Cement & Concrete Composites 34 (2012) 18–24

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Geopolymers based on a coarse low-purity kaolin mineral: Mechanical strength as a function of the chemical composition and temperature ☆

Oswaldo Burciaga-Diaz, Jose Ivan Escalante-Garcia *, Alexander Gorokhovsky

Centro de Investigación y de Estudios Avanzados (Cinvestav Saltillo), Saltillo, Coahuila, CP 25000, Mexico

A R T I C L E I N F O

Article history:
Received 7 July 2010
Received in revised form 9 August 2011
Accepted 10 August 2011
Available online 22 August 2011

Keywords:
Geopolymers
Strength
Metakaolin
Coarse mineral
Statistical analysis
Alkali activated cement

A B S T R A C T

A coarse mineral with 70% kaolinite and 30% quartz was calcined and chemically activated by alkaline solutions of Na_2SiO_3 and NaOH. The compressive strength evolution was investigated as a function of the curing temperature at 20 and 80 °C, and the molar ratios of SiO_2/Al_2O_3 (2.64–4.04) and Na_2O/Al_2O_3 (0.62–1.54). For curing at 20 °C, the best composition was $SiO_2/Al_2O_3 = 2.96$ and $NaO/Al_2O_3 = 0.62$, reaching 85 MPa at 28 days. Curing at 80 °C had a positive effect on the strength development only in the first 3 days. X-ray diffraction of the geopolymeric formulations showed the formation of amorphous silicoaluminates of similar nature. The microstructure consisted of unreacted quartz and metakaolinite particles in a matrix of silicoaluminate polymer and condensed silica gel from the unreacted sodium silicate.

1. Introduction

Geopolymers materials, from the alkaline activation of silicoaluminate raw materials, have recently received wide attention in view of their advantages over other cementitious materials, like Portland cement. Some of the advantages are high strength, low environmental impact, chemical resistance and thermal stability. They are also called geocements [1], and result from the polymerization of aluminosilicate monomers in an alkaline solution; the products obtained are considered ceramic-like materials. Two advantages can be mentioned of geopolymers in relation to traditional ceramic processing: (a) ceramic-like materials, stable at high temperatures [2–4], can be processed at room temperature departing from a plastic moldable paste, and (b) if firing of raw materials is required, it takes place before any chemical reaction takes place, for kaolinite the temperatures are lower than 750 °C. Among the most widely used raw materials to prepare alkali activated silicoaluminate cements are coal ash from power stations [1,5,6] and kaolinite mineral clays, the latter is commonly of fine particle size and high purity as reported by many authors [2,7–9].

Among the most important factors that influence the properties of synthesized geopolymers is the chemical composition of the geopolymeric mixtures, which has been addressed by a limited number of authors. Rowles and O'Connor [8], investigated variations of the chemical compositions for a high purity metakaolin, the reported molar compositions were: Si:Al at 1.08–3 (equivalent molar ratios of $2.16 < SiO_2/Al_2O_3 < 6$) and Na:Al at 0.52–2.0 (equivalent molar ratios of $0.52 < Na_2O/Al_2O_3 < 2$), the activating solutions were derived from silica fume and sodium hydroxide. Their samples were cured at 75 °C for 24 h and 7 days at ambient temperature. The highest strength of 64 MPa was for Si:Al of 2.5 and Na:Al of 1.29 ($SiO_2/Al_2O_3 = 5$ and $Na_2O/Al_2O_3 = 1.5$). Fletcher et al. [10] assessed compositional ranges of $0.5 < SiO_2/Al_2O_3 < 300$ and $0.66 < Na_2O/Al_2O_3 < 87$ using metakaolin, NaOH and amorphous silica and alumina. The latter work was addressed towards structural characterization and reported only relative strength values for samples cured overnight. In a more recent study [11], the effect of the molar ratio Na_2O/SiO_2 was reported as an important factor that influences the mechanical and morphological characteristics of pastes of fly ash activated with NaOH solutions. The results revealed that $Na_2O/SiO_2 = 0.40$ pastes had a denser appearance, which was in agreement with results of compression strength tests.

The temperature of curing, or that at which the initial reactions take place, is also an important factor that influences the strength development. Curing at temperatures above ambient are normally reported to favor the development of high compressive strength [2,4,8,11]. Nonetheless, the effect of temperature on the compressive strength is not completely clear and it has not been systematically addressed in the literature. One report data [12] indicated that curing at 50–80 °C improved the strength when compared

---

☆ Research funded by Project of Fondos Mixtos CONACYT-ZACATECAS ZAC-2001-C01-4201.

* Corresponding author.
E-mail address: ivan.escalante@cinvestav.edu.mx (J.I. Escalante-Garcia).

0958-9465/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2011.08.001

with curing at room temperature, while results from another report [13] showed that curing at 65 °C promoted higher early strength values compared to 25 °C, nevertheless after 28 days the strengths of two geopolymers were fairly similar.

