

# The formation of crystalline phases in metakaolin-based geopolymers in the presence of sodium nitrate

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Abstract Geopolymers generated by alkali-activation of amorphous aluminosilicate sources are considered as an alternative immobilizing matrix for hazardous and nuclear wastes. Low and intermediate level nuclear waste streams are often highly alkaline saline solutions containing various concentrations of nitrate salts. The aim of the research project presented here was to study the effect of nitrate ions on the formation and evolution of metakaolin-based geopolymeric systems at moderate temperatures, i.e., at 40 °C. Metakaolin was alkali-activated using NaOH solutions of varying concentrations, yielding H<sub>2</sub>O:OH<sup>-</sup> ratios of 5.50, 9.15, 13.75, and 27.50. Sodium nitrate was added to the activation solutions at a constant [NO<sub>3</sub><sup>-</sup>]: [OH<sup>-</sup>] ratio of 0.25. Most geopolymeric mixtures were designed to obtain a Na2O:Al2O3 ratio of 1.00 for nitrate-free mixtures, or 1.25 for those including sodium nitrate. In addition, the effect of deviation from these values (Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios of 0.84 and 1.20 for nitrate-free samples, 1.04 and 1.50 for nitrate-bearing samples) was also studied. The samples were cured in sealed containers at 40 °C for periods ranging from 1 day to 3 months. The products were characterized by X-ray diffractometry, Fourier transform midinfrared spectroscopy, and scanning electron microscopy as well as by compressive strength measurements. The results demonstrate the influence of composition, alkalinity, SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio, Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio, nitrate concentration, and curing times on the mineralogy of the geopolymeric

E. Ofer-Rozovsky elyaofer@technion.ac.il matrix. Various crystalline phases such as zeolite A, zeolite X, and nitrate-bearing phases, namely nitrate sodalite and nitrate cancrinite, were identified among the reaction products. The sequence of phase evolution in these geopolymeric systems was elucidated.

## Introduction

Geopolymers are aluminosilicate binders that are synthesized by alkali-activation of natural materials such as clays, or of industrial by-products such as coal fly ash and slags. The geopolymeric backbone is composed of silicate (SiO<sub>4</sub>) and aluminate (AlO<sub>4</sub>) groups. Cations are incorporated into the geopolymer structure as counter ions to the negatively charged aluminate groups. Due to the combination of metal-binding properties with chemical stability and good mechanical properties [1, 2], these materials have been proposed as candidate matrices for hazardous waste immobilization, including nuclear wastes [3–5].

The geopolymerization process is initiated by the hydrolysis of T–O–T (T = Si, Al) bonds in the raw material, followed by condensation of the resultant alumina and silica monomers into short oligomers, which further condense to form an inorganic polymeric network known as the geopolymeric amorphous phase [6, 7]. This amorphous geopolymer may undergo further reorganization to yield crystalline structures, which are thermodynamically favored over the amorphous structure [6, 8–10]. The concentration and nature of the alkali cations, the stoichiometric ratio between silicate and aluminate groups, the water content of the mix and the curing conditions, all influence the geopolymerization reaction rates as well as the structure and properties of the resulting product [2, 6, 11–13]. Low-silica content (SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>  $\leq$  2), high alkali

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cation content, and elevated temperatures are all known to promote the formation of crystalline phases, most often zeolites or similar related phases, within the amorphous matrix [10, 14–17]. Immobilization of hazardous metal ions was reported for non-crystalline geopolymers prepared from various aluminosilicate sources, suggesting effective adsorption on the amorphous gel due both to its ability to bind cationic species to the negatively charged aluminate groups as well as to its dense structure [18–20]. Zeolites are able to bind ions in their various cages and cavities and have been reported to incorporate some hazardous metals and radionuclides, sometimes irreversibly, depending on the size of the cation and the zeolite structure [21-24]. Geopolymeric matrices that combine both specific binding sites for cations, such as zeolites, and non-specific adsorption sites within the dense amorphous matrix may therefore advantageous hazardous be for waste immobilization.

The formation of geopolymers by alkali-activation of metakaolin (MK), a commonly used pozzolanic material, is widely described in the literature. The formation of various crystalline phases within MK-based geopolymers has been reported for different Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O ratios and curing conditions. Crystalline phases most often identified in MK-based geopolymers are zeolite A, hydroxysodalite [11, 25, 26], and zeolites X and Y from the faujasite family [17]. Other zeolites, such as zeolites P, R, and S have also been reported [27].

Several research groups examined the impact of the different anionic species on the properties of geopolymers [20, 28]. The formation of zeolites from the faujasite family (X and Y) in the presence of nitrate and sulfate ions at 90 °C was reported, while at room temperature these crystalline phases were not observed. The influence of nitrate, sulfate, chloride, and carbonate anions on the compressive strength was studied in geopolymeric systems prepared from slags [29] or fly ash [30]. Decrease in compressive strength due to the presence of the anionic species was reported in the former case, while no effect was found in the latter.

The aim of the present study was to investigate the effects of the main ions often present in nuclear w streams, i.e., sodium and nitrate, on the formation evolution of MK-based geopolymeric systems. M specifically, we were interested in understanding the cesses that determine the composition of the amorph

crystalline matrix, including the transformations that occur in such systems at a moderate temperature of 40 °C. To achieve this goal, geopolymers containing NaNO<sub>3</sub> as a model waste were prepared from metakaolin (MK) using a series of NaOH-based activation solutions of varying alkalinities. Nitrate-free samples were prepared as a reference system. No additional silica source was used, yielding low-silica geopolymer formulations, which are known to enhance the formation of crystalline phases. The geopolymerization process and the transformations that took place within the resulting matrices were followed over a period of 3 months.

#### Materials and methods

Metakaolin (MK, PowerPozz<sup>TM</sup>) conforming to ASTM C-618, Class N Specifications for Natural and Calcined Pozzolans, was supplied by Advanced Cement Technologies (Blaine, Washington USA). Tables 1 and 2 present the manufacturer's data for chemical composition and physical properties of metakaolin, respectively.

#### **Preparation of geopolymers**

Table 3 presents the mix formulations used in this study. Reference (nitrate-free) formulations contained metakaolin that was alkali-activated using NaOH solutions of varying concentrations, yielding  $H_2O:OH^-$  (dilution factor = d) ratios of 5.50, 9.15, 13.75, and 27.50, which correspond to approximately 9, 5.5, 4, and 2 M NaOH, respectively. The solid:solution ratios in most samples were adjusted to obtain a Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.00, assuming a Al<sub>2</sub>O<sub>3</sub> content of 44 % in MK. To study the effect of this ratio on geopolymerization, several samples of d = 5.50 and 13.75 were also prepared with different solid:solution ratios, yielding Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios of 1.20 and 0.84.

 Table 2 Physical characterization of raw metakaolin

BET (m	<sup>2</sup> /g) Der	Density (g/cm <sup>3</sup> )		Particle size distribution				
			D10	(µm)	D5	0 (µm)	D90 (µm)	
23.5	2.6		<2		<4.	.5	<25	
							LOI <sup>a</sup>	
TO	NL-0	NEO	K O	DO		50	Ι	

< 0.40

< 0.05

< 0.20

< 0.50

<0.50 %

Table 1 Chemical composition of raw metakaolin

51-53	42-44	<2.20	< 0.2	<3.00			
<sup>a</sup> LOI: loss on ignition, 950 °C							

Fe<sub>2</sub>O<sub>3</sub>

< 0.10

Oxides, weight (%)

 $Al_2O_3$ 

SiO<sub>2</sub>

Samples containing nitrates were prepared in a similar manner and at the same alkali concentrations as the reference experiments (similar H<sub>2</sub>O:OH<sup>-</sup> ratios which resulted in similar water:MK ratio, expressed as H<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio, Table 3). Sodium nitrate was introduced to the activation solutions at a constant NaNO<sub>3</sub>:NaOH (NO<sub>3</sub><sup>-</sup>:OH<sup>-</sup>) ratio of 0.25, thus leading to a Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.25 in most samples. The effect of the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio was studied by varying the solid:solution ratio to obtain Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios of 1.50 and 1.04 (corresponding to 1.20 and 0.84 without nitrate) with dilution factors of d = 5.50 and 13.75, respectively.

MK was mixed manually with the activation solution at ambient temperature until homogenous paste texture was obtained. The samples were cast into sealed polypropylene containers (50 ml) and cured at 40 °C  $\pm$  3 for periods ranging from 1 day to 3 months.

#### **Characterization techniques**

The structural evolution of the geopolymeric products was monitored using XRD and FTIR measurements, complemented by compressive strength measurements (Amsler press 100 kN). The XRD analysis was conducted using a SIEMENS D5000 diffractometer using CuK<sub> $\alpha$ </sub> radiation at 20 kV, 5 mA, and a scanning speed of 0.9° min<sup>-1</sup>. Samples were screened from  $2\theta = 5^{\circ}$  to  $2\theta = 80^{\circ}$ . Spectra of nitrate-free geopolymers are presented up to  $2\theta = 60^{\circ}$ since no additional information was observed in the range of  $2\theta = 60^{\circ}$ -80°. FTIR spectra were collected in the range of 500–1500  $\text{cm}^{-1}$  using a BRUKER Vector 22 FTIR spectrometer in transmittance mode, with 2  $\text{cm}^{-1}$  resolution.

Samples for XRD and FTIR measurements were ground manually using a mortar and pestle. FTIR samples were prepared by pressing a mixture of 2–5 mg ground sample with 100 mg dry KBr into pellets (French Press LCAD cell, BLA, type: C2P1). Samples of the starting materials, metakaolin and NaNO<sub>3</sub>, were prepared in a similar manner.

XRD spectra were normalized with respect to the anatase diffraction line at  $2\theta = 25.68^\circ$ , which was observed in all diffraction patterns. Quartz and anatase are present as impurities in MK, and remain unaltered throughout the geopolymerization process. FTIR spectra were normalized with respect to the integrated intensity in the 900–1300  $\text{cm}^{-1}$  range, which is attributed to the asymmetric stretching vibration of T-O-T (T = Al, Si) bonds. Normalization to sample weight was also performed, yielding similar results. Table 4 summarizes the major absorbance bands due to T-O, T-O-T, and N-O vibrations and their respective identification. In addition, a wide band around 1440 cm<sup>-1</sup> was observed in many of the geopolymer spectra. This band is attributed to the stretching vibrations of the C = O bond due to partial carbonation of the geopolymers at the high alkaline concentrations used in the research [26, 30].

Compressive strength measurements were performed using sets of 3–5 replicate cylindrical samples with a 26.5mm diameter and height. Samples were polished and then dried for 24 h in an oven at 40 °C before testing.

Table 3 Activation solution compositions and mix formulations in terms of molar ratios

Sample	Activation solution	18		Mix formulations			
	$H_2O: OH^-, d$	H <sub>2</sub> O:Na <sub>2</sub> O	NO <sub>3</sub> : OH <sup>-</sup>	Na <sub>2</sub> O: Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O:Al <sub>2</sub> O <sub>3</sub>	NO <sub>3</sub> :Al <sub>2</sub> O <sub>3</sub>	
1	5.50	11.0	0	1.00	11.0	0	
2	5.50	11.0	0	1.20	13.2	0	
3	5.50	11.0	0	0.84	9.2	0	
4	9.15	18.3	0	1.00	18.3	0	
5	13.75	27.5	0	1.00	27.5	0	
6	13.75	27.5	0	1.20	33.0	0	
7	13.75	27.5	0	0.84	23.1	0	
8	27.50	55.0	0	1.00	55.0	0	
9	5.50	8.8	0.25	1.25	11.0	0.50	
10	5.50	8.8	0.25	1.50	13.2	0.60	
11	5.50	8.8	0.25	1.04	9.2	0.42	
12	9.15	14.6	0.25	1.25	18.3	0.50	
13	13.75	22.0	0.25	1.25	27.5	0.50	
14	13.75	22.0	0.25	1.50	33.0	0.60	
15	13.75	22.0	0.25	1.04	22.9	0.42	
16	27.50	44.0	0.25	1.25	55.0	0.50	

SEM images were obtained using a Jeol 5300 scanning electron microscope (SEM). The fractured surface of specimens was observed after moderate drying at 50 °C for 24 h and coating with Au.

# Results

# Geopolymerization in the absence of nitrate: a reference study

Activation at a low dilution factor (high alkali concentration): d = 5.50

Figures 1 and 2 present the XRD patterns and FTIR spectra, respectively, of samples activated at d = 5.50 as a function of curing time. The data from XRD and FTIR measurements are complementary and enable us to follow the processes taking place within the forming geopolymer matrix. While the diffraction pattern of the raw metakaolin (MK) exhibited a broad hump with maximal intensity at  $2\theta = 23.3^{\circ}$  (in addition to the diffraction peaks of anatase, TiO<sub>2</sub>, Powder Diffraction File (PDF) #00-075-1537, and quartz, SiO<sub>2</sub>, PDF #01-085-0457), which are impurities, the broad hump in the diffraction pattern obtained after 1 day of curing is centered around  $2\theta = 30.6^{\circ}$ . This change is indicative of the formation of the amorphous geopolymer gel, as was shown in several previous studies [16, 26, 31].

Rearrangement of the amorphous phase into crystalline phases could be discerned after 2 days of curing as evidenced by the appearance of distinct diffraction peaks. These peaks were attributed to two zeolitic phases, zeolite A (PDF #00-039-0222) and a zeolite from the faujasite family, (PDF #00-012-0246), which is most probably zeolite X. The formation of these two phases was previously reported for MK-based geopolymers [17], as well as in Na-geopolymeric systems prepared from different raw materials such as fly ash [32, 33] and oil shale ash [34]. The relative intensity of these diffraction peaks as well as the

ratio between signal height and width increased during the first week of curing, indicating a gradual increase in the amount of the crystalline material during this time period. The diffraction patterns observed after 1 month (not shown) and 3 months were, however, very similar to those observed after 1 week, indicating that the extent of reorganization after the initial week of curing is limited.

The main IR absorbance band of aluminosilicate materials, which is attributed to asymmetric stretching  $v_3$  of the T–O–T bonds (T = Si, Al) appears between 900 and 1200 cm<sup>-1</sup>. Figure 2 shows that the maximal intensity of this band, which appeared at 1092 cm<sup>-1</sup> in the raw material (MK), shifted to 987 cm<sup>-1</sup> within 1 day of curing. The shift toward a lower frequency was due to the incorporation of Al within the generated aluminosilicate framework of the geopolymer, which resulted in a higher average T–O–T angle and consequently lower bond energies and lower frequencies [31]. A further decrease in the frequency of this band was observed with increasing curing time, implying that Al incorporation into the geopolymer backbone continued. The maximal intensity of this band reached the frequency of 977 cm<sup>-1</sup> after 3 months of curing.

The progress of the geopolymerization process can also be followed through the T-O symmetric stretching and OH bending vibrations of terminal T-OH groups [12, 16, 30] which appear in the 830–870  $\text{cm}^{-1}$  region of the spectrum (Fig. 2). Three vibrations were observed in this region after day 1 of curing  $(865, 844, 840 \text{ cm}^{-1})$  suggesting the existence of several different chemical environments around the T-OH groups. After 2 days of curing, only a single band at 865  $\text{ cm}^{-1}$ remained, indicating a more homogeneous speciation at this stage of the process. It is worth noting that the change in speciation after 2 days of curing was concurrent with the appearance of XRD diffraction peaks indicating the formation of zeolitic phases (Fig. 1). The T-OH band shifted to a lower frequency of 848  $\text{cm}^{-1}$  after 1 week of curing, then to  $835 \text{ cm}^{-1}$  after 1 month, and it was no longer observed after 3 months of curing, indicating a reduction in the rate of rearrangements within the geopolymer matrix at this time.

Table 4 FTIR absorbance signals of phases observed for raw materials and in MK-based geopolymers (cm<sup>-1</sup>), T = Si, Al

Phase in geopolymeric matrix	T-O-T stretching mo	de	N-O symmetric stretching mode	References
	Symmetric (SBUs)	Asymmetric		
Metakaolin	798	1092		[16]
Sodium nitrate			820, 1383	[38]
Amorphous geopolymer	650-800	975–990		[25]
Zeolite A (LTA)	556, 671	975–990		[16, 25]
Zeolite X (FAU)	695, 746	975–990		[16], this paper
Nitrate sodalite (SOD)	661, 730	990	1383	[36, 37]
Nitrate cancrinite (CAN)	575, 622, 682	961, 999, 1041, 1120	1415–1435	[38]

Fig. 1 XRD patterns of MK and geopolymerization products after activation with NaOH (d = 5.50) for different curing times





Fig. 2 FTIR spectra of MK and geopolymerization products after activation with NaOH (d = 5.50) for different curing times

The 500–800 cm<sup>-1</sup> region in the FTIR spectrum is assigned to T–O–T symmetric stretching modes. Metakaolin exhibited a single band in this region of the spectrum, at 798 cm<sup>-1</sup>, which is assigned to the symmetric stretching of either Al–O–Al [16, 25] or Si–O–Si [30]. This band was no longer observed after 1 day of curing, indicating the rapid dissolution of the raw material. A wide vibration band at  $650-800 \text{ cm}^{-1}$  was observed in the same region of the spectrum after 1 day of curing. Demortier et al. reported similar results in a FTIR study of zeolite precursor gels, and attributed this wide absorbance band to symmetric vibrations of T-O-T bonds in the amorphous phase of the gel [25]. The rearrangements within the geopolymer matrix were reflected in this region of the spectrum by a gradual resolution of this wide band into specific absorbance bands associated with the secondary building blocks (SBUs) of zeolites and related crystalline structures. A band at  $556 \text{ cm}^{-1}$ , which was previously assigned to the double ring unit of zeolite A (D4R), was clearly observed after 2 days of curing together with a small hump at 671  $\text{cm}^{-1}$ , which has also been assigned to zeolite A [25]. The identification of these bands with zeolite A is in agreement with the XRD data. Two additional vibration bands at 695 and 746  $\rm cm^{-1}$ were observed from day 3 (data not shown) and onwards. Similar results were reported by Fernandez-Jimenez et al. who attributed these bands to the sodalite units in both zeolite A and zeolite X [16]. Based on the XRD data, we suggest that these specific FTIR vibrations correspond to the double rings (D6R) or the sodalite units in zeolite X. As in the other regions of the spectrum, here again the changes that occurred between 1 week and 3 month of curing were very minor, since the dissolution of raw MK is very fast under these alkaline conditions, and the condensation of geopolymer as well as the rearrangement process, is immediate.

Activation at higher dilution factors (lower alkali concentrations): d = 9.15, 13.75, 27.50

Activation of MK by solutions of lower alkalinity and consequently higher water content (i.e., *d* values of 9.15, 13.75, and 27.50), is known to delay the geopolymerization process [12]. Despite slower reaction rates under these conditions, the formation of the amorphous geopolymer gel was detected after 1 day of curing by both XRD (a wide hump centered around  $2\theta = 30.6^{\circ}$ ) and FTIR (a broad band in the 650–800 cm<sup>-1</sup> range), as seen for d = 13.75 in Figs. 3 and 4, respectively. Similar results were obtained for d = 9.15 and d = 27.50. The absorbance band of the terminal T–OH groups, observed at 865 cm<sup>-1</sup> between 1 day and 3 days of curing (Fig. 4), with maximal relative intensity during the second day of curing, is an indication that the geopolymeric matrix had undergone rearrangements during this period.

Rearrangement of the geopolymer gel leading to the formation of crystalline phases was slower for d = 13.75 than in the case of highest alkalinity described in above "Activation at a low dilution factor (high alkali concentration) d = 5.50" section (Fig. 1). Zeolite A was the only crystalline phase observed after 1 week of curing at all higher dilutions. Figure 5 presents an SEM image showing the presence of cubic structures, which is the well-known morphology of zeolite A crystals. Zeolite X was detected by XRD at later times, either after 1 month or 3 months, depending on the alkalinity of the activation solution (d = 9.15 and 13.75, respectively), whereas it appeared

after only 2 days in the most alkaline conditions at d = 5.50 (Fig. 1). Figure 6 shows the diffraction patterns of samples prepared using activation solutions of varying alkalinities after 3 months of curing. It is seen that the relative intensity of zeolite X diffraction peaks was highest at d = 5.50 and decreased with decreasing alkalinity. At the lowest alkalinity used (d = 27.50), diffraction peaks due to zeolite X were not observed even after 3 months of curing.

FTIR spectra for the same samples (Fig. 7) show similar trends. The frequency of the maximal intensity of the T–O–T asymmetric band observed after 3 months of curing increased with the decrease in alkalinity of the activation solution, shifting from 977 cm<sup>-1</sup> for samples with the highest alkalinity (d = 5.50) to 1006 cm<sup>-1</sup> for the lowest alkalinity (d = 27.50). This shift indicates slower dissolution of MK and a lesser degree of Al incorporation into the geopolymeric backbone during condensation of the geopolymer at lower alkaline concentrations. In the SBU region (500–800 cm<sup>-1</sup>) of the FTIR spectra, in which the bands at 556 and 671 cm<sup>-1</sup> are associated with zeolite A and those at 695 and 746 cm<sup>-1</sup> are associated with zeolite X, a decrease in the relative intensity of bands associated with zeolite X was observed with decreasing alkalinity.

The set of results presented above indicates that the main parameter affecting the rate of reactions was the activation solution alkalinity, which is determined by the  $H_2O:OH^-$  ratio, denoted *d*. In addition to the lower dissolution rates at higher *d* values, the local concentration of the dissolved monomers was also lower, resulting in lower

Fig. 3 XRD patterns of MK and geopolymerization products after activation with NaOH (d = 13.75) during the initial curing period





Fig. 4 FTIR spectra of MK and geopolymerization products after activation with NaOH (d = 13.75) for different curing times



Fig. 5 SEM images of MK-based geopolymers after alkali-activation with NaOH (d = 9.15)

condensation rates. Another indication of slow condensation rates was the development of compressive strength. While geopolymer monoliths obtained at d = 5.50 reached compressive strength values of  $6.00 \pm 1.5$  MPa after 3 months of curing, monoliths obtained at d = 9.15resembled dry clay in texture and attained very low compressive strength values (0.5 MPa). At the highest dilutions tested (d = 13.75 and d = 27.50), the condensation stage was extremely slow and no monolith structures were obtained after 3 months of curing at 40 °C, in agreement with Katz [35].

#### Varying the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio

Varying the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio in the geopolymer mixture at two alkaline concentrations, d = 5.50 and d = 13.75, influenced the crystalline phase distribution in the resulting geopolymers. This is demonstrated by comparing the XRD and FTIR data of samples prepared at d = 5.50 with three different Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios following 3 months of curing (Figs. 8, 9, respectively). At the lowest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio (0.84), diffraction signals attributed to zeolite A were much more dominant than those attributed to zeolite X; at higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios (1.00 and 1.20) both zeolite A and zeolite X were detected by XRD (Fig. 8). As expected, FTIR spectra were in agreement with the XRD data; the bands at 695 and 746 cm<sup>-1</sup>, which are associated with zeolite X, are not clearly resolved for mixtures with the lowest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio, but are well defined in the FTIR spectra of samples of the higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios (Fig. 9). Moreover, the relative intensity of signals associated with zeolite X in both XRD and FTIR increased with the increasing Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio, indicating that this ratio had a strong influence on the conditions under which zeolite X is generated.

At the highest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio studied (Na<sub>2</sub>O:Al<sub>2</sub> O<sub>3</sub> = 1.20), at d = 5.50, evidence of structural rearrangements could still be detected after 3 months of curing, as indicated by the presence of the T–OH absorption band at 845 cm<sup>-1</sup> (Fig. 9). In contrast, this band was no longer observed at this time at lower Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios. The deceleration of geopolymerization processes that occurs when the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio is decreased can be also observed by examining the position of the T–O–T asymmetric band. After 3 months of curing, this band appeared at 990 cm<sup>-1</sup> for samples prepared at Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> = 0.84, while at higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios it was observed at a lower frequency of 977 cm<sup>-1</sup>, indicating a higher extent of Al incorporation into the geopolymer.

Similar trends were observed in XRD and FTIR data of samples prepared at d = 13.75 with varying Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios.

#### Geopolymerization in the presence of nitrate

Activation at a low dilution factor (high alkali concentration): d = 5.50

Introduction of sodium nitrate into the activation solution had a great impact on the rate of the geopolymerization







Fig. 7 FTIR spectra of MK and geopolymerization products after 3 months of activation with NaOH for different d

reaction as well as on the nature of the resulting products. Figure 10 displays the diffraction pattern of the geopolymeric matrix formed at d = 5.50 in the presence of nitrate as a function of curing time. The FTIR absorbance spectra of similar samples are presented in Fig. 11. Well-developed crystalline phases were identified by XRD after 1 day (Fig. 10). The main diffraction peaks were associated with nitrate sodalite, Na<sub>8</sub>Al<sub>6</sub>(SiO<sub>4</sub>)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub> (PDF #04-009-1879), a mineral from the feldspathoid family, while weak diffraction peaks associated with nitrate cancrinite, Na<sub>8</sub> Al<sub>6</sub>(SiO<sub>4</sub>)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (PDF #00-038-0513), an additional member of the feldspathoid family, were also observed for all curing times. It should be mentioned that nitrate cancrinite and nitrate sodalite share many structural features, resulting in similar diffraction patterns. The diffraction pattern of nitrate cancrinite contains peaks at  $2\theta = 24.30^{\circ}, 27.48^{\circ}, 37.00^{\circ}, \text{ all of which are of relatively}$ high intensity, enabling unambiguous identification of this phase. On the other hand, the only diffraction peak attributed to nitrate sodalite that does not overlap peaks attributed to nitrate cancrinite diffraction appears at  $2\theta = 60.03^{\circ}$ and is of relatively low height. A minor increase in signal height was observed for both of these phases during the 3 months of curing, with no additional changes in the XRD pattern during the curing period between 1 week and 3 months. The overlapping of the diffraction peaks of the two feldspathoids makes it difficult to unambiguously identify the trends in signal heights of a specific feldspathoid.

The FTIR data presented in Fig. 11 correspond well with the XRD results. The main absorbance band of the asymmetric stretching vibration of T–O–T bonds (T = Si, Al) shifted from a frequency of  $1092 \text{ cm}^{-1}$  in the raw material (MK) to 990 cm<sup>-1</sup> in the geopolymeric matrices after 1 day of curing, as observed for the nitrate-free samples after the same time (Fig. 2). Two bands at 661 and 730 cm<sup>-1</sup> are clearly resolved in the SBUs region





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Fig. 9 FTIR spectra of geopolymerization products after 3 months of activation with NaOH (d = 5.50) for different Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios

 $(500-800 \text{ cm}^{-1})$  after 1 day of curing. These frequencies were previously assigned to the symmetric T–O–T stretching vibrations of the sodalite framework in carbonate sodalite [36]. Based on the XRD results and the relatively high nitrate concentration in this sample, we can conclude that these bands are due to the aluminosilicate framework of nitrate sodalite.

The absorbance in the  $1380-1440 \text{ cm}^{-1}$  region is attributed to N-O symmetric stretching modes of nitrate ions [37]. The position of the band is highly dependent on the chemical environment to which the nitrate ion is exposed. A single band at 1383 cm<sup>-1</sup> was observed for crystalline NaNO<sub>3</sub> or for nitrate ion in aqueous solution, as well as for the nitrate sodalite phase. An additional band at 1415  $\text{cm}^{-1}$  appeared in FTIR spectra due to nitrate ions intercalated in the nitrate cancrinite structure, in which nitrate ions reside in two chemically different environments [38, 39]. The absorbance band at 1415  $\text{cm}^{-1}$  can be clearly observed in the FTIR spectrum from day 1 (Fig. 11) and its appearance, together with the two bands at 578 and  $624 \text{ cm}^{-1}$ , both of which were previously attributed to nitrate cancrinite support the identification suggested by the XRD data. The presence of the two phases, nitrate sodalite and nitrate cancrinite, indicates that part of the nitrate ions were incorporated within the crystalline phases in the geopolymeric matrix. The FTIR spectrum obtained after 3 months of curing was essentially the same as that obtained after 1 day of curing, and was in agreement with XRD data for the same samples.

The combined data from XRD and FTIR measurements suggest that the formation of crystalline phases was faster in the nitrate-bearing systems compared with the nitratefree systems. Additional evidence for the accelerated reaction rate in the nitrate-containing systems was obtained from the development of compressive strength which was followed over a period of 90 days. Figure 12 shows that the increase in compressive strength was more rapid in the presence of nitrate compared with the corresponding **Fig. 10** XRD patterns of geopolymerization products after activation with NaOH (d = 5.50) and NaNO<sub>3</sub> for different curing times





Fig. 11 FTIR spectra of MK and geopolymerization products after activation with NaOH (d = 5.50) and NaNO<sub>3</sub> for different curing times

nitrate-free samples. The compressive strength of nitratebearing samples reached a value of  $9.0 \pm 0.8$  MPa after 3 days of curing and did not vary significantly in the following 87 days. This time-to-stabilization corresponds well with the XRD and FTIR data which showed no change in phase distribution after a similar period. Slower development of compressive strength was observed for nitratefree samples in which strength increased gradually over 28 days of curing. Note that all samples, with and without nitrate, were prepared with an activation solution of the same d and water:MK ratio (Table 3). However, due to the addition of NaNO3 to the activation solution, the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio in the nitrate-bearing samples was higher than in the corresponding nitrate-free samples. As shown above, the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio may influence geopolymerization kinetics and product distribution. Moreover, nitrate anions  $(NO_3^{-})$  are known to have a structure forming ability, which may also enhance the reactions rates [28, 40]. Thus, the higher rate of strength development in the nitrate-bearing system was most probably due to the faster kinetics. Nevertheless, the nature of the different crystalline phases identified in the systems may also influence the compressive strength of the geopolymeric products obtained.

# Activation at higher dilution factors (lower alkali concentrations): d = 9.15, 13.75, 27.50

The reduced alkalinity had a pronounced effect on the rate of geopolymerization in the nitrate-bearing systems, as presented above for the nitrate-free formulations ("Activation at higher dilution factors (lower alkali concentrations): d = 9.15, 13.75, 27.50" section). The XRD (Fig. 13) and FTIR (Fig. 14) data for systems activated at

Fig. 12 Development of compressive strength of geopolymers activated at d = 5.50 without nitrate (solid line, left vertical axis) versus geopolymers activated in presence of nitrate (dashed line, right vertical axis) presented in logarithmic scale (base 10)



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d = 13.75 show that during the first 2 days of reaction, the geopolymeric product consisted only of an amorphous phase. Diffraction peaks of a crystalline phase, zeolite A, were first observed after 3 days of curing. This sequence of phase transformations is supported by the FTIR data. Two wide bands characteristic of the symmetric stretching of T-O-T groups in the amorphous product were detected in the  $650-800 \text{ cm}^{-1}$  range of the spectra during the first 2 days of curing (Fig. 14). Starting from day 3, the absorbance at  $556 \text{ cm}^{-1}$ , which is characteristic of zeolite A, was resolved. The enhanced absorbance in this region of the spectrum was concurrent with the increase in intensity of two distinct absorbance bands in the T-OH region (835,  $870 \text{ cm}^{-1}$ ), demonstrating once again that the rearrangement in geopolymer systems occurs via the T-OH terminal groups.

The appearance of a crystalline phase, in this case zeolite A, was delayed compared with nitrate-bearing samples activated at d = 5.50, but was earlier than in the nitrate-free samples activated at d = 13.75 (Fig. 5), demonstrating again that the reorganization of the amorphous phase into a crystalline phase was faster in the presence of NaNO<sub>3</sub>. Similar results were obtained for samples activated at d = 9.15 and d = 27.50 (not shown).

Figure 15 shows the evolution of the diffraction patterns for geopolymer matrices formed using the three lower alkalinity activation solutions (d = 9.15, 13.75, 27.50) from 1 week to 3 months of curing. Figure 16 presents the corresponding FTIR spectra for d = 9.15, 13.75. Although zeolite A was the only crystalline phase observed in all three dilutions after 1 week of curing, the extent of rearrangement thereafter and the product composition at 3 months depended greatly on the activation solution dilution.

When an activation solution of d = 9.15 was used, zeolite X and nitrate sodalite were both observed in the diffraction pattern after 1 month of curing, in addition to zeolite A. Diffraction peaks attributed to nitrate cancrinite were observed after a 3-month curing period. It is worth noting that the intensity of the diffraction peaks due to zeolite A at 3 months was lower than at 1 month, suggesting a possible transformation of the zeolite to nitrate sodalite and nitrate cancrinite. FTIR spectra were found to be a more sensitive analytical tool than XRD in this case, providing additional information to that obtained by XRD. Initial indications of the presence of nitrate cancrinite, namely the N-O band at 1425 cm<sup>-1</sup>, could be observed in the FTIR spectrum at 1 month at d = 9.15. In the SBU region of the spectrum, the bands attributed to nitrate sodalite (661 and 730  $\text{cm}^{-1}$ ) were clearly observed. In addition, the relative intensity of absorbance at 556  $cm^{-1}$ associated with zeolite A decreased, and a new absorbance peak at 578 cm<sup>-1</sup> appeared. A further decrease in absorbance at 556 cm<sup>-1</sup> was observed after 3 months of curing, together with the resolution of additional bands in the SBU region of the spectrum (624 and 681  $\text{cm}^{-1}$ ) and in the asymmetric stretching region (961, 1037, and 1123  $\text{cm}^{-1}$ ). These bands, together with the band at  $578 \text{ cm}^{-1}$ , were previously assigned to different T-O-T bonds in nitrate cancrinite [39]. Furthermore, the N–O symmetric

Fig. 13 XRD patterns of MK and geopolymerization products after activation with NaOH (d = 13.75) and NaNO<sub>3</sub> during the initial curing period





Fig. 14 FTIR spectra of geopolymerization products after activation with NaOH (d = 13.75) and NaNO<sub>3</sub> for different curing times

stretching mode at 1425 cm<sup>-1</sup> due to nitrate cancrinite which was observed for the first time after 1 month of curing at d = 9.15 had enhanced intensity and was split into two distinguishable bands after 3 months of curing. The greater spectral resolution of the spectrum of nitrate cancrinite after curing for 3 months indicates a higher content of this phase. These results provide further evidence for the transformation of zeolite A to nitrate sodalite and nitrate cancrinite.

At lower alkalinity (d = 13.75), diffraction peaks due to nitrate sodalite as well as FTIR absorbance bands due to this phase (661, 730 cm<sup>-1</sup>) appeared after 1 month of curing. In addition, a small shoulder at 1425 cm<sup>-1</sup> could also be seen after 3 months of curing, suggesting that the formation of nitrate cancrinite under these conditions was also initiated. It is worth noting that the formation of nitrate cancrinite was not detected by XRD in this case. At the least alkaline environment (d = 27.50), zeolite A was the only crystalline phase observed, even after 3 months of curing at 40 °C.

Figure 17 presents the FTIR absorbance of the nitratebearing geopolymeric systems prepared at different dilutions after a 3-month curing period. Absorbance at 990 cm<sup>-1</sup>, attributed to T–O–T asymmetric stretching, was observed for all four dilutions. All other FTIR absorbance bands corresponded to the vibration modes of phases identified by XRD. The relative intensities of the N–O absorbance bands at 1425 and 1383 cm<sup>-1</sup> vary for the different activation solutions. The relative intensity of the band at 1425 cm<sup>-1</sup>, which is due to nitrate cancrinite, increased when dilution was reduced from d = 27.50 to d = 9.15. In addition, the bands at 1123, 1037, and 961 cm<sup>-1</sup>, which are also assigned to nitrate cancrinite, were also more clearly resolved, indicating a higher



Fig. 15 XRD patterns of geopolymerization products after activation with NaOH and NaNO<sub>3</sub> for different d and for curing periods of 1 week (1 w), 1 month (1 m), and 3 months (3 m). A-zeolite A, X-Zeolite X, S-nitrate sodalite, C-nitrate cancrinite, T-anatase, Q-quartz

amount of nitrate cancrinite. Nevertheless, at d = 5.50 the intensity of all bands due to nitrate cancrinite was lower than at d = 9.15.

It is known that the transformations within the geopolymeric matrix or similar zeolite precursor gels take place through dissolution and recondensation [41, 42]. It is therefore proposed that despite the initial high rate of reaction at d = 5.50 ("Activation at a low dilution factor (high alkali concentration): d = 5.50" section), the low water content in the samples activated at this dilution did not facilitate the rearrangement processes after the geopolymeric monolith was formed. As a result, further transformations in the geopolymeric system, and particularly the transformation from nitrate sodalite to nitrate cancrinite, were inhibited, in agreement with Barnes et al. who also failed to observe the conversion of carbonate sodalite to carbonate cancrinite without liquid media [36, 42].

#### Varying the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio

The effect of the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio on the formation of nitrate-bearing geopolymers was examined using two activation solutions, d = 5.50 and d = 13.75 (Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios of 1.04 and 1.50, in addition to 1.25 presented above).

After 1 week of curing at d = 13.75, zeolite A was the only crystalline phase observed by XRD for all three Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios (Fig. 18). Whereas no significant changes were seen in the XRD data for the low Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.04 between 1 week and 3 months, a higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.25 resulted in enhanced rearrangements within the geopolymer, as indicated by diffraction peaks attributed to nitrate sodalite and zeolite A that were observed after 3 months (Fig. 18, middle line in the 3-month graph). At the highest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.50, zeolite A was no longer observed after 3 months of Fig. 16 FTIR spectra of geopolymerization products after activation with NaOH (d = 9.15, d = 13.75) and NaNO<sub>3</sub> for different curing times





Fig. 17 FTIR spectra of geopolymerization products after 3 months of activation with NaOH and NaNO<sub>3</sub> for different d

curing. The nitrate-bearing feldspathoids, nitrate sodalite and nitrate cancrinite, were the only crystalline phases detected (Fig. 18, line 3 in the 3-month graph).

The FTIR results for the samples prepared with d = 13.75 (Fig. 19) are in good agreement with the XRD

results: the transformation of zeolite A into nitrate sodalite and nitrate cancrinite that occurred between 1 week and 3 months of curing was identified by the decrease in the band at 556 cm<sup>-1</sup>, attributed to zeolite A at a Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.25, together with an increase in the bands attributed to nitrate sodalite (at 661 and 730  $\text{cm}^{-1}$ ) and of nitrate cancrinite (at 1415  $\text{cm}^{-1}$ ), the latter of which was not identified by XRD. This transformation was most evident at the highest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.50, as no absorbance of zeolite A was detected in the IR spectrum after 3 months of curing. IR absorbance bands at 1425 and at 1435  $\text{cm}^{-1}$  are attributed to the nitrate vibrations in nitrate cancrinite. Bands due to nitrate cancrinite were also observed in the SBU region (578, 622, 682, 781  $\text{cm}^{-1}$ ) as well as in the T– O-T region (1042, 1120 cm<sup>-1</sup>). The band at 799 cm<sup>-1</sup> was unidentified. An increase in the absorbance bands