

Conference Paper

Influence of the Kaolinite Calcination Conditions on the Compressive Strength of Geopolymer

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Abstract

Among the cementitious materials, geopolymers not only attract interest due to the low emission of CO₂ in their manufacturing process, but also because of their good mechanical and chemical properties, together with their resistance to fire. They can be made from different raw materials including various wastes from industrial activities and mineral extraction. In this study, metakaolin was obtained from kaolinite calcined under different conditions. In this case kaolinite is a by-product of sand extraction. It was observed that the calcination conditions (kiln heating rate, calcination time and temperature) had a strong influence on the compressive strength of geopolymer after 28 days of cure. They also affected the composition of the geopolymer, which was prepared by mixing metakaolin, alkaline sodium silicate and sodium hydroxide solution. Compressive strengths in the range from 10 MPa to 50 MPa may be observed, depending on the combination of these factors. A factorial design of experiments allowed the isolation of the effect of each factor and its interactions, offering new insights into the complexity of the geopolymeric reactions and highlighting the need for a rigid control of the calcination conditions of kaolinite and the composition of the geopolymer samples to obtain the desired compressive strength.

Keywords: kaolinite, calcination, metakaolin, geopolymer, compressive strength.

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1. Introduction

The manufacturing of Portland cement requires high energy consumption and generates emission of large amounts of CO₂. About 5% of all CO₂ emissions from human activity are originated from the production of Portland cement [1]. A significant growth of the cement industry is expected in the coming decades, especially in the developing countries [2]. Interest in geopolymers, whose production emits less CO₂, is growing due to the possibility of reducing greenhouse gas emissions from Portland cement.

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Geopolymers, so named by Joseph Davidovits [3], are cementitious binders formed by alkali activated aluminosilicates. They have high mechanical strength, stability at high temperatures and in alkaline or acidic media. Synthesis occurs by means of polymerization or polycondensation reactions from the dissolution of SiO_4^{4-} and AlO_4^{5-} ions of the aluminosilicates in a highly alkaline solution. After dissolution, these ions are transported in the solution and rearranged in structures of polysialates, poly(siloxo-sialato) or poly(disiloxo-sialato) forming a three-dimensional network predominantly amorphous, composed of SiO_4 and AlO_4 tetrahedra [4]. The sources of aluminosilicates can be calcined clays, fly ash and some industrial residues, which makes geopolymers a sustainable product with interesting market potential [5].

In this study, samples of kaolinite from the company GH Areias were used (located in Inhaúma, Minas Gerais, Brazil). The samples had different greyish colors according to the depth at which they were collected. The gray coloration becomes darker at greater depths. In this company the kaolinite is a by-product of sand extraction for civil construction. Due to the difficulty of commercialization, the kaolinite is considered a residue, being stored in piles. The objective is to develop geopolymers from this kaolinite in order to obtain products with higher added value.

2. Materials and Methods

The kaolinite samples were characterized by X-ray diffraction, X-ray fluorescence, particle size distribution, specific surface area, density, infrared spectroscopy, and thermal analysis. They 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 metakaolin was obtained by calcination of the kaolinite in trays in a muffle kiln under the conditions shown in Table 1. The calcining temperatures were chosen based on the results of thermal analysis.

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 at 350 rpm for 10 minutes to remove air bubbles. After 24 hours at room temperature the hardened samples were desmolded. Based on the stoichiometric composition of 45 wt% of metakaolin (MK), 33 wt% of sodium silicate (SS) and 22 wt% of NaOH solution, seven compositions were made according to a simplex design done with Minitab (Figure 2). The two compositions

TABLE 1: Calcination conditions of the kaolinite to obtain metakaolin

First design				
Temperature (°C)	800			
Heating rate (°C/min)	1	10		
Calcination time (hour)	1	2.8	4	8
Second design				
Temperature (°C)	700		800	
Heating rate (°C/min)	1	Code: -1	10	Code: +1
Calcination time (hour)	4		8	

that presented the best workability, best solidified product with lower porosity and no efflorescence were chosen. These compositions were referred to as A (55 wt% MK, 25 wt% SS and 20 wt% NaOH) and B (50 wt% MK, 35 wt% SS and 15 wt% NaOH). The geopolymer samples of compositions A (code: -1) and B (code: +1) were characterized for compressive strength based on the Brazilian Standard NBR 5739: 2007 [6], after 28 days of curing at room temperature, in a 273 kN press at a loading rate of 30 MPa/min.