Kaolin minerals are an abundant natural resource readily commercially available, as an additive to portland cement concretes or to produce geopolymers, with a fine particle size and high purity; nonetheless, not all the resources are of high purity. The objective of this work is to determine if a relatively coarse and low purity kaolin mineral can be successfully used to produce alkali-activated cementitious geopolymeric materials of low cost and environmental impact. The investigation addressed the effects of the chemical composition, curing temperature and age on the compressive strength, as well as the kind of reaction products and microstructural features. The chemical composition, in terms of the molar ratios SiO_2/Al_2O_3 and Na_2O/Al_2O_3, was varied by using different concentrations of SiO_2 and Na_2O in the formulations by means of the addition of sodium silicate and NaOH solutions.

2. Experimental

The mineral used in this study was obtained from a deposit located in Zacatecas, Mexico. The chemical composition of the kaolin, determined using X-ray fluorescence spectrometry, was of (wt.%) 57.89 SiO_2, 30.04 Al_2O_3, 0.8 TiO_2, 0.14 Fe_2O_3, and other minor constituents, loss on ignition at 900 °C was of 10.3% due to dehydroxilation of the kaolinite fraction. X-ray diffraction (XRD) indicated that quartz was the main impurity in the mineral, which reduced the grindability. The mineral was ball milled and in the resulting material 50%, 75% and 90% passed the 14.5, 98 and 212 μm, respectively. This is, coarser than commercially available high purity kaolin which normally passes the 45 μm sieve. The ground mineral was fired 3 h at 750 °C to induce the formation of reactive Metakaolin (MK). The MK was chemically activated with solutions of sodium silicate ($SiO_2 = 62.3\%$, $Na_2O = 19.2\%$ and $H_2O = 18.5\%$: modulus $M = 3.24$) and sodium hydroxide pellets blended in proportions intended to cover a relatively wide range of variation.

The following considerations were taken into account for the preparation of the formulations. MK is known to be reactive and quartz to be inert in alkaline environments at those temperatures normally used for curing of cementitious materials [14]. Taking into account the losses on ignition and assuming that all Al_2O_3 was present as MK (based on XRD data analysis), the mineral was estimated to contain ~70% of MK. On this basis a "reactive" fraction was considered, which excluded the quartz, and its chemical composition was defined and used as the base for the preparation of the analyzed formulations.

The variables considered to investigate the alkaline activation process were: SiO_2/Al_2O_3 (S/A) molar ratios of: 2.64, 2.96, 3.27 and 4.04; Na_2O/Al_2O_3 (N/A) molar ratios of: 0.62, 0.93, 1.24 and 1.54. A total of 16 pastes were formulated in which the water/MK weight ratio was kept fixed at 0.5 to obtain a consistency able to be molded in cubes of 2.5 cm. The specimens were cured for the first 24 h in two routes: (a) in the molds at 20 ± 2 °C and (b) in the molds at 80 ± 4 °C. The subsequent curing for up to 28 days, for both regimens, was at dry storage at 20 ± 2 °C. The molded samples were cured covered with plastic film to avoid water evaporation which is necessary for the reactions of gepolymerization [11]. As pointed in the introduction, curing at 80 °C was chosen as some reports have concluded that curing at temperatures above ambient normally favor the development of high compressive strengths, and also it has also been reported that curing at 80 °C results in better strength compared to curing at 50 and 65 °C [11].

For the characterization of the specimens, the compressive strength was measured (Controls, 50-c7024, Italy) from four cubes at 1, 7, 14 and 28 days. These results were statistically analyzed through a fully factorial experimental design ($4^3 \times 2^1$) in order to have a better understanding about of the influence of the studied variables and their interactions on the compressive strength.

Table 1
Factors and levels considered.

Factors	Levels
A = SiO_2/Al_2O_3 ratio	2.64; 2.96; 3.27; 4.04
B = Na_2O/Al_2O_3 ratio	0.62; 0.93; 1.24; 1.54
C = Curing time (days)	1; 7; 14; 28
D = Curing temperature	20 °C; 80 °C

The statistical significance of the variables was quantitatively determined by means of an analysis of variance (F-ANOVA test) with a confidence level of 95% using the next mathematical model [15,16].

$$y_{ijkl} = \mu + A_i + B_j + C_k + D_l + AB_{ij} + AC_{ik} + AD_{il} + BC_{jk} + BD_{jl} + CD_{kl} + e_{ijkl} \quad (1)$$

where y_{ijkl} is the value of response variable estimated at i, j, k and l factor levels; μ is the general mean of the estimated value of the treatment; A_i, B_j, C_k, D_j represent the single effects of the factors considered; AB_{ij}, AC_{ik}, AD_{il}, BC_{jk}, BD_{jl}, CD_{kl} represent the effect of the combined interactions among the factors; and e_{ijkl} represents the random error associated with the combination of the mathematical treatments. The used methodology was the same explained in detail in a previous work [17], and Table 1 summarizes the nomenclature employed in the variables and levels definition.

