Young's modulus. Le *et al.* (Le *et al.*, 2023) report values of 13985.84 to 33657.87 MPa for geopolymer foams formed from an industrially supplied material based on metakaolin and an alkaline potassium activator, similar values compared to those reported in the present investigation for z = 2 values.

Table 4 shows the ANOVA statistical analysis to determine the main effects and the interactions on Young's modulus of geopolymers. Again, the p-value was used to determine the significance level of each term. It is common to label the term as insignificant if the p-value is greater than 0.05. In the analysis, it is observed that z had the most significant main effect on Young's modulus again, followed by a small significant effect of molarity. But, the interaction between both factors does not have a significant influence.

The regression equation for compressive strength is expressed as:

$$Ym = -49.533 + 1.505M + 59.469z - 0.046M^2 - 0.1049Mz - 15.118z^2 \quad (3)$$

Where Ym is Young's modulus, M is the molarity, and z is the silicon units. with an R^2 value of 98.69 %.

The compressive strength function is shown in Figure 4 as a contour plot of equation 3. Once again, a curvature can be observed both in the sense of molarity and z, so it is possible to indicate that both factors are significant in the statistical analysis. In addition, it is again observed that Young's modulus depends more on z. Again, this graph can be used to estimate Young's modulus at any molarity and z within the regime of this experiment.

The optimization of the compressive strength and Young's modulus, as well as the interaction of both factors, will depend entirely on the requirements and application that is given to the material.

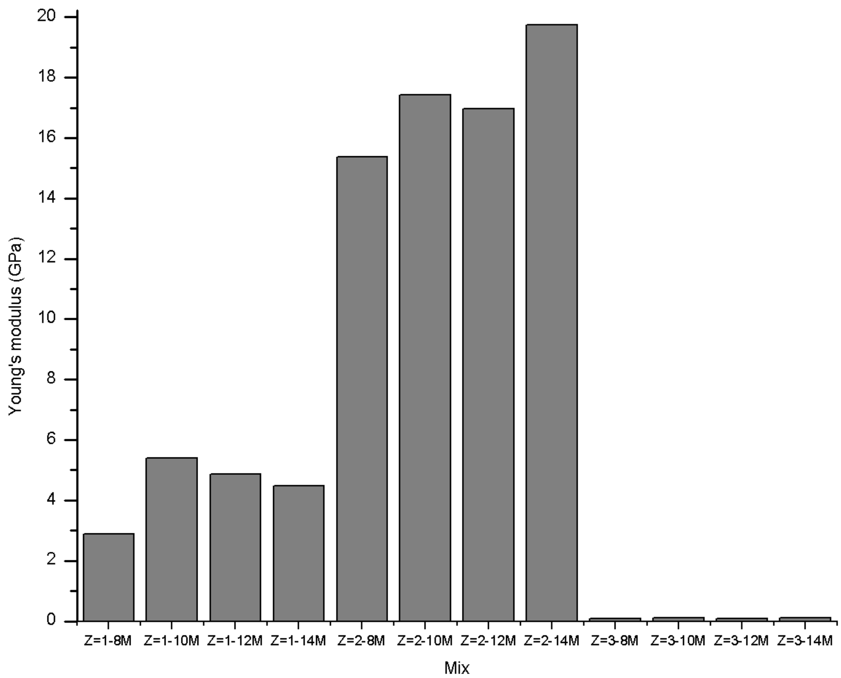

Fig. 3: Young's modulus of the geopolymer samples.