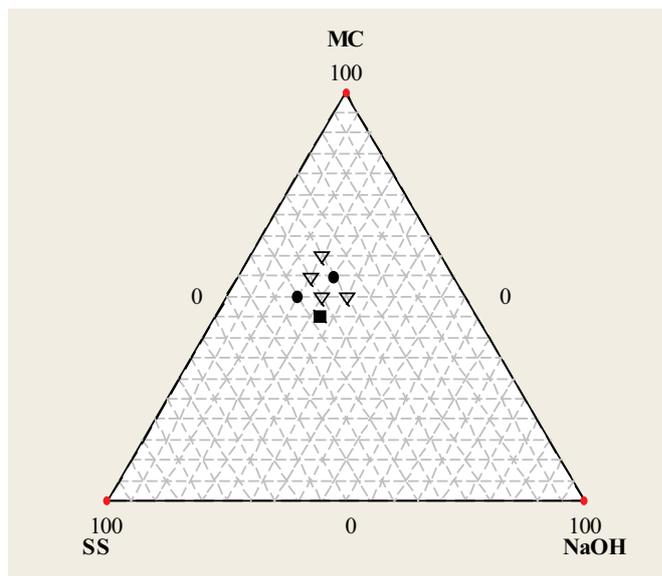


Figure 1: Simplex design where the square is the stoichiometric composition and the circles is the compositions A and B choice.

The first design of Table 1 comprised 16 runs (8 runs for each composition, A and B, respectively). The second design was a 2⁴ factorial design where the factors were calcination temperature (T), calcination time (CT), heating rate (HR), and composition (C) with 16 runs. The response was the compressive strength (CS) of the samples. Five or four specimens were measured for each run.

3. Results and Discussion

Despite the difference in coloration, the kaolinite samples showed very similar X-ray diffractograms, with kaolinite as the major phase and quartz as a minority phase. X-ray fluorescence also revealed similarity between the samples, except for the Mn and Cr contents, as well as the loss of mass on calcination, as shown in Table 2. Only the loss of mass on calcination correlates to the color tone, suggesting that the color is related to the presence of organic matter, since the calcined materials had slight to no color differences. The density of the samples varied between 2.54 g/cm³ and 2.62 g/cm³, probably due to quartz and organic matter contents. The mean particle size varied between 7.75 μm and 11.05 μm.

TABLE 2: Composition of the kaolinite samples (X-rays fluorescence)

Composition	Sample		
	Light gray	Gray	Dark grey
MgO (wt%)	0.16	<0.10	0.20
Al ₂ O ₃ (wt%)	29.23	28.32	25.60
SiO ₂ (wt%)	51.02	48.92	48.68
P (ppm)	3421	3385	3593
S (ppm)	111	110	121
K ₂ O (wt%)	2.14	2.34	2.32
CaO (wt%)	0.38	0.39	0.31
Ti (ppm)	4660	4551	4662
V (ppm)	112	110	113
Cr (ppm)	69	96	42
Mn (ppm)	93	230	150
Fe ₂ O ₃ (wt%)	3.38	3.67	5.10
Ni (ppm)	19	11	16
Cu (ppm)	26	25	26
Zn (ppm)	85	126	80
Zr (ppm)	173	140	180
Ba (ppm)	592	580	591
Loss of mass on calcination(%)	12.73	15.37	16.40

Thermal analysis of the samples reveals an endothermic peak around 500 °C (differential scanning calorimetry, DSC), which is related to the dehydroxylation of kaolinite (Figure 2). Around 250 °C there is a small peak that is probably related to the burning

of organic matter. There is another small peak around 580 °C, which may be related to the transition from alpha-quartz to beta-quartz. At 980 °C there is an exothermic peak, related to mullite formation.