After the analysis of compressive strength, fragments of chosen samples were afterwards dried in acetone for characterization by X-ray diffraction (XRD, Philips D-Expert, Netherlands) and scanning electron microscopy (SEM, Philips ESEM-XL, The Netherlands) equipped with Energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Mechanical properties

This section presents contour graphs which were produced using the statistical software package Minitab 15, such graphs provide a two dimensional view of the compressive strength development of the analyzed formulations. Fig. 1 shows the influence of the molar ratios S/A vs. N/A on the strength development for all compositions cured at 20 °C as a function of time for 1, 7, 14 and 28 days. The black points on the interjections of the dotted lines represent the chemical compositions of the elaborated formulations. After 1 day, is noteworthy that samples with $S/A < 2.96$ showed values of compressive strength of up to 12 MPa. The N/A ratio also influenced the development of strength, as increasing this ratio from 0.62 to 0.93 favored the strength; nonetheless further increases up to 1.54 had a negative effect. It was also noticeable that those formulations with $S/A \geqslant 3.27$ did not develop strength regardless of the N/A ratio. The setting time of the latter was of 1–3 days and showed high viscosity, which reduced their workability. Fletcher et al. [10] reported setting times of 24 h at 65 °C for geopolymers with $S/A = 3.3$ and twice as much water; strengths up to 3 days were reported also as low. This finding suggests that with the increase of the S/A ratio the alkaline solution becomes less chemically active towards the structure of the silicoaluminate promoting slower reaction processes during the early ages of curing.

After 7 days of curing, the formulations with $S/A > 3.27$ rapidly increased their strength reaching up to 50 MPa for N/A of 0.93 and 1.24. On the other hand, for $S/A = 2.96$ the N/A of 0.62 and

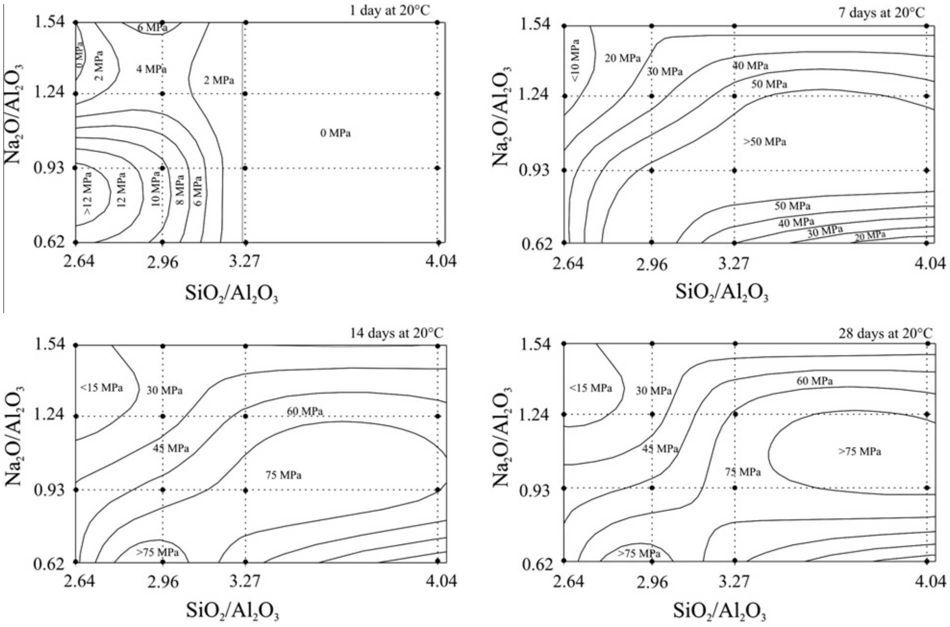


Fig. 1. Influence of the S/A vs. N/A ratio on the compressive strength development for all geopolymeric compositions cured at all times at 20 °C.

0.93 resulted more favorable for strengths above 50 MPa, whereas for N/A ⩾ 1.24 the strength was lower than 30 MPa. After 14 and 28 days it was evident that the reaction processes continued as all formulations showed noticeable strength gains. After 28 days, the formulations with S/A = 4.04 and N/A = 0.93 reached strengths >75 MPa, the binder with the highest strength (85 MPa) was that of S/A = 2.96 and N/A = 0.62. On the other hand those geopolymers with S/A = 2.64 and N/A = 1.24 and 1.54 developed strengths lower than 15 MPa.

From the results it is clear that for all of the formulations investigated, the curing time influences the strength development as the reactions gradually proceed over time. However, it is noteworthy that at any given curing age, those formulations of N/A = 0.93 always developed the highest strength regardless of the S/A ratio.

Fig. 2 presents the influence of the molar ratios S/A vs. N/A on the strength development for the same compositions from Fig. 1 but after initial curing for 24 h at 80 °C. It was clear that after 1 day of curing the higher temperature accelerated the reactions and induced higher early strengths relative to the curing at 20 °C for 24 h. After 1 day, the formulations with ratios (S/A–N/A) of 2.96–0.62, 2.96–0.93 and 3.27–0.93 developed strengths of around 30–40 MPa, but during the subsequent curing at 7 days, the strength gain was not considerable, and the values reached were lower than those samples cured at 20 °C. After 14 days the areas between the iso-response lines within the graphs increased and the strength values similarly increased, this indicates that all formulations developed mechanical resistance to similar levels. The relatively small change observed in the area patterns from 14 to

