



Research Paper

Modeling the compressive strength of metakaolin-based geopolymers based on the statistical analysis of experimental data

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ABSTRACT

The relationship between the compressive strength of metakaolin-based geopolymer samples and different processing conditions has been investigated for both potassium and sodium based geopolymer systems. Cubic geopolymer samples were prepared by mixing the slurry for 1 h in a thermostatic bath at 0 °C. >1200 samples have been tested to gather enough data to carry out a meaningful statistical analysis. All the data evaluation and model development have been carried out extensively using R. The variation of curing and aging time, curing temperature, SiO₂/Al₂O₃ and H₂O/Al₂O₃ molar ratios has been accounted for via the application of statistical models whose reliability has been suitably checked. Curing has been performed in a sealed container at 100% relative humidity. Aging has been conducted in a climate chamber kept at 75% of relative humidity using an oversaturated solution of NaCl. Curing time has proved a positive relationship with compressive strength while aging time does not show evidence of any significant effect. Curing temperature negatively affects compressive strength. Increasing the SiO₂/Al₂O₃ molar ratio results in an increase of the compressive strength within a certain range of values for the ratio; however, above a threshold (3.8 for the potassium-based and 3.4 for the sodium-based geopolymer system) the mechanical properties decrease. The H₂O/Al₂O₃ molar ratio displayed an inverse proportionality with the compressive strength except for the sodium-based geopolymer, where the mechanical properties initially increased. A further comprehensive and statistically sound model has been proposed that allows us to predict the strength of geopolymer samples as a function of process variables and their composition, ranging in a rather wide set of values.

1. Introduction

Geopolymers represent an innovative green binder that can compete with ordinary Portland cement as a structural material in construction. They are a class of inorganic polymers derived from the reaction of alumino-silicate minerals with aqueous solutions of alkali metal oxides or hydroxides. The alumino-silicate source is often a clay (e.g., kaolinite) which underwent a calcination process to extract the chemisorbed water and foster its reactivity; calcination temperatures are typically lower than those necessary for the clinker production, and the CO₂ footprint of the process is significantly lower. Moreover, calcined clay, e.g., metakaolin, can be substituted by a waste product, such as fly ashes, foundry slugs, or construction wastes, reducing the environmental impact of geopolymer even further (Davidovits, 1991).

It is essential to standardize the manufacturing process and testing

procedure to enable the widespread adoption of geopolymers. This standardization ensures consistent quality and performance across various production batches, reducing the risk of defects or failures. Furthermore, it simplifies the supply chain and allows for manufacturer interoperability. The testing procedure also requires rigorous standardization to ensure the reliability and durability of the final product. The lack of unified testing methods could lead to misleading results, compromise safety standards, and slow the acceptance of this new technology in the market. Additionally, standardization can facilitate research and development, as it provides a common foundation on which further innovations can be built. It also assists in comparing different geopolymer formulations, driving the evolution of more efficient and effective materials. Lastly, establishing international standards could expedite regulatory approval, thus accelerating the integration of geopolymers into existing infrastructures. As it stands, there are several

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studies that report on the influence of processing conditions and geopolymer composition on their compressive strength (Vora and Dave, 2013; Lahoti et al., 2017b). However, these studies often consider only a very limited number of samples and conditions. Such narrow scope of investigation not only reduces the representativeness of the results, but also fails to account for the complex interaction of various parameters affecting geopolymer properties. In reality, the compressive strength of geopolymers, much like any other construction material, is a function of a multitude of variables. This lack of consideration can lead to significant differences between laboratory results and the actual performance of geopolymers in real-world conditions (Lisboa and Danubia, 2006; Lahoti et al., 2017a). Without these considerations, it becomes difficult to predict long-term performance, durability, and safety of geopolymers. There is a clear need for more comprehensive and systematic studies that take into account a broader set of influencing factors. These should aim to create robust mathematical models capable of predicting geopolymer performance under diverse conditions, further aiding in the standardization of geopolymer production and testing processes.

Indeed, there is a conspicuous lack of extensive and comprehensive statistical studies that simultaneously consider both the chemical, specifically composition (Duxson et al., 2005a, 2005b; Thakur et al., 2009), and processing aspects such as curing and aging conditions (Muñiz-Villarreal et al., 2011; Nurrudin et al., 2018). While these individual studies make significant contributions to our understanding of specific aspects, they don't necessarily provide a holistic view of the overall process and the multitude of factors that can influence the properties of geopolymers. This holistic perspective is crucial to enable the creation of an optimized, standardized, and reproducible manufacturing protocol for geopolymers.

Ghanbari et al. were the first ones to attempt modeling the mechanical properties of geopolymers, taking into consideration both process conditions and composition (Ghanbari et al., 2017). However, there is a notable exclusion in their methodology, specifically the failure to account for the curing and aging condition - a significant facet in the manufacturing process of geopolymers. Furthermore, the quantity of samples tested in their study appears insufficient to provide statistically relevant trends, and the authors do not provide a comprehensive model accounting simultaneously for all parameters considered. The study we report in this paper aims to bridge this gap by concurrently considering both chemical and processing variables in a systematic and statistically robust manner.

From a chemical standpoint, the reaction starts with the metakaolin particles' dissolution operated by alkaline solutions. Gelation results from the hydrolysis-polycondensation of aluminum and silicon-containing dissolved species, resulting in a complex gel network swollen by water trapped in the pores. The aluminosilicate gel is composed of primary globular polymeric entities 0.8–2.0 nm in diameter, whose packing density is influenced by the reaction rate and by the water content (Colomban, 1998). Structural reorganization of the network occurs by continued reaction and expulsion of the water, that tends to coalesce into larger pores. Both curing and aging conditions affect the development of the geopolymer network. Both the curing duration and holding temperature influence the kinetics of polycondensation with an impact on the early-stage network formation (Mo et al., 2014). The aging stage, on the other hand, is linked to the later-stage reorganization and to the expulsion of water (Khale and Chaudhary, 2007a, 2007b; Emdadi et al., 2015). In fact, it is typically carried out in an open environment with relative humidity <100%; therefore, water evaporation impacts on the pore refinement occurring within the material during this stage. Steins et al. (Steins et al., 2014) identified several structural changes of porosity over time through SANS SAXS and BET analyses: further densification of the solid network and a partial closure of the porosity at the nanometer scale both contributed to the refinement of the porosity; such decrease in the pore accessibility may be linked to the ongoing reactions.

It should be noted that the source of aluminosilicates has a

tremendous impact not only on the composition but also on the reaction kinetics and on the final microstructure. Even reducing the study to only metakaolin as reference material, variations in the SiO₂/Al₂O₃ ratio, the particle size distribution and the calcination temperature all influence the kinetics of dissolution and therefore the architecture of the condensed network, and ultimately, the mechanical response of the material. Kuenzel et al. (2013) made an attempt at studying the effect of different kinds of metakaolin on the mechanical properties of geopolymers; however, they concluded that the comparison between geopolymers made from different MK samples is deemed difficult by the high variations in critical defect size, hampering the collation of results of other papers even more.