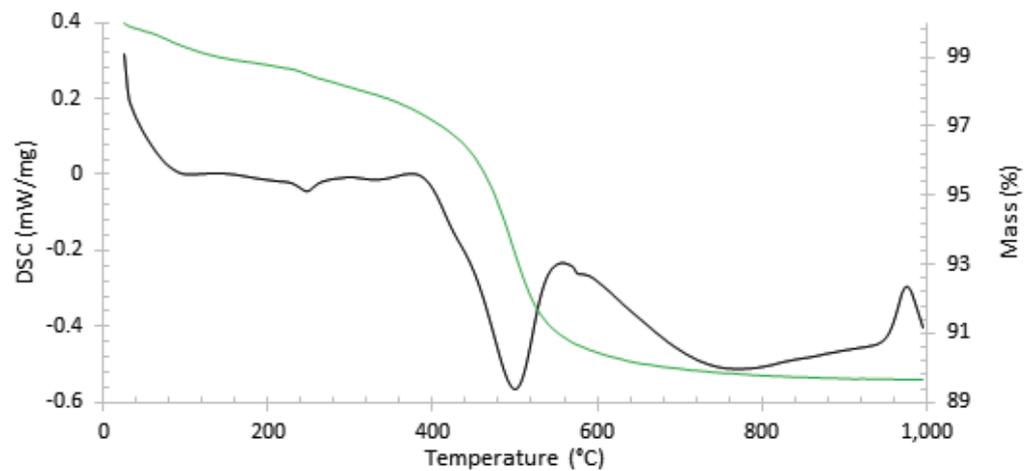


Figure 2: Typical result of thermal analysis of kaolinite samples after drying at 120 °C for 24 hours in air. Heating rate: 10 °C/min, atmosphere: N₂.

Figure 3 shows an example of infrared spectra of kaolinite samples before and after the calcination at 800 °C (formation of metakaolin). Typical bands of kaolinite in the range of 3697-3621 cm⁻¹ related to OH stretching disappear after calcination and bands for wavenumbers smaller than 1500 cm⁻¹ become indefinite, indicating amorphous material. The loss of crystallinity after calcination could also be observed by X-ray diffraction, except for the presence of quartz that was already present as a minor phase in kaolinite.

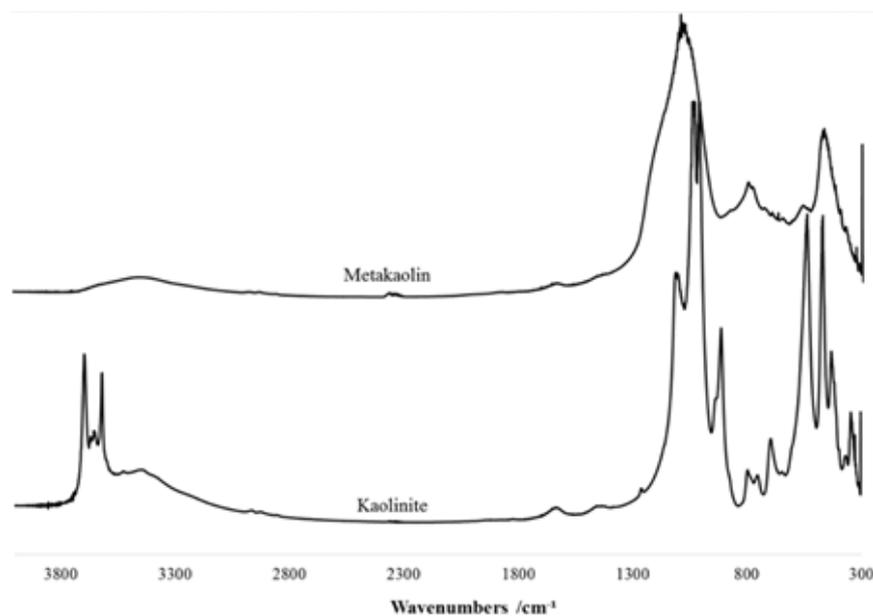


Figure 3: Infrared spectra of the kaolinite and the metakaolin.

Table 3 shows the decrease of the specific surface area of a kaolinite sample after calcination at 800 °C with varying heating rate (1 and 10 °C/min) and calcination time (4 h and 8 h), treated as a 2² factorial design. Figure 4 shows the main effects and interaction plots. The influence of heating rate is greater than the one of calcination time. Concerning the interaction between heating rate and time, the influence of the heating rate is greater at the shorter calcination time.