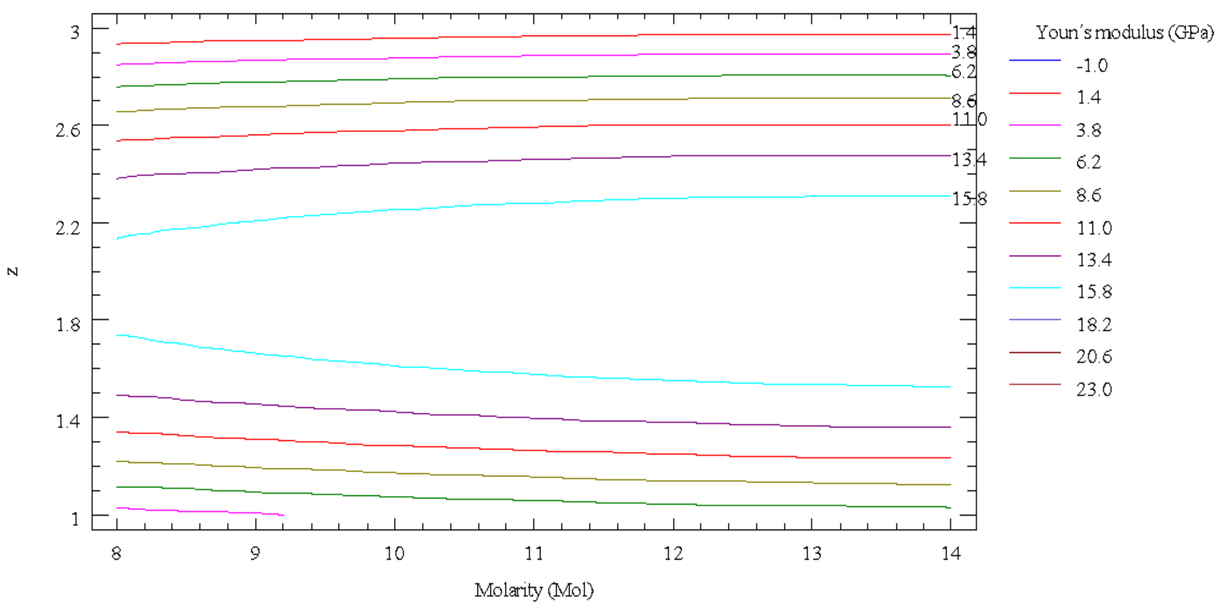

Fig. 4: Contour plot of Young's modulus versus molarity and z.

Table 4: Analysis of Variance for Young's modulus.

Source	Sum of Squares	Gl	Mean Square	F- Value	P- Value	Remarks
A: Molarity	14.24	1	14.24	15.38	0.0005	Significant
B: z	111.64	1	111.64	120.61	0.0000	Significant
AA	1.22	1	1.22	1.32	0.2599	Negligible
AB	1.32	1	1.32	1.43	0.2423	Negligible
BB	1828.44	1	1828.44	1975.49	0.0000	Significant
Total error	25.92	28	0.93			
Total (corr.)	1982.85	35				

3.3 Fourier Transform Infrared (FTIR)

Figure 5 shows the FTIR analysis of sample number 10, which corresponds to the sample that provides the highest value of compressive strength and Young's modulus. A band of great intensity is observed at 977 cm^{-1} that corresponds to an asymmetric tension of the Si-O-R bonds (where R corresponds to Si or Al tetrahedra). Some authors mention that this band indicates that the geopolymerization reaction has been successfully carried out.

Furthermore, the bands observed at 782 cm^{-1} and 693 cm^{-1} are related to the asymmetric stretching vibrations of Si-O-Si and Al-O-Si that confirm the geopolymerization process (Ahmed *et al*., 2023). In addition, a band at 1643 cm^{-1} is seen that corresponds to the tension vibration of the H-OH band.

The band at 3396 cm^{-1} can be related to a stretching of the O–H bond, which is attributed to hydrogen bond interactions, the low-intensity band at 1380 cm^{-1} was assigned to an O-C-O bond, it is inferred that it is due to a reaction with CO_2 from the atmosphere (Chuewangkam *et al*., 2022; Fu et al., 2021; Louati *et al*., 2016). Salimi and Salimi (2016) studied the adsorption of CO_2 using Al_2O_3-SiO_2 composites, finding that this type of material is capable of capturing CO_2. In addition, Hossain and Akhtar (2023) carried out an exhaustive study on the use of geopolymers for the capture of atmospheric CO_2, finding that geopolymers stand out in capturing and mitigating the effects of CO_2. Furthermore, they found that this type of materials can be used as catalysts or precursors for the conversion of CO_2 into other value-added chemicals.

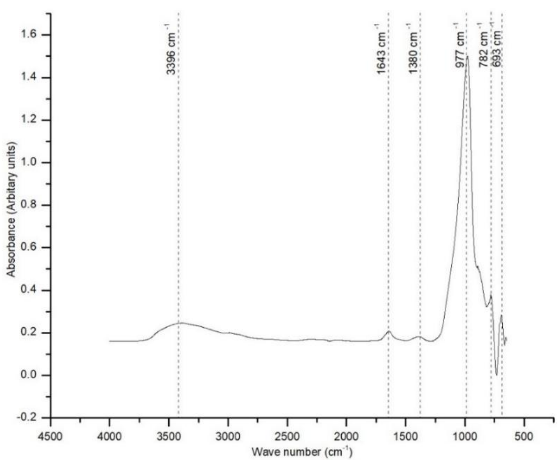

Fig. 5: FTIR spectra of sample z = 2; 14 M.

3.4 X-Ray Diffraction Analysis (XRD)

Figure 6 shows the diffractograms obtained from samples labeled 3, 8, 10, and 13 of geopolymers corresponding to z = 1 - 10 M, z = 2 - 10 M, z = 2 - 14 M, and z = 3 - 10 M, respectively. This arrangement allows us to observe how the change in molarity and the change in silicon units affects the structure of the materials. In the diffractograms,

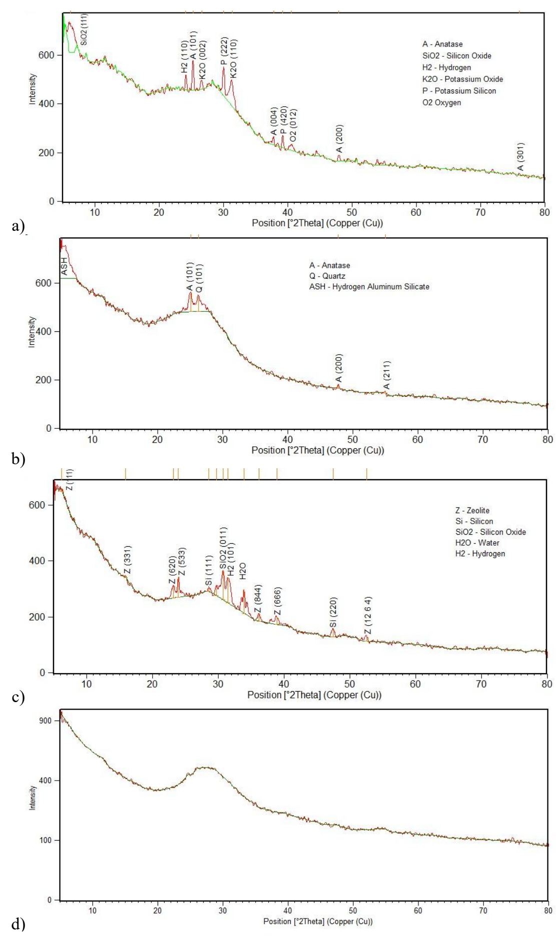

Fig. 6: X-ray diffractogram of the geopolymer samples 3, 8, 10, 13.

an amorphous halo is observed between 20 and 30°, according to Davidovits, this halo is established for geopolymers obtained from an aluminosilicate gel (K-A-S-H), which provides the resistance of the geopolymer (Davidovits, 1994; Guzmán-Aponte *et al*., 2019). This amorphous halo is more clearly observed in Figure 8 d), which corresponds to sample 13, which is inferred to be because the increase in molarity causes complete alkaline activation, corroborating the compression strength results mentioned previously. In addition, in Figures 8 a) and 8 b) the presence of traces of some chemical compounds such as anatase from the TiO_2 present in the composition of the metakaolin is observed, which indicates that the alkaline activation was not carried out completely (Villaquirán *et al*., 2014). Finally, in Figure 8 c) the slight presence of the amorphous halo that corresponds to the geopolymers is observed, in addition to the presence of zeolites, it is inferred that the conditions under which the alkaline activation was carried out allowed the production of geopolymer-zeolite hybrid materials. These materials can be used as adsorbents or as membranes in separation processes (Rozek *et al*., 2019).

Conclusion

A statistical analysis has been carried out to determine the effect of molarity and the amount of number of silicon units (z), as well as the interaction of both variables on the compressive strength and Young's modulus properties of metakaolin-based geopolymers. The analysis revealed that both molarity and z have a significant effect on the compressive strength and Young's modulus, with the effect of z being much more significant. The compressive stress experiments of the geopolymers formulated with z=2 and molarity between 8 and 14 gave a value above 20 Mpa. This value favors the use of geopolymers in the construction industry as binders to replace Portland cement, but its applications are not limited to this use, since its applications have been expanded depending on the requirements of the material, being able to interact and modify the oxide ratios to generate the optimal mechanical properties for each application. It is also observed that the molarity between 10 M and 14 M does not significantly modify the results, so it could represent a saving in manufacturing costs when using 10 M. Furthermore, the XRD analysis showed that an increase in molarity influenced the correct alkaline activation, which produced an increase in the compressive strength of the geopolymers. In addition, it was observed that increasing the silicon units at z = 3 produced a geopolymer-zeolite hybrid material, which can be used as an absorbent or membrane for catalytic processes, including CO_2 capture.

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