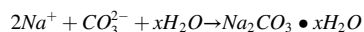
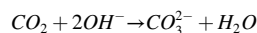
With this work, we aimed at addressing this issue and at proposing a predictive model, based on a statistical analysis of the collected experimental data. We limited our study to single aluminosilicate, alkali silicate and alkali hydroxide sources, and we developed a standardized procedure for the production and characterization of samples. The proposed model has the potential to inform the production of geopolymers of given characteristics by appropriate selection of formulation and processing parameters.

2. Experimental

2.1. Design of Experiments

All the experiments were conducted on both potassium- and sodium-based geopolymers, as they are both extensively used and possess different properties. The compressive strength of the geopolymers was evaluated for varying conditions alleged to affect their microstructure and performance, namely the curing and aging time, curing temperature, silica to alumina ratio and water to alumina ratio (Hardjito et al., 2004; Moradikhrou and Esparham, 2020).

In order to limit the number of experimental variables and curb the collection of experimental data, the geopolymer composition was changed solely in terms of SiO₂/Al₂O₃ ratio and H₂O/Al₂O₃ ratio, whereas the Na₂O or K₂O/Al₂O₃ ratio was always held constant at 1; this corresponds to the composition at which the positive charge of the alkaline cation fully stabilizes the Al coordination from [Al]^{VI} to [Al]^{IV} while limiting the material susceptibility to carbonation reactions. In natural carbonation, atmospheric CO₂ reacts with hydroxide, i.e., an acid-base reaction is established (Zhang et al., 2014; Sani et al., 2016). However, in geopolymeric materials, the main driving factor to efflorescence in geopolymeric materials is the availability of Na⁺ or K⁺ and OH⁻ as shown in the following equations (for Na⁺):



Thus, the efflorescence development potential observed by the total alkalinity value of the samples leachate may be due to the alkalinity resulting from the hydroxide (OH⁻) and carbonate (CO₃²⁻) ions. Excessive efflorescence and, consequently, leaching and carbonation on the surface and inside the pores can reduce geopolymers' compressive and tensile strength. L. Simão et al. (Simão et al., 2021) studied a new approach to controlling the efflorescence in geopolymeric material. In their work, they studied, in particular, different Na₂O/Al₂O₃ ratios concluding that a value of about 1 showed a higher compressive strength value. Nevertheless, the number of factors and possible combinations that could be considered limits the possibility for a straightforward evaluation of the relationship between the compressive strength and the whole set of conditions and precludes the prediction of geopolymer performance. Hence, a factorial design of experiments approach was followed in this investigation for a wide, yet specific selection of conditions. Experimental conditions for each considered varying factor were selected based on the analysis of a wide range of papers reporting

different processing conditions and resulting material's characteristics, and cover the widest range considered appropriate for typical geopolymer materials (Ismail et al., 2011; Timakul et al., 2015; Verma et al., 2022). Additionally, a pilot set of experiments was carried out to tune the geopolymer composition and the curing temperature to provide the lowest strength variability. The resulting design of the experiments is summarized in Table 1 and in the following detailed.

The effect of **curing and aging time** on the compression strength was evaluated on geopolymer samples of composition $K/Na_2O \cdot 3.4SiO_2 \cdot Al_2O_3 \cdot 18H_2O$ cured at 40 °C for C days and aged afterward for A days, with (C, A) varying in the set $\{1, 7, 28\} \times \{0, 7, 21, 28, 56\}$.

The effect of **curing temperature** on the compression strength was evaluated on geopolymer samples of composition $K/Na_2O \cdot 3.4SiO_2 \cdot Al_2O_3 \cdot 18H_2O$ cured for 1 day at T degrees (°C) and aged for 7 days at room temperature, with T varying in the set $\{25, 40, 50, 60, 75, 90\}$. Curing and aging time conditions were selected in the pilot experiments as the ones providing the lowest standard deviation values, besides being the most suited in term of general processing approach and times.

The effect of the **SiO₂/Al₂O₃ molar ratio** on the compression strength was evaluated on geopolymer samples with ratio selected in the set $\{2.6, 3.0, 3.4, 3.8, 4.2\}$, cured at 40 °C for 1 day and aged for 7 days. The H₂O/Al₂O₃ ratio was kept at 18, as this value provides geopolymer systems with a rheology suitable for a variety of processing methodologies, including casting.

The effect of the **H₂O/Al₂O₃ ratio** on the compression strength was evaluated on geopolymer samples with ratio selected in the set $\{11, 13, 15, 18, 20, 22, 25\}$, cured at 40 °C for 1 day and aged for 7 days; the SiO₂/Al₂O₃ ratio was kept at 3.4.

2.2. Samples preparation

To manufacture the samples, metakaolin (Argical 1200s, Imerys, France) was mixed with an alkaline solution for 1 h in a thermostatic bath at 0 °C; The primary purpose of the thermostatic bath is to slow down the geopolymeric reaction that is taking place while mixing to better assess the influence of curing time on the compressive strength. The alkaline solution was obtained by dissolving sodium (SS2942 Ingessil Italy) or potassium silicates (Kaslov 205 PQ Corporation) and sodium or potassium hydroxides (Sigma Aldrich) into distilled water. After that, the slurry was poured into 10x10x10 mm³ silicone molds; the choice of relatively small molds serves the purpose of enabling the production of a great number of specimens while limiting the volumes of material to be processed. This way, each set of specimens can be produced in a single batch, assuring better homogeneity among the set. The molds were placed in a sealed container at a constant 100% relative humidity (RH), achieved by placing a water container within the chamber and monitoring RH using a hygrometer, to proceed with the curing process in different conditions placing the samples in the oven. Curing refers to the time (days) that geopolymer samples remain in the aforementioned conditions inside the silicone mold in a sealed container. After curing, the samples are removed from the mold and placed in a climate chamber at a constant 75% RH, achieved by placing a supersaturated NaCl solution within the chamber (which acts as water regulator) and monitoring using a hygrometer. The duration of this

Table 1
Design of Experiments: tested variables and conditions.

Variable	Conditions						
Curing (days)	1	7	28				
Aging (days)	0	7	21	28	56		
Curing temperature (°C)	25	40	50	60	75	90	
Si/Al ratio	2.6	3.0	3.4	3.8	4.2		
H ₂ O/Al ₂ O ₃ ratio	11	13	15	18	20	22	25

second step is referred to as aging time (days). The relatively high value of RH maintained during aging is motivated by preliminary tests showing a tendency to crack for geopolymer samples aged otherwise. For all conditions studied in this work, boiling tests and FT-IR analyses were conducted to assess the complete consolidation of materials (especially for low curing and aging times).