TABLE 3: Effect of heating rate and calcination time on the decrease of the specific surface for design 1 (see Table 1)

Heating rate	Time	$S_{g, \text{initial}}$ (m ² /g)	$S_{g, \text{calcined}}$ (m ² /g)	ΔS_g (m ² /g)
-1	-1	24.23	19.75	-4.48
+1	-1		16.35	-7.88
-1	+1		18.57	-5.66
+1	+1		16.51	-7.72

S_g : specific surface

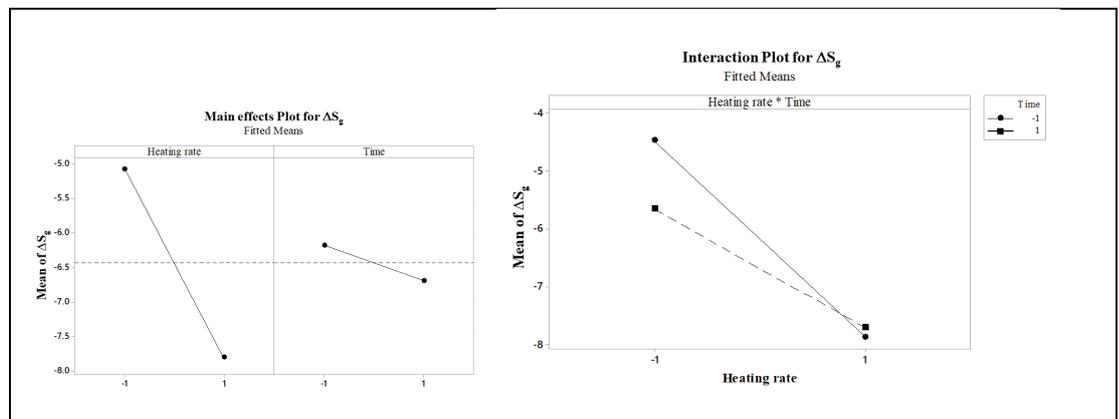


Figure 4: Main effects and interaction plots for the specific surface of the metakaolin, calculated with Minitab

Table 4 shows the results of the compressive strength tests performed on the geopolymer samples after 28 days of curing for the first design including the sample composition. Figure 5 shows a comparison based on the Tukey test assuming equal variances, calculated with Minitab. By comparing Figures 4a and 4c and 4b and 4d, one observes that composition A produced higher strength compressions for the heating rate of 10 °C/min. By comparing Figures 4a and 4b and 4c and 4d, one observes that the heating rate of 10 °C/min produces higher compressive strengths. Figures 4a to 4d shows that higher calcination times tends to produce higher compressive strengths.

Based on these results the second design of Table 1 was performed in order to study also the influence of the calcining temperature. Table 5 shows the results obtained for the compressive strength. This Table is a replicate of the experiments of the data of

TABLE 4: Results of compressive strength for the first design of Table 1

CT	HR	C	CS (MPa)				
1.0	1	A	31.21	43.98	43.52	22.02	13.24
1.0	10	A	22.83	13.87	20.85	27.83	39.68
1.0	1	B	14.00	10.32	20.34	23.90	12.32
1.0	10	B	15.00	15.13	17.71	13.36	16.77
2.8	1	A	22.86	30.85	18.04	21.54	20.13
2.8	10	A	24.64	27.97	15.53	*	17.27
2.8	1	B	21.26	21.46	22.22	18.45	22.47
2.8	10	B	21.50	31.42	16.75	16.22	33.46
4.0	1	A	30.87	37.27	34.12	24.67	*
4.0	10	A	47.65	49.34	43.33	40.72	43.81
4.0	1	B	36.52	31.99	33.51	45.15	33.56
4.0	10	B	26.82	27.95	25.94	26.60	29.46
8.0	1	A	38.09	44.09	26.92	43.29	31.81
8.0	10	A	50.60	51.00	67.08	46.94	50.32
8.0	1	B	29.65	31.11	29.90	24.19	30.95
8.0	10	B	39.92	41.46	43.25	43.86	48.81

CT: calcination time (hours), HR: heating rate (°C/min), C: composition, CS: compression strength

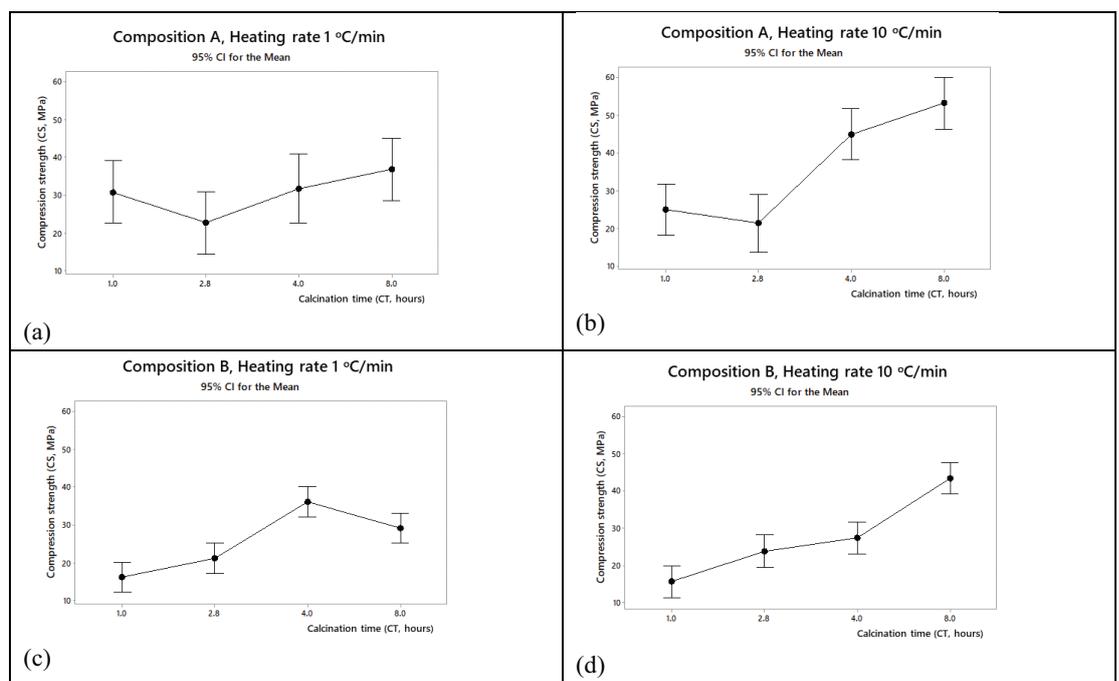


Figure 5: Comparisons of the results of compressive strength (Table 4) based on the Tukey test using pooled standard deviation to calculate the intervals

Table 4 related to the calcination times of 4 and 8 hours for calcination at 800 °C. A two-sample t test for means comparison with a confidence level of 95% indicated there is no difference between these replicates.

TABLE 5: Design matrix and responses (compression strength) for the 2⁴ factorial design

C	CT	HR	T	CS (MPa)			
-1	-1	-1	-1	34.23	42.14	38.14	39.18
+1	-1	-1	-1	26.97	25.65	23.01	23.23
-1	+	-1	-1	12.96	11.65	19.91	18.33
+1	+1	-1	-1	28.24	14.63	17.76	15.75
-1	-1	+1	-1	32.46	35.89	28.24	32.26
+1	-1	+1	-1	28.30	29.20	26.70	28.32
-1	+1	+1	-1	23.07	19.76	23.64	21.41
+1	+1	+1	-1	12.60	13.16	13.05	13.31
-1	-1	-1	+1	29.39	34.74	31.49	23.26
+1	-1	-1	+1	35.48	30.84	32.80	32.83
-1	+1	-1	+1	36.26	41.50	40.81	29.83
+1	+1	-1	+1	28.25	30.38	28.24	29.68
-1	-1	+1	+1	44.77	42.01	38.84	41.17
+1	-1	+1	+1	25.71	27.05	24.92	25.79
-1	+1	+1	+1	48.26	48.81	44.77	47.99
+1	+1	+1	+1	38.70	39.97	41.39	41.82

C: composition, CT: calcination temperature, HR: heating rate, T: calcination time

The data of Table 5 were analyzed with Minitab. A non-hierarchical empirical model including only the significant interactions is

$$\begin{aligned}
 CS (MPa) = & 29.87 - 3.17C + 1.50HR + 5.69T - 1.87CT - 1.29C * HR + 1.81HR * T \\
 & + 1.23HR * CT + 4.86T * CT - 0.97C * HR * T - 0.91C * T * CT \\
 & + 0.87HR * T * CT + 2.63C * HR * T * CT
 \end{aligned}
 \tag{1}$$

SE_{coef} = 0.39, S = 3.09, R² = 92.01%, R²_{adj} = 90.13%, R²_{pred} = 87,42%. C, HR, CT and T are coded factors.

This model has many significant interactions between the main factors, which indicates the complexity of the geopolymetric reactions and how they are influenced by the conditions of the metakaolin production. According to this model, the maximum compression strength, obtained for C = -1 (composition A), HR = +1 (10 °C/min), T = +1

(800 °C), and CT = +1 (8 hours), is between 40.9 MPa and 54.5 MPa for a confidence of 95%, calculated with the response optimizer of Minitab.

The most important term in the model of equation (1) is the interaction between the calcination temperature and the calcination time ($T \cdot CT$). This interaction is synergic, that means, for 700 °C (-1) the calcination time should be 4 hours (-1) and for 800 °C (+1) the calcination time should be 8 hours (+1) to produce higher compressive strengths. The combination of 700 °C for 8 hours or 800 °C for 4 hours is deleterious for the compressive strength. In overall, the compressive strength is lower at 700 °C when compared with 800 °C, as shown in the cube plot of Figure 6. It can also be observed that with the combination of composition, calcination temperature, calcination time and heating rate samples of geopolymer with very different compressive strengths can be obtained.

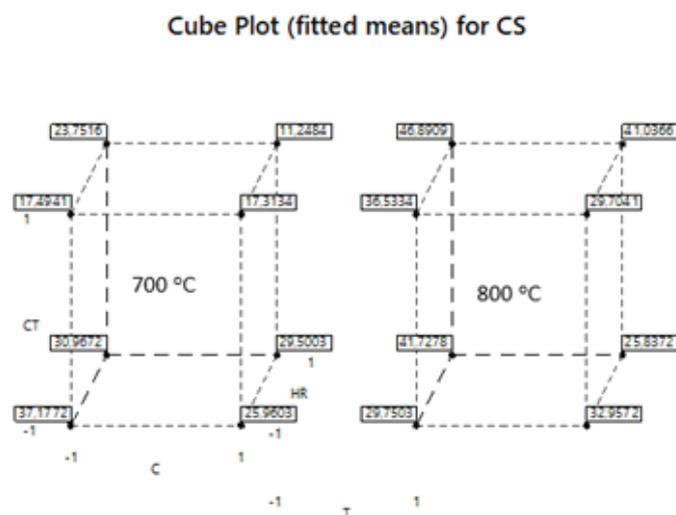


Figure 6: Cube plot for the compressive strength (CS) based on the empirical model of equation (1). T: calcining temperature, C: composition, HR: heating rate

Figure 7 shows the compressive strength (CS) as a function of the decrease of the specific surface (ΔS_g) in the calcination. A correlation exists for composition A, but it is not clear for composition B. For composition A, the compressive strength increases with the decrease of the specific surface.

4. Conclusion

Samples of geopolymer were obtained with the use of kaolinite generated as a by-product from sand extraction in the municipality of Inhaúma (Minas Gerais, Brazil). The samples of kaolinite were calcined at different temperatures, times and heating rates

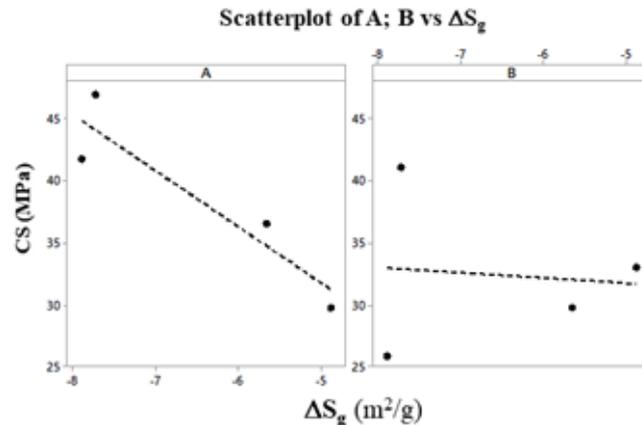


Figure 7: Compressive strength of geopolymer samples (CS) as a function of the decrease of the specific surface (ΔS_g) in the calcination of kaolinite.

of the kiln. 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. According to the empirical model calculated from a 2^4 factorial design, the compressive strengths observed may range from 10 MPa to 55 MPa, revealing the need for a rigid control over these factors to obtain geopolymer samples with the desired compressive strength.

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