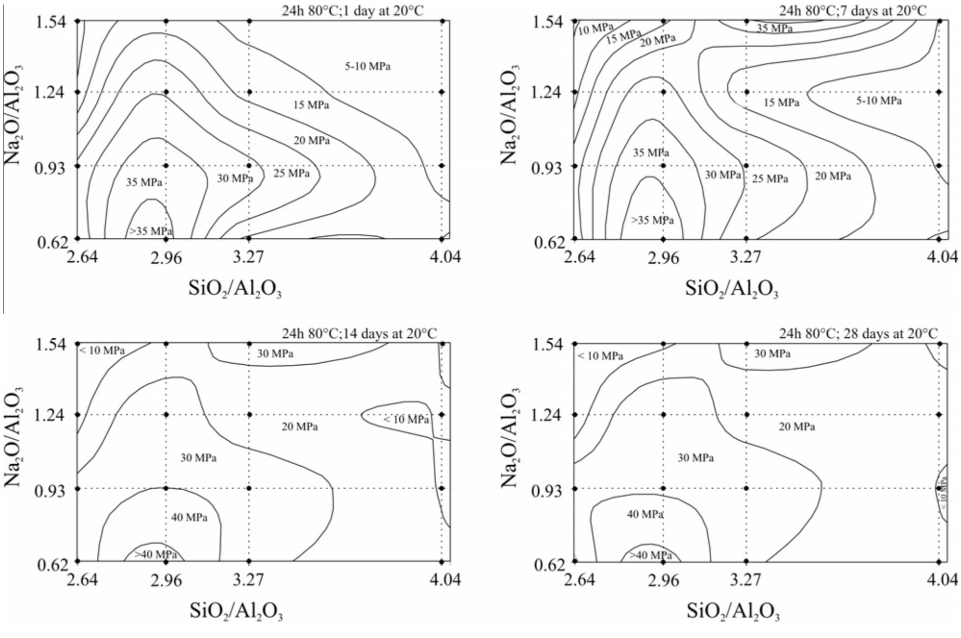


Fig. 2. Influence of the S/A vs. N/A ratio on the compressive strength development for all geopolymeric compositions cured 24 h at 80 °C and up to 28 days at 20 °C.

Table 2
F-ANOVA results obtained to evaluate the effect of the considered factors on the compressive strength with a confidence level of the 95%.

Factors	DF	SC	QM	$F_{cal.}$	F_{tab}	Significance[a]
A	3	5485.77	1828.59	27.00	2.73	S
B	3	7691.75	2563.92	37.86	2.73	S
C	1	2927.08	2927.08	43.23	3.97	S
D	3	7494.76	2498.25	36.89	2.73	S
AB	9	5696.25	632.92	9.35	2.01	S
AC	3	674.02	224.67	3.32	2.73	S
AD	9	1164.00	129.33	1.91	2.01	NS
BC	3	4404.23	1468.08	21.68	2.73	S
BD	9	1110.05	123.34	1.82	2.01	NS
CD	3	7153.64	2384.55	35.22	2.73	S
e[b]	81	5484.80	67.71			

DF = Freedom degrees, SC = Sum of squares, QM = Quadratic mean, F_{cal} = Calculated value of F, F_{tab} = Table value for F at a level of significance of 95%, S = Significant, NS = Not significant.

[a] Significance = $F_{cal} > F_{tab}$ = S, $F_{cal} < F_{tab}$ = NS.

[b] e = Experimental error.

28 days suggests small strength gains of the analyzed geopolymers. At these ages the highest values (>40 MPa) were for formulations of S/A = 2.96 and N/A = 0.62, similar to the case of Fig. 1; moreover, the pattern of the effect of the N/A ratio was the same as described for curing at 20 °C. Compositions with (S/A–N/A) of 2.96–0.62 were the more benefited from curing at high temperature. For compositions of S/A > 3.27, curing at 80 °C eliminated the long setting times previously noted at 20 °C, the higher curing temperature probably enhanced the reactions of dissolution and condensation of products.

3.2. Statistical analysis of strength

Table 2 summarizes the results of F-ANOVA to evaluate the effect of considerer variables and their interactions on the results of compressive strength of alkali-activated samples. After the statistical analysis, the order of statistical importance of the factors on strength development was: Curing time–Curing temperature < N/A molar ratio < S/A molar ratio, which are discussed below.

From Fig. 3a it is clear that the temperature and time of curing had a strong influence on the strength development after 28 days. After 1 day of curing at 80 °C the mean strength was of about 17 MPa; whereas at 20 °C the mean was lower than 5 MPa. However, after 7 days the specimens cured at 20 °C increased notably their strength reaching values greater than those of specimens cured at 80 °C. The trend of increasing strength on time was maintained for 28 days at 20 °C for all formulations reaching a mean value of about 40 MPa. In contrast, those samples cured at 80 °C the mean strength value remained practically unchanged.

The above could be explained by considering that on the early ages, the higher temperature promoted an intense dissolution of the MK and condensation of geopolymeric products with a heterogeneous distribution in the matrix, probably with a relatively high porosity. Moreover, the higher temperature also promotes rapid water evaporation which, together with the relatively fast paste densification, made the diffusion of species more difficult and thus limited the advance of the reaction processes and the increase of the compressive strength. In contrast, the specimens cured at lower temperature experimented an opposite effect in which the dissolution of the reactive species occurred slowly and the condensation of reaction products took place more homogeneously due to the longer retention of water within the microstructure, as a consequence the diffusion processes and formation of products continued on time up to a point in which the consumption of reactants and the densification of the matrix of reaction products became in the limiting factors.

According to Fig. 3b the mean value of compressive strength increased as the N/A ratio augmented from 0.63 to 0.93 and then decreased with the further increases of N/A up to 1.54. Although the molar ratio Na_2O/SiO_2 (N/S) was not a variable of study in this work, it was included in the upper part of Fig. 3b, its effect on the compressive strength is similar to that of the Na_2O/Al_2O_3. It is well know that when the alkaline solution comes into contact with the silicoaluminate mineral, a strong dissolution of the Si–O–Al and Al–O–Al species is promoted, Si and Al are released out of the mineral towards the alkaline medium [18,19]. The increase of the Si and Al concentration in the aqueous medium promote the process of formation of oligomers such as Si–OH and Al–OH and improve the effectiveness in the condensation of geopolymeric products with high mechanical properties. In this case is possible that higher amounts of NaOH, manifested by the higher N/A ratios from 0.62 to 0.93 or N/S from 0.24 to 0.36, favored the formation of geopolymers. However, N/A and N/S ratios above 0.93 and 0.36, respectively, limited the processes of geopolymerization manifested by lower mean strength values. The latter is in agreement with Panias et al. [18], who concluded that the formation of oligomeric precursors, necessary for the formation of geopolymers, is inhibited under extremely high NaOH concentrations. This means that the species at equilibrium at highly alkaline conditions shifts towards the formation of mononuclear species minimizing the concentration of oligomeric silicate species in the aqueous phase and thus, limiting the process of polycondensation of geopolymeric species mechanically strong. Moreover, also is probable that under such conditions, some of the Na present in high concentration did not participate in the reaction processes promoting carbonation and cracking of the binders. This was observed mainly in samples cured at 80 °C.

Another statistically important variable for the geopolymerization process was the overall S/A molar ratio. Fig. 3c shows that the strength increased with the S/A ratio from 2.64 to 2.96 and reduced for S/A > 2.96. Theoretically, Si–O–Si bonds are stronger

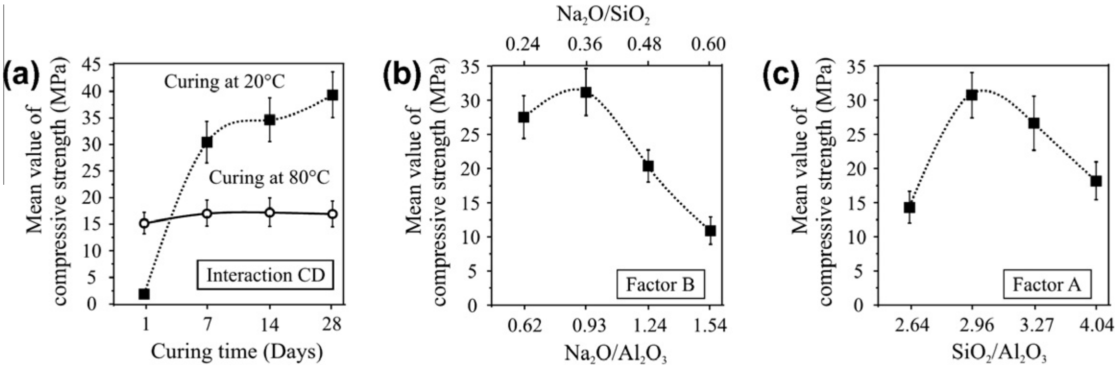


Fig. 3. Influence of the factors Curing time–Curing temperature (a); Na_2O/Al_2O_3 molar ratio (b); and SiO_2/Al_2O_3 molar ratio on the compressive strength (c).

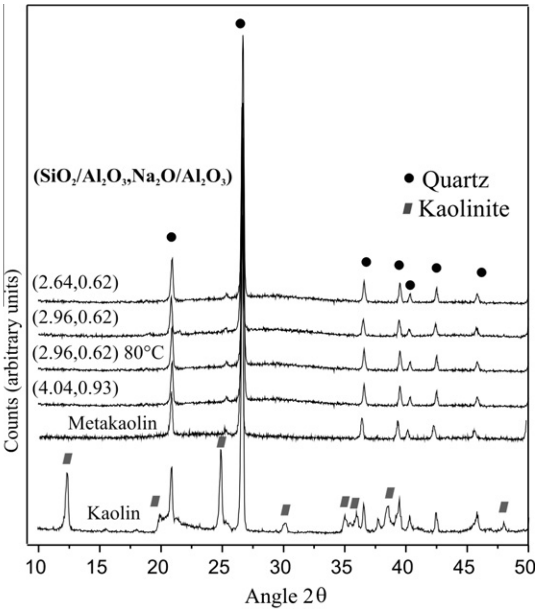


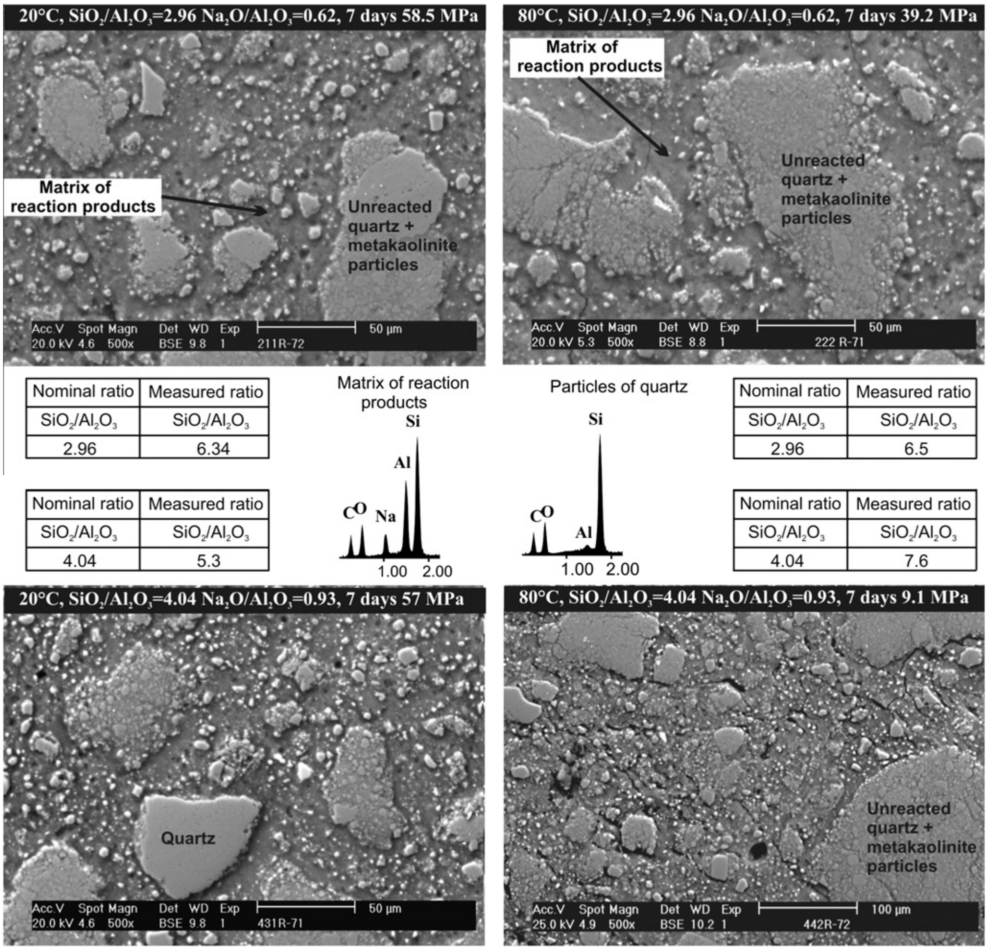
Fig. 4. X-ray diffraction patterns for various geopolymeric compositions.

than Si–O–Al and Al–O–Al linkages, meaning that the strength of geopolymers should increase with S/A ratio since the density of Si–O–Si bonds increases with S/A ratio [20–22]. By considering this, it could be expected that the continuous increase of the S/A ratio would positively affect the mechanical properties of the obtained cements. However, the experimental results showed that this only occurs within a certain range of composition, this is possibly because an alkaline solution with relatively high amounts of soluble silicate species is chemically less aggressive and more prone to condensation which limits the dissolution of the aluminosilicate mineral [17,19,23].

3.3. Microstructural characterization

Fig. 4 shows the XRD patterns of selected compositions that showed high and low strengths; the kaolin and MK are included for reference, showing prominent reflections of quartz. After firing the reflections of kaolinite disappeared and an amorphous hump showed at 15–30° 2θ. After the alkaline activation, the quartz peaks remained, confirming that it did not take part in the reactions, also there was no formation of new crystalline products. The amorphous hump of the MK shifted to the right to a range of 20–35° 2θ indicating the formation of aluminosilicate products of amorphous character. Although the strengths of the various formulations were different, XRD indicated that the products formed were of similar nature.

Fig. 5 presents backscattered electron images of microstructures for various formulations cured at 20 °C and 80 °C. A total of 10 EDS spot analyses were taken on the matrix of geopolymeric products for each analyzed cement. The results, together with those from XRD, indicated that the reaction products are formed


20°C, SiO_2/Al_2O_3=2.96 Na_2O/Al_2O_3=0.62, 7 days 58.5 MPa

80°C, SiO_2/Al_2O_3=2.96 Na_2O/Al_2O_3=0.62, 7 days 39.2 MPa

20°C, SiO_2/Al_2O_3=4.04 Na_2O/Al_2O_3=0.93, 7 days 57 MPa

80°C, SiO_2/Al_2O_3=4.04 Na_2O/Al_2O_3=0.93, 7 days 9.1 MPa

Nominal ratio	Measured ratio
SiO_2/Al_2O_3	SiO_2/Al_2O_3
2.96	6.34

Nominal ratio	Measured ratio
SiO_2/Al_2O_3	SiO_2/Al_2O_3
4.04	5.3

Nominal ratio	Measured ratio
SiO_2/Al_2O_3	SiO_2/Al_2O_3
2.96	6.5

Nominal ratio	Measured ratio
SiO_2/Al_2O_3	SiO_2/Al_2O_3
4.04	7.6

Fig. 5. Microstructures and chemical composition of some geopolymers, scanning electron microscopy microstructures (backscattered electron images).

by an amorphous gel composed of Si, Al and Na commonly called N–A–S–H [5,17]. The measured S/A ratios were above those initially targeted (that would be attained after complete reactions), which suggest incomplete metakaolin reaction and an excess of SiO_2. The matrix appears to be a mixture of amorphous silicoaluminate reaction products finely intermixed with silica gel that condensed from the unreacted sodium silicate. For samples cured at 20 °C, the reaction products had molar ratios $SiO_2/Al_2O_3 < 6.34$ (calculated from EDS measurements), however for samples cured at 80 °C the ratio was greater than 6.5. This increase of SiO_2/Al_2O_3 suggests that a major condensation of silica gel was promoted by the increase of the temperature.

At 20 °C the condensed silica gel and geopolymeric gel (from reaction of MK) promoted the densification of the matrix, enhancing the compressive strength. For samples cured at 80 °C the silica condensation was not enough to increase the strength due to the low quantity of geopolymeric gel (N–A–S–H) formed and the rapid evaporation of water, which resulted in a significant amount of unreacted particles and in the formation of microcracks as observed more markedly in the micrograph corresponding to a molar ratio S/A = 4.04.

The microstructures showed large composite mineral particles partially reacted and bonded by the described reaction products, these particles were constituted of quartz (brighter gray due to higher average atomic number) intermixed with metakaolinite (darker gray), some particles of pure quartz were also noted. The large particles of quartz observed performed well as a filler in the material and perhaps trapped some metakaolin impeding its reaction.

4. Discussion

The best molar ratios reported by Rowles and O'Connor [8], in terms of strength, were for pastes with S/A = 5.0 and N/A = 1.29 which after curing at 75 °C 24 h and 7 days at 20 °C reached 64 MPa. Their EDS measured ratios were S/A = 5.72, higher than the target ratios (as also noted in our results), however N/A = 0.86 was lower than the target value. The authors used a wet sample preparation to leach out unreacted Na from the samples to ensure that only reacted Na was measured, but some Si could have also been removed. These results evidenced that part of the activating solution remained unreacted. From our work, the closest composition to that quoted was of S/A = 4.04 and N/A = 1.24, with lower strengths under 20 and 10 MPa after curing at 20 and 80 °C, respectively. In contrast to the commonly reported recommendations and advantages of an initial curing at 60–80 °C, the best strengths reported by our investigations were systematically obtained after curing at 20 °C. The geopolymer of S/A = 2.96 and N/A = 0.62 reached 58.5 MPa after 7 days, which increased to 85 MPa after 28 days. However, the measured S/A ratios were of 6.3 and N/A = 0.75, which evidenced the incomplete reactions.

After curing at 80 °C, the measured ratio N/A in the microstructures was higher than in samples cured at 20 °C. This demonstrates that the dissolution of the Al from the MK was limited by the increase of the temperature. On the other hand an excess of Na could not take place in the reaction processes which also limited the further production of geopolymeric gel giving place to the formation of microstructures mechanically weak as previously discussed.

The resulting properties are interesting considering that the starting mineral is cheap based on the coarse particle size and its low content of kaolinite (∼70%). The discrepancies in behavior relative to other authors [8] could derive from differences in the mineral and the nature of the activating solution preparation.

The very slow setting for geopolymers based on metakaolin with high $Na_2O/H_2O = 25$ was attributed to incomplete reactions as indicated by NMR [10]. Our compositions of $S/A \geqslant 3.27$ displayed very slow setting for Na_2O/H_2O of 7–13, slow reactions could also be the cause and a possible explanation could be as follows. For $S/A \geqslant 3.27$ the contents of colloidal SiO_2 in the activating solution (higher sodium silicate amounts) were higher than in compositions of S/A = 2.96 (highest strength). According to [19], the degree of silicate ion polymerization in the alkaline solution climbs with the rise in the silica concentration, so as the concentration of silicon in the alkaline solution increases, the number and structural complexity of larger oligomers increases [20,21]. When a solution with these characteristics comes into contact with the silicoaluminate mineral in order to produce a geopolymer, the oligomers react relatively slow with the Al. The phases formed are nonetheless moderately stable and may retard the subsequent reaction of the material as the dissolution of acidic components from the MK is insufficient to saturate the solution. The silica gel begins to harden slowly while a substantial portion of mineral has yet to react and only small amounts of geopolymeric gel have formed [19]. However, such hardening is favored by the increase in the temperature, water losses or a reduction of pH. Based on the above mentioned, the lack of strength development after curing at 80 °C could be attributed to slow chemical reactions after a rapid engulfing of unreacted mineral grains by dense layers of the reaction products formed quickly in the first hours, limiting further dissolution of MK. That could explain why the measured S/A ratios after cured at 80 °C were higher than in samples cured at 20 °C.

5. Conclusions

1. A calcined mineral with a relatively high average of particle size and low content of metakaolinite (70%MK–30% Quartz) can be used to produce geopolymeric materials of high compressive strength. The costs are reduced as less grinding is required and the presence of quartz reduces the amounts of alkaline agents required, with no detriment on the mechanical properties.
2. This study has also shown that the SiO_2/Al_2O_3 and Na_2O/Al_2O_3 molar ratios have a strong effect on the strength development. The optimal ratios that yielded the greatest compressive strength were $SiO_2/Al_2O_3 = 2.96$ and $Na_2O/Al_2O_3 = 0.62$, 0.93. For greater SiO_2/Al_2O_3 ratios, good final compressive strengths were registered, but the setting time was very long.
3. Curing at 80 °C for 24 h was favorable for a rapid strength gain only at early ages for any given SiO_2/Al_2O_3 ratio; however, at later ages, the highest compressive strengths were obtained after curing at 20 °C.
4. The matrix of reaction products was constituted of amorphous silicoaluminate products intermixed with silica gel that condensed from the unreacted sodium silicate. Many unreacted mineral particles remained, which consisted of large quartz crystals intermixed with metakaolinite.

References

[1] Shi C, Krivenko PV, Roy D. Alkali-activated cements and concretes. London and New York: Taylor and Francis; 2006. ISBN 10: 0-415-70004-3.

[2] Barbosa VFF, MacKenzie KJD. Synthesis and thermal behaviour of potassium sialate geopolymers. Mater Lett 2003;75(203):1477–82.

[3] Mackenzie KJD. What are these things called geopolymers? A physico-chemical perspective. Ceram Trans: Am Ceram Soc 2003;153:175–86.

[4] Barbosa VFF, MacKenzie KJD. Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate. Mater Res Bull 2003;38:319–31.

[5] Palomo A, Grutzek MW, Blanco MT. Alkali activated fly ashes a cement for the future. Cem Concr Res 1999;29:1323–9.

[6] van Jaarsveld JGS, van Deventer JSJ, Lukey GC. The characterization of source materials in fly ash based geopolymers. Mater Lett 2003;57:1272–80.

[7] Davidovits J. Geopolymers: inorganic polymeric new materials. J Therm Analysis 1991;37:1633–56.

[8] Rowles M, O'Connor B. Chemical optimization of the compressive strength of aluminosilicate geopolymers synthesized by sodium silicate activation of metakaolinite. J Mater Chem 2003;13:1161–5.
[9] van Jaarsveld JGS, van Deventer JSJ, Lukey GC. The effect of composition and temperature on the properties of fly ash and kaolinite based geopolymers. J Chem Eng 2002;89:63–73.
[10] Fletcher RA, MacKenzie KJD, Nicholson CL, Shimada S. The composition range of aluminosilicate geopolymers. J Eur Ceram Soc 2005;25:1471–7.
[11] de Vargas Alexandre S, Dal Molin Denise CC, Antônio CF, da Silva Felipe José, Pavão Bruno, Veit Hugo. The effects of Na_2 O/SiO_2 molar ratio, curing temperature and age on compressive strength, morphology and microstructure of alkali-activated fly ash-based geopolymers. Cem Concr Comp 2011(33):635–60.
[12] Khalil MY, Merz E. Immobilization of intermediate-level wastes in geopolymers. J Nucl Mater 1994;211(2):141–8.
[13] Davidovits J. Man-made rock geosynthesis and the resulting development of very early high strength cement. J Mater Educ 1994;16(2 and 3):91–139.
[14] Escalante JI, Campos-Venegas K, Gorokhovsky A, Fuentes AF. Cementitious composites of pulverized fuel ash and blast furnace slag activated by sodium silicate: effect of Na_2O concentration and modulus. Adv App Ceram 2006;105(4):201–8.
[15] Montgomery DC, Rounger GC. Applied statistics and probability for engineers. New York: Jhon Wiley and Sons; 2003. ISBN 0-471-20454-4.
[16] Ostle B. Estadistica aplicada. México: Limusa; 1990.
[17] Burciaga-Diaz O, Escalante-Garcia JI, Arellano-Aguilar R, Gorokhovsky A. Statistical analysis of strength development as a function of various parameters on activated metakaolin/slag cements. J Am Ceram Soc 2010;93(2):541–7.
[18] Panias D, Giannopoulou IP, Perraki T. Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers. Colloid Surf 2007;301:246–54.
[19] Criado M, Jiménez AF, Palomo A. Effect of the SiO_2/Na_2 O ratio on the alkali activation of fly ash. Part II: ^{29}Si MAS-NMR survey. Micropor Mesopor Mater 2008;109:525–34.
[20] Duxon P, Provis JL, Lukey GC, Mallicoat SW, Kirven WM, van Deventer J. Understanding the relationship between geopolymers composition, microstructure and mechanical properties. Colloid Surf A: Physicochem Eng Aspects 2005;269:47–58.
[21] Duxson P, Jiménez AF, Provis JL, Lukey GC, Palomo A, van Deventer J. Geopolymer technology: the current state of the art. J Mater Sci 2007;42:2917–33.
[22] Monzó M, Jiménez AF, Vicent M, Palomo A, Barbara A. Activación alcalina de metacaolín efecto de la adición de silicato soluble y de la temperatura de curado. Bol Soc Esp Ceram V. 2008;47(1):35–43.
[23] Criado M, Jiménez AF, Palomo A. Alkali activation of fly ash: effect of the SiO_2/Na_2O ratio Part I: FTIR study. Micropor Mesopor Mat 2007;106:180–91.