2.3. Mechanical characterization

The compressive strength was measured using a universal testing machine (Galdabini Quasar 25) with a crosshead speed 0.5 mm/min; the compression surfaces of the samples were lightly sanded before testing, and 20 samples for each condition were analyzed.

2.4. Data analysis

The statistical analysis has been conducted on the collected data using the R software for statistical computing https://cran.r-project.org/web/packages/report/vignettes/cite_packages.html, an open-source environment available under the GNU General Public License, primarily written in C, Fortran and R itself.

The relationships between the compressive strength and composition, curing temperature, curing and aging conditions were preliminary explored by means of box and whiskers plots - *boxplots* -, widespread graphical tools that summarize an empirical distribution by building a box delimited by its first and third quartile and cut by its median as a measure of central tendency. The box is then possibly provided by whiskers extending to the spread of the data, and by outliers which are individually plotted.

Results of the exploratory data analysis, discussed in the following section, suggested a broad adequacy of linear models with polynomial trends and Analysis of Covariance (ANCOVA) to evaluate significant effects of composition, curing temperature, curing and aging conditions. ANCOVA refers to regression problems to model the expected variation of continuous responses as a function of both qualitative (as the alkaline cation on which the geopolymer formulation is based upon) and quantitative predictors (e.g., the SiO₂/Al₂O₃ molar ratio and the H₂O/Al₂O₃ ratio), possibly interacting among them.

To evaluate the effect of the considered experimental factors *ceteris paribus*, model specification also accounted for possible random variations in the experimental conditions, such as the sample geometric density or its volume, and kept it in the resulting model whenever resulted significant. A general formulation of the considered models to explain the expected variation of the compressive strength $E(\sigma)$ for varying experimental factors F on sodium or potassium geopolymer is the following:

$$E(\sigma) = \begin{cases} \beta_0 + \beta_1 F + \dots + \beta_k F^k & \text{Alkaline Cation K} \\ \gamma_0 + \gamma_1 F + \dots + \gamma_k F^k & \text{Alkaline Cation Na} \end{cases}$$

Details on the estimated models for the different experiments, along with the associated residuals analysis and indexes of goodness of fit are illustrated in the next section.

The samples were labelled as: KCxAy or NaCxAy, where:

- K and Na identify the alkaline cation on which the geopolymer formulation is based on;
- x, expressed in days, is the curing time (curing temperature was kept constant at 40 °C);
- y, expressed in days, is the aging time.

3. Results and discussion

3.1. Effect of curing and aging time

Fig. 1 reports the mechanical test results for all the selected curing

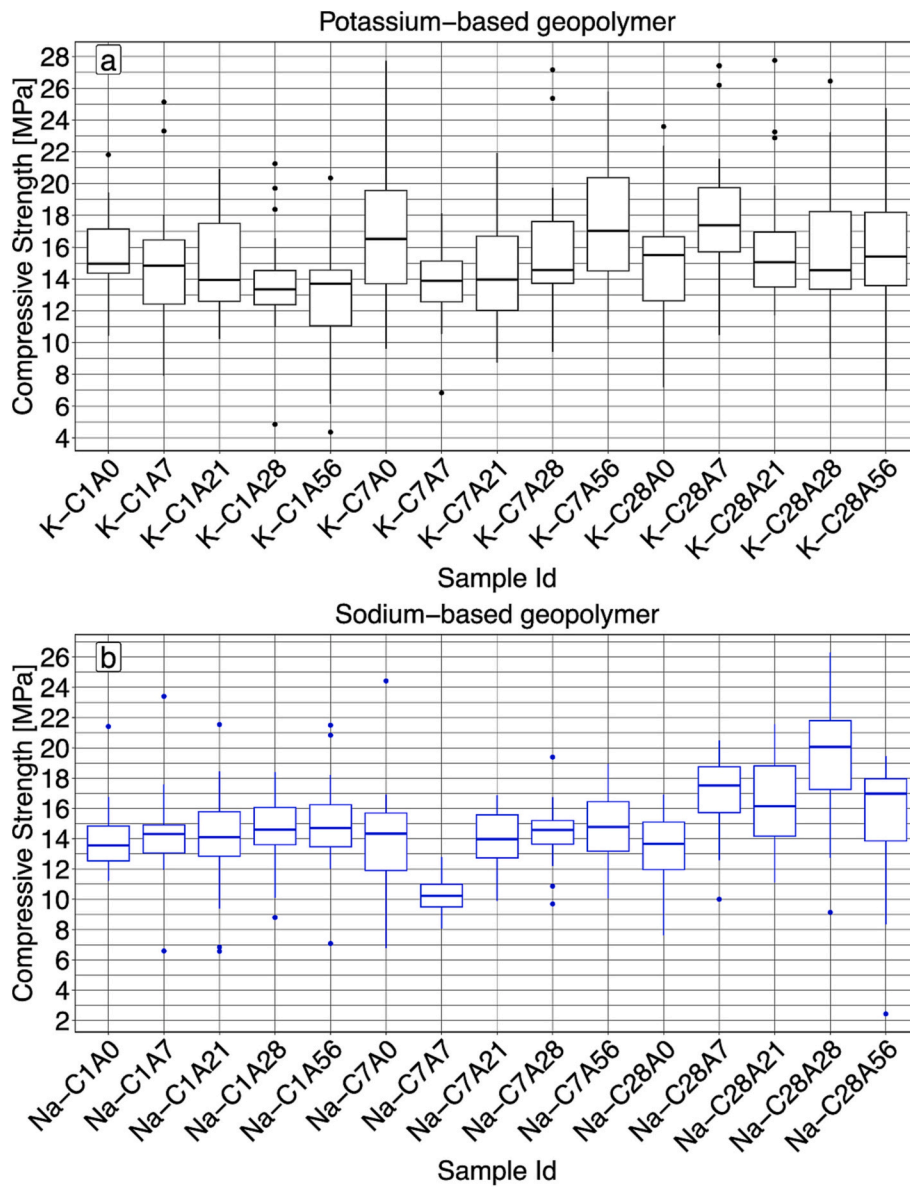


Fig. 1. Overview of the effect of curing time (at fixed curing temperature = 40 °C) and aging conditions on compression strength. a) Potassium-based geopolymer, b) Sodium-based geopolymer.

and aging conditions. Due to the difference in behavior between these two types of geopolymer, the conditional distributions of compressive strength vs curing were analyzed, depending on the amount of aging and of curing.

Fig. 2a and b show the empirical distribution of compressive strength vs aging time for different curing times and, respectively, the empirical distribution of compressive strength vs curing time for different aging times, in both potassium- and sodium-based samples.

As a general remark, potassium geopolymers show a broadly higher compressive strength. A positive linear association between compressive strength and curing time appears, yet possibly of different intensity in potassium- and sodium-based geopolymer samples. The relationship between compressive strength and aging time appears less evident and of interest for sodium geopolymers only.

The above considerations suggest the formulation of the following model:

$$E(\sigma) = \begin{cases} \beta_0 + \beta_1 C + \beta_2 A & \text{Alkaline cation K} \\ (\beta_0 + \gamma_0) + (\beta_1 + \gamma_1)C + (\beta_2 + \gamma_2)A & \text{Alkaline cation Na} \end{cases} \quad (1)$$

where C is the curing time and A is the aging time.

The estimated parameters, along with their standard errors and significance are summarized in Table 2; their analysis validates and strengthens our previous, qualitative findings.

On average, a higher compressive strength of potassium geopolymers than sodium-based ones, amounting to about 2 MPa, is confirmed and significant in accordance with previous reports (Lizcano et al., 2012). The drop in strength observed for both potassium and sodium-based geopolymers at 7 days of curing and 7 days of aging still needs to be fully understood, but it is most likely related to the stage of pore refinement reached by the material. After 1 day of curing, the polycondensation reactions are still far from being completed (Sagoe-Crentsil and Weng, 2007) and little water is expected to be produced. After 7 days of curing, however, there might already be considerable water coalescence (Archez et al., 2021); while its effect cannot be appreciated at 0 days of aging, the subsequent evaporation in the following 7 days generate large pores that limit the strength of the material. With additional aging time, the microstructure continues to develop, and the material shows an increase in its strength. After 28 days of curing, the

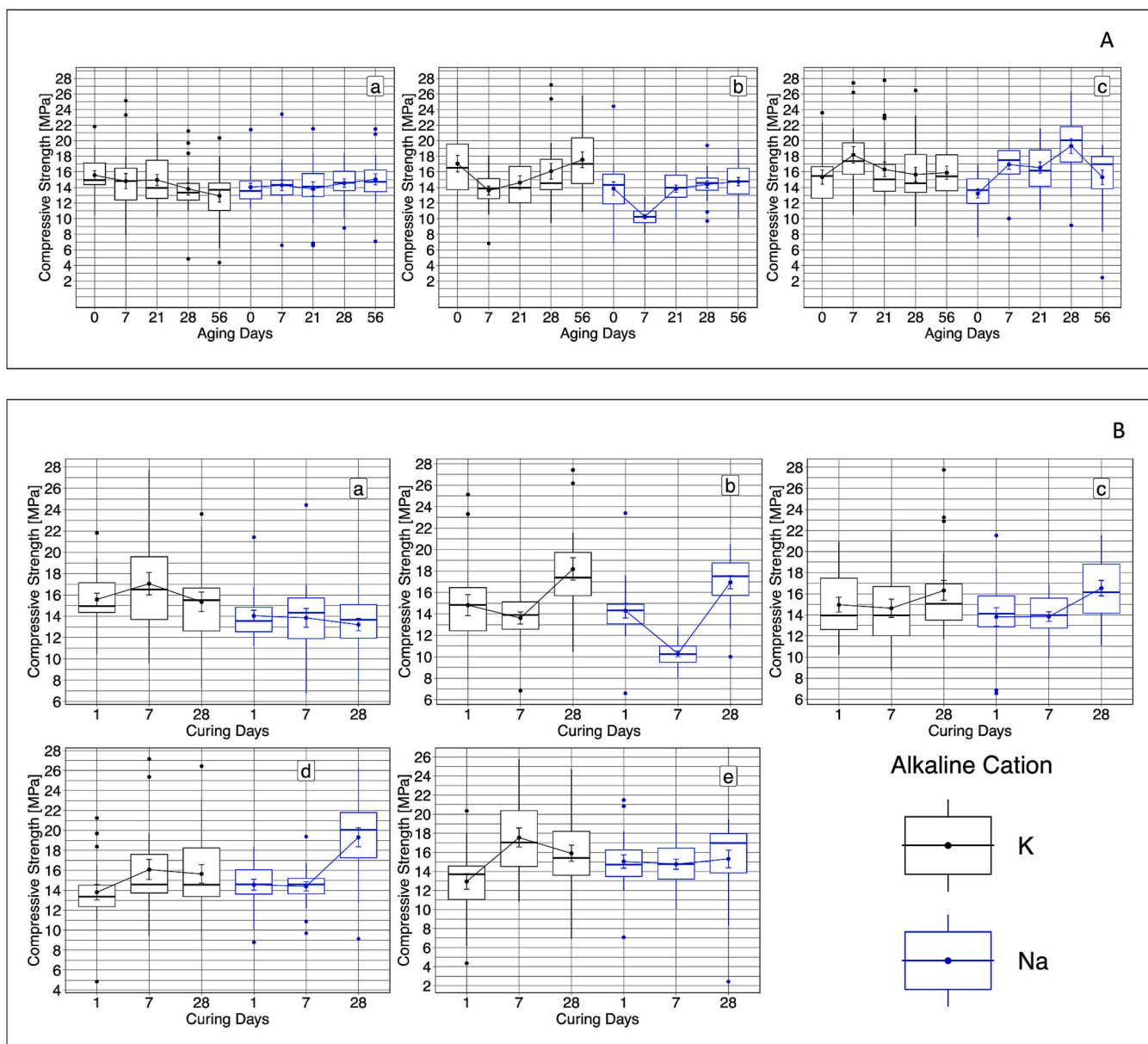


Fig. 2. (A) Empirical distribution of compressive strength vs curing age (at fixed curing temperature = 40 °C) for curing times 1 day (a), 7 days (b), 21 days (c). (B) Empirical distribution of compressive strength vs curing time (at fixed curing temperature = 40 °C) for aging times 0 days (a), 7 days (b), 21 days (c), 28 days (d), 56 days (e).

Table 2

Estimates, standard errors and level of significance of parameters in Eq. 1; F statistics, R², DF (Degree of Freedom). Significance levels: 0 ‘****’, 0.001 ‘***’, ‘×’ 1.

Parameter	Estimate (standard error)	Significance
β_2	14.98 (0.39)	***
γ_0	-2.00 (0.55)	***
β_1	0.06 (0.02)	**
γ_1	0.09 (0.02)	***
β_2	-0.01 (0.01)	
γ_2	0.03 (0.01)	**

R² = 0.07; F-statistic: 9.424 on 5 and 590 DF ***

reactions are mostly completed, and the subsequent aging has a lower influence. This hypothesis will need to be validated with further investigation on the materials’ porosity; however, the combination of 7 days of curing and 7 days of aging can be deemed undesirable for both

material systems studied here.

Curing time has a slight, yet fully significant, effect on increasing the expected compressive strength in both potassium- and sodium-based geopolymers, quantifiable in an average increase of ~0.06 and ~0.14 MPa for each additional day of curing, respectively. The slight increase in strength could be explained by the fact that the temperature accelerates the geopolymerization reaction. Keeping the samples at 40 °C for longer times forces the reactions toward the product, helping to consume all the reagents and therefore resulting in the development of a more complete geopolymer network. The greater concentration of Si-O-Si bonds with respect to Si-O-Al bonds can be held responsible for higher values for the compressive strength (Jong and Jr, 1980). This trend is in agreement with previous experiments carried out considering similar conditions (Rangan et al., 2010).

Aging time has a slight positive effect on sodium geopolymers quantifiable in an average increase of about 0.03 MPa for each additional day of aging; conversely, it does not result in significantly

affecting potassium-based geopolymers. The result can be explained considering by the fact that the geopolymerization reaction rate for the Na-based geopolymer is slower (Botti et al., 2021).

In Fig. 3a, model residuals are plotted versus the predicted values of the compressive strength, according to the estimated model; while residuals are comprehensively high, the plot does not show any trend, thus suggesting an overall correct model specification; the normal quantile-quantile plot (Fig. 3b) compares the empirical quantiles of the residuals with the theoretical quantiles of a normal density. Except for some data at the tail of the distribution, which depart from the general trend, the linearity of the points indicates that model errors comply with Gaussianity, hence the whole inference about the model, relying on such assumption, can be considered reliable. Furthermore, the scale-location plot (Fig. 3c) does not present any trend, hence does not show violations of the hypothesis of homoscedasticity of the error term and guarantees the efficiency of the estimates.

Besides a general adequacy and reliability of the estimated model, the value of the R^2 indicates that curing and aging time can explain about the 8% only of the variability of compressive strength, hence requiring inclusion of further experimental factors in the model.

3.2. Effect of curing temperature

Fig. 4 shows the empirical distribution of compressive strength vs curing temperature.

Temperature seems to negatively affect the average compressive strength of samples, yet up to some threshold. Above such value, the trend changes, getting less clear. This suggests modeling the data as specified in the following:

$$E(\sigma) = \begin{cases} \beta_0 + \beta_1 T + \beta_2 I_{T>60} & \text{Alkaline cation K} \\ (\beta_0 + \gamma_0) + (\beta_1 + \gamma_1) T + \gamma_2 I_{T>40} & \text{Alkaline cation Na} \end{cases} \quad (2)$$

where T is the temperature and I_A is dummy variable taking value 1 when event A occurs, and value 0 otherwise. In this case, event A refers to the temperature exceeding a certain threshold. The estimated parameters, along with their standard errors and significance are summarized in Table 3. Some main remarks are discussed in the following.

The model does not prove any evidence of a linear relationship between the expected compressive strength and the curing temperature, neither before nor after the selected thresholds, and for none of the cations (the associated parameter β_1 and γ_1 are indeed not significant).

With low curing temperature, there is no evidence of a different expected compressive strength between the two cations (the γ_0 is also not significant).

In both types of geopolymers there is evidence of a threshold curing temperature that shifts the expected compressive strength toward lower

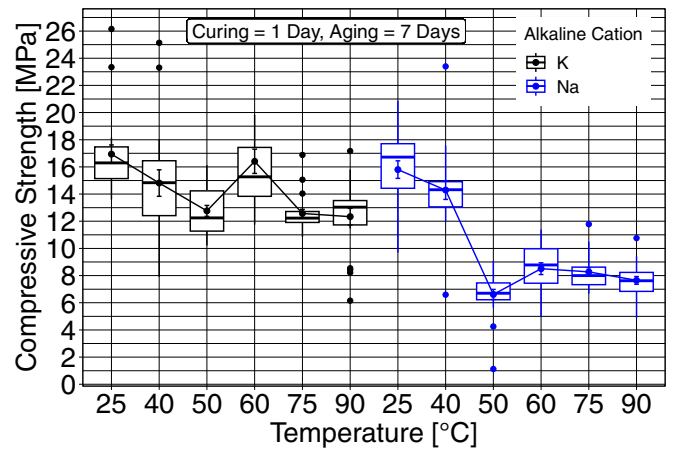


Fig. 4. Empirical distribution of compressive strength vs curing temperature.

Table 3

Estimates, standard errors and level of significance of parameters in Eq. 2; F statistics, R^2 , DF (Degree of Freedom). Significance levels: 0 ‘***’, 0.001 ‘**’, ‘×’ 1.

Parameter	Estimate (standard error)	Significance
β_0	16.04 (1.22)	***
γ_0	-0.17 (1.72)	
β_1	-0.005 (0.04)	
γ_1	-0.02 (0.05)	
β_2	-1.99 (1.17)	.
γ_2	-6.87 (1.05)	***

$R^2 = 0.59$, F-statistic: 48.16 on 5 and 232 DF, significance ***

values, especially in sodium-based geopolymers. The expected shift is estimated to amount to about -1.99 MPa for potassium-based geopolymers when the temperature exceeds a threshold of 60 °C, and to about -6.87 MPa for sodium-based geopolymers when the temperature exceeds a threshold of 40 °C. These patterns demonstrate consistency with preceding scholarly research (Ghanbari et al., 2017). Nevertheless, at this stage of the investigation, the reason behind this behavior is still unclear. Systematic NMR structural investigations of the samples should be carried out to assess any diversity in the developed network, but this is beyond the scope of the present work. An overall negative impact of the curing temperature on the compressive strength could be explained by the fact that the rate of polycondensation and water evaporation in the geopolymer both increase with increasing curing temperature; the latter promotes the formation of larger, macropores, which are believed to be more interconnected than micro and mesopores (Ramón et al., 2011). Consequently, the presence of macropores can decrease mechanical strength (Rovnaník, 2010). Similar trends have been found in other works under similar conditions (Bakria et al., 2011; Lee et al., 2016).

The model is overall informative (F test is significant) and the R^2 suggests that the temperature can explain almost 60% of the total variability. Nevertheless, residual analysis (reported in Fig. 5) indicates some weak deviations from the model assumptions, especially with reference to the hypothesis of normal errors. While this is likely to be due to the presence of some outliers (see also Fig. 4), these results warn to use some caution in considering reliable the inference associated to such model.

3.3. Effect of the SiO_2/Al_2O_3 molar ratio

Fig. 6 shows the empirical distribution of the compressive strength and silica to alumina ratio and clearly shows a quadratic trend for both

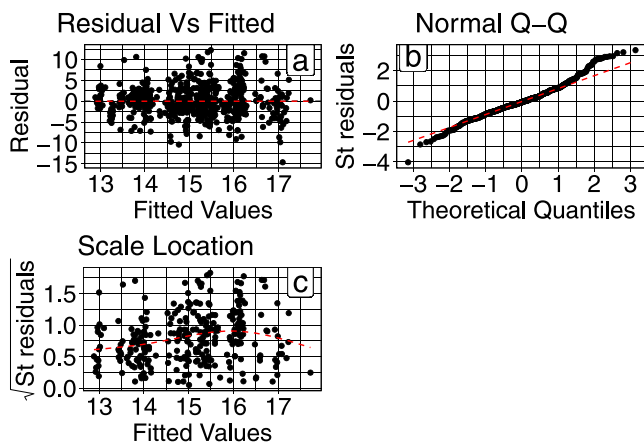


Fig. 3. Residual analysis of the curing-aging estimated model in Eq. 1. a) Residual vs Fitted values, b) Normal Q-Q plot, c) Scale-Location.

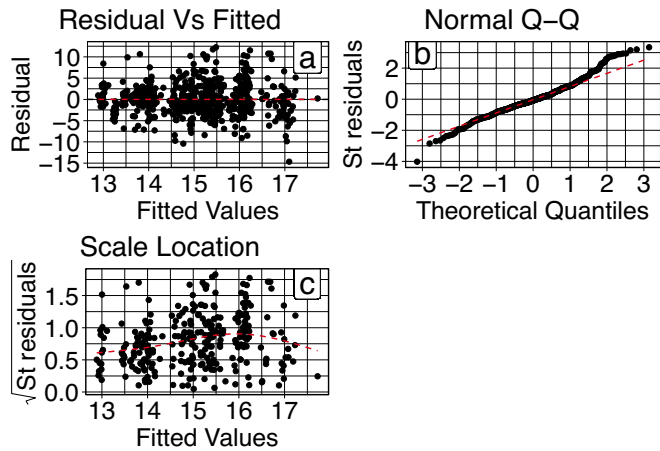


Fig. 5. Residual analysis of the estimated model in Eq. 2.

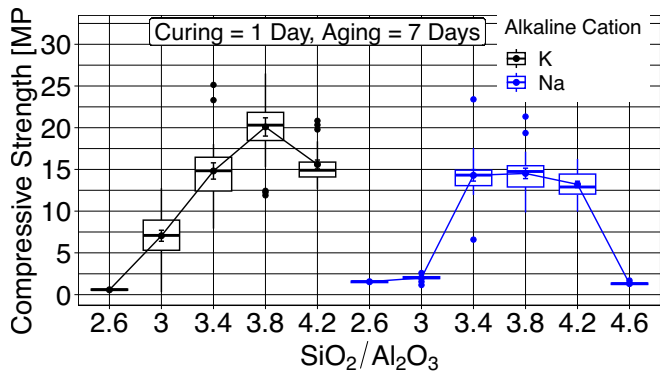


Fig. 6. Empirical distribution of compressive strength vs $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio.

types of geopolymers.

The following model is thus adopted:

$$E(\sigma) = \left\{ \begin{array}{l} \beta_0 + \beta_1 \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} + \beta_2 \left(\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} \right)^2 \quad \text{Alkaline Cation K} \\ (\beta_0 + \gamma_0) + (\beta_1 + \gamma_1) \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} + (\beta_2 + \gamma_2) \left(\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} \right)^2 \quad \text{Alkaline Cation Na} \end{array} \right\} \quad (3)$$

The estimated parameters, along with their standard errors and significance are summarized in Table 4. Some main remarks are discussed in the following.

The estimated model confirms a significant quadratic, concave trend linking the expected compressive strength and the silica to alumina ratio. Knowing that the Al component of metakaolin tends to dissolve more easily than the Si component (Weng et al., 2002), we can assume that more $\text{Al}(\text{OH})_4^-$ species are readily available for condensation with respect to $\text{Si}(\text{OH})_4$ ones. This is particularly true for the systems with low values of the $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio: condensation is likely to have occurred between aluminate and silicate species, producing poly(sialate) polymer structures. With increasing Si content, the overall higher amount of silicate species promotes the reaction between them, resulting in oligomeric silicates; the dominance of the latter leads to better mechanical properties with increasing $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio.

Above a certain threshold for the $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio (3.8 for both potassium and sodium-based geopolymers) the mechanical strength drops significantly. This decrease could be linked to the fact that, for

Table 4

Estimates, standard errors and level of significance of parameters in Eq. 3; F statistics, R^2 , DF (Degree of Freedom). Significance levels: 0 ‘***’, 0.001 ‘**’, ‘×’ 1.

Parameter	Estimate (standard error)	Significance
β_0	-148.99 (15.84)	***
γ_0	-13.67 (19.05)	
β_1	85.71 (9.5)	***
γ_1	10.02 (11.23)	
β_2	-11.01 (1.39)	***
γ_2	-1.96 (1.61)	

$R^2 = 0.75$, F-statistic: 130.6 on 5 and 212 DF, significance ***

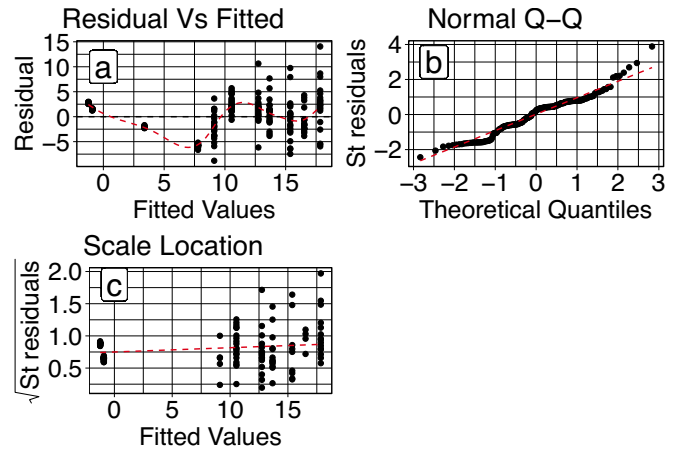


Fig. 7. Residual analysis of the estimated model in Eq. 3.

higher concentration of SiO_2 , the dissolution of metakaolin becomes more difficult, resulting in the permanence of unreacted metakaolin in the final material acting as a point of defect.

Data trends are in good agreement with data present in the literature (Duxson et al., 2005a, 2005b); however, the compressive strength values, on average, are lower than those generally reported in the literature. It is worth noticing that the amount of water in the formulations is relatively high compared to the literature ($\text{H}_2\text{O} / \text{Al}_2\text{O}_3 = 18$, whereas generally a range of 11–13 is employed), leading to a generally more porous structure and hence limited strength.

On average, the silica to alumina ratio explains the expected variation of the compressive strengths with no difference between the two types of geopolymers (γ parameters result all not to be significant).

The residual analysis suggests that (Fig. 7) model does not show evident violation of the hypotheses and is consequently to be considered reliable. It also shows a very good fit of the data, with the silica to alumina ratio showing to be a major responsible for explaining the variability of the compressive strength ($R^2 = 0.75$).

3.4. Effect of the $\text{H}_2\text{O} / \text{Al}_2\text{O}_3$ molar ratio

Fig. 8 shows the empirical distribution of the compressive strength and $\text{H}_2\text{O} / \text{Al}_2\text{O}_3$ molar ratio.

This ratio seems to negatively affect the average compressive strength of the samples. Potassium-based geopolymer samples show a clearly visible decreasing trend, while sodium-based ones show at the beginning (from $\text{H}_2\text{O} / \text{Al}_2\text{O}_3 = 11$ to 13) an increase in the compressive strength. Exceeding $\text{H}_2\text{O} / \text{Al}_2\text{O}_3 = 13$ results in a decrease of the compressive strength, but with a higher slope than for the potassium-based geopolymer system until $\text{H}_2\text{O} / \text{Al}_2\text{O}_3 = 22$, where a plateau is reached.

The statistical model is the following:

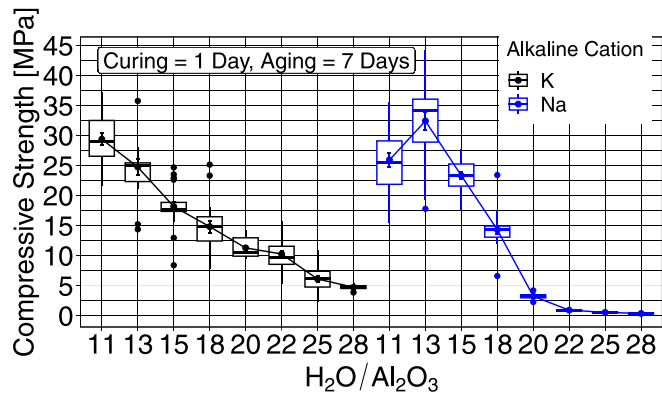


Fig. 8. Empirical distribution of compressive strength vs H₂O / Al₂O₃ ratio.

reported in Fig. 9). The fitting of the data could be improved even more using a polynomial with a higher degree (from 2 to 3). However, some of the hypotheses underlying the model are not fully satisfied (slightly heteroskedasticity in Fig. 9c) and so for this reason the estimates are not completely reliable.

3.5. Comprehensive model

To separate the possible effect of each condition all other things being equal, a full factorial design of experiments should be conducted. Nevertheless, in the experimental unfeasibility of varying so many conditions, a comprehensive model has been estimated. The model attempts the ambitious aim of explaining the variability of the compressive strength of metakaolin-based geopolymers by accounting for all the factors considered so far, namely curing and aging time, curing temperature and composition (SiO₂/Al₂O₃ and H₂O/Al₂O₃ molar ratios). Among several alternative formulations, the best model has been selected, specified as follows:

$$E(\sigma) = \begin{cases} \beta_0 + \beta_1 \left(\frac{H_2O}{Al_2O_3}\right) + \beta_2 \left(\frac{H_2O}{Al_2O_3}\right)^2 & \text{Alkaline Cation K} \\ (\beta_0 + \gamma_0) + (\beta_1 + \gamma_1) \left(\frac{H_2O}{Al_2O_3}\right) + (\beta_2 + \gamma_2) \left(\frac{H_2O}{Al_2O_3}\right)^2 & \text{Alkaline Cation Na} \end{cases} \quad (4)$$

$$E(\sigma) = \begin{cases} \beta_0 + \beta_1 C + \beta_2 A + \beta_3 T + \beta_4 I_{T>60} + \beta_5 \frac{SiO_2}{Al_2O_3} + \beta_6 \left(\frac{SiO_2}{Al_2O_3}\right)^2 + \beta_7 \frac{H_2O}{Al_2O_3} + \beta_8 \left(\frac{H_2O}{Al_2O_3}\right)^2 & \text{Alkaline Cation K} \\ (\beta_0 + \gamma_0) + (\beta_1 + \gamma_1) C + (\beta_2 + \gamma_2) A + (\beta_3 + \gamma_3) T + \beta_4 I_{T>40} + (\beta_5 + \gamma_5) \frac{SiO_2}{Al_2O_3} + (\beta_6 + \gamma_6) \left(\frac{SiO_2}{Al_2O_3}\right)^2 + (\beta_7 + \gamma_7) \frac{H_2O}{Al_2O_3} + (\beta_8 + \gamma_8) & \text{Alkaline Cation Na} \end{cases} \quad (5)$$

The estimated parameters, along with their standard errors and significance are summarized in Table 5. Some main remarks are discussed in the following.

The estimated model confirms a significant quadratic decrease in the compressive strength value linked to an increase on the H₂O/Al₂O₃ molar ratio. This trend is in accordance with the literature (Ismail et al., 2011; Xie and Kayali, 2014) As previously mentioned, increasing the water content (increasing the H₂O/Al₂O₃ molar ratio) increases the porosity of the final structure (Khale and Chaudhary, 2007a, 2007b). Pores act as a defect point and therefore a higher porosity significantly lowers the compression strength of the final product.

The model shows a very good fit of the data (high R² and low residual

Table 5

Estimates, standard errors and level of significance of parameters in Eq. 4; F statistics, R², DF (Degree of Freedom). Significance levels: 0 *****, 0.001 ***, ‘×’ 1.

Parameter	Estimate (standard error)	significance
β ₀	64.89 (4.76)	***
γ ₀	18.48 (0.52)	***
β ₁	-3.99 (0.51936)	**
γ ₁	-1.65 (0.73)	*
β ₂	0.07 (0.01)	***
γ ₂	0.09 (0.01)	***

R² = 0.83, F-statistic: 303.3 on 5 and 314 DF, significance ***.

The estimated parameters, along with their standard errors and significance are summarized in Table 6.

The model is essentially consistent with the results emerging from the marginal models discussed above, yet some further significance has arisen when accounting for all the factors involved.

Curing time is confirmed to positively affect the expected compressive strength in both types of geopolymers, with a larger effect on sodium-based cations. Aging time is also confirmed to have a moderate positive effect on the compressive strength of sodium-based geopolymers only. Same goes for the H₂O/Al₂O₃ molar ratio, negatively affecting the compressive strengths with a quadratic trend.

The silica to alumina ratio also maintains the expected quadratic effect on both types of geopolymer, yet accounting for all the involved factors allows for a significant difference between the trends of the two cations to arise. Sodium-based geopolymers show a larger parabolic curvature, suggesting both a slower increase and a slower decrease after the maximum is reached.

Variation of all the involved experimental condition is globally able to explain about 73% of the total variability of the compressive strength. Residual analysis (reported in Fig. 10) is overall satisfactory: slight evidence of the violation of the hypothesis of normality is evident at the tails of the distribution only. We posit that this is due to either small changes in the experimental conditions (beyond our control), or to some measurement errors, leading to a few outlier values of the compressive

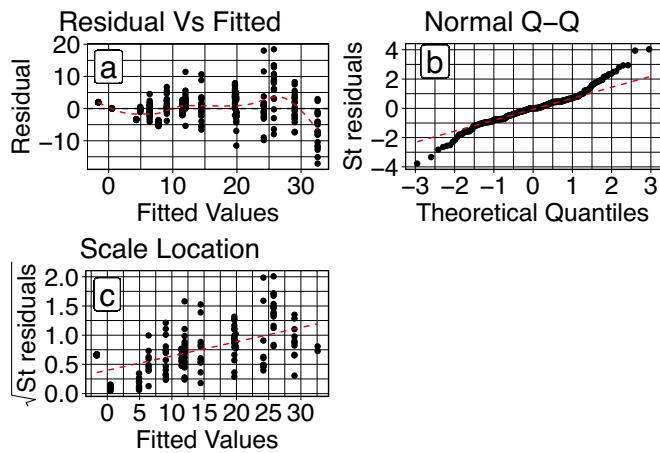


Fig. 9. Residual analysis of the estimated model in Eq. 4.

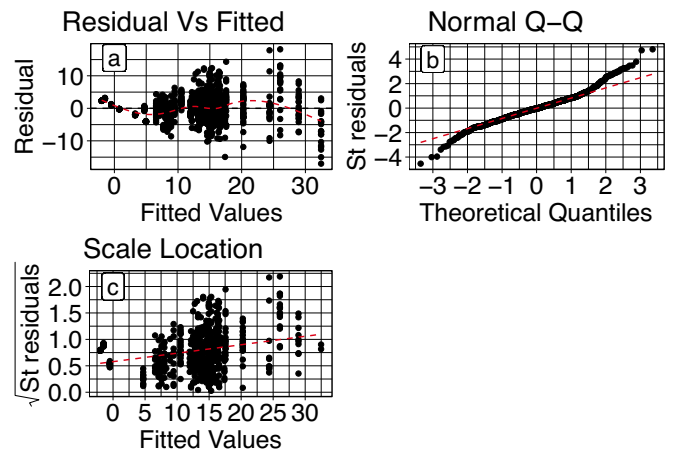


Fig. 10. Residual analysis of the global model.

strength. Also, a limited trend in the scale location plot suggests a moderate heteroskedasticity of the errors, which might reduce the efficiency of the estimates. Nevertheless, the standard errors are overall rather small with respect to the estimates, hence their possible increase because of the loss of efficiency can be considered tolerable and does not undermine the whole reliability of the model.

3.6. Model limitations

It's important to note that the current model is strictly limited to describing the compressive strength within the boundaries set by the conditions chosen for this study. As such, the results may not be directly extrapolated to different processing conditions. This presents a potential area for future development, where the model could be refined and validated across a broader set of conditions. At this juncture, the model is most reliable for small sample sizes. One of the key challenges we've identified is the introduction of a size effect factor to consider samples with varying dimensions. Size effects can significantly influence material properties, particularly in the case of geopolymers where the microstructure plays a key role in determining performance. Therefore, future work will focus on developing and validating a size effect factor to ensure that our model can accurately predict the behavior of geopolymers regardless of sample size.

4. Conclusions

Three different statistical models have been proposed to account for the experimental relationship between the compressive strength of potassium and sodium-based geopolymer samples and different process parameters and their composition. For all models, the errors have been computed and analyzed to assess their statistical reliability. We can conclude that:

- Curing time shows a positive relationship with compressive strength.
- Aging time has a slight positive effect on sodium geopolymers, and it does not significantly affect potassium-based geopolymers.
- Curing temperature negatively affects compressive strength. In fact, increasing the curing temperature led to a decrease in the compressive strength values.
- The SiO₂/Al₂O₃ ratio shows a significant quadratic concave trend with compressive strength. Increasing this ratio provides an increase in the compressive strength up to a certain threshold which is different for potassium and sodium-based geopolymers. Above the threshold, increasing SiO₂/Al₂O₃ led to a decrease in the mechanical properties.
- The potassium-based geopolymer system shows an almost linearly inverse proportionality between compressive strength and the H₂O/Al₂O₃ molar ratio. The sodium-based geopolymer system displays an increase of compressive strength at the beginning (from H₂O/Al₂O₃ = 11 to 13). Above H₂O/Al₂O₃ = 13, a linear decrease can be observed until H₂O/Al₂O₃ = 20, while after this threshold a plateau is reached.

A final comprehensive statistical model has been proposed that is able to predict the compressive strength of both potassium and sodium based geopolymers as a function of some process variables (curing and aging time, curing temperature) and the geopolymer formulation (SiO₂/Al₂O₃ and H₂O/Al₂O₃ molar ratios).

The observed differences in the mechanical strength of the samples as a function of the different parameters considered can be attributed, according to the literature, to variations in the characteristics of the geopolymer network developed under the different processing conditions.

Further work will aim to add greater variability to the model in order to achieve a better description capability of the compressive strength dependencies on the processing condition; moreover, more efforts will be devoted to the further validation of the proposed model for different starting raw materials (e.g., fly ash) and for composite materials using a geopolymer phase as matrix. Moreover, the model is strictly limited to describing the compressive strength inside the boundaries set by the conditions chosen to design the entire work. At this stage, the model is reliable for small samples; more work is ongoing to introduce a size effect factor to consider samples with different dimensions.

Nevertheless, the fact that the model is based on the testing of >1200 samples all prepared in a consistent way and provides a reasonable fitting of data, lends appropriate consistency to the statistical model proposed.

Table 6

Estimates, standard errors and level of significance of parameters in Eq. 5; F statistics, R², DF (Degree of Freedom). Significance levels: 0 ****, 0.001 ***, . ** 1.

β_0	-95.45 (13.68)	***	γ_0	1.90	.
β_1	0.06 (0.02)	***	γ_1	0.05 (0.02)	.
β_2	-0.007 (0.01)		γ_2	0.04 (0.01)	**
β_3	-0.06 (0.02)	*	γ_3	0.03 (0.04)	.
β_4	0.38 (0.90)		γ_4	-4.51 (1.27)	***
β_5	83.43 (7.23)	***	γ_5	11.18 (8.79)	.
β_6	-10.67 (1.05)	***	γ_6	-2.14 (1.25)	.
β_7	-3.66 (0.36)	***	γ_7	-1.46 (0.50)	**
β_8	0.06 (0.008)	***	γ_8	0.02 (0.01)	.

R² = 0.73, F-statistic: 199.1 on 17 and 1236 DF ***

Credit author statement

Mattia Muracchioli prepared the samples, analyzed the data and wrote the draft of the manuscript;

Giovanna Menardi analyzed the data and contributed to the writing of the manuscript;

Marco Lorenzo D'Agostini contributed to the sample preparation and to the writing of the manuscript;

Giorgia Franchin and Paolo Colombo contributed to the analysis of the data and to the writing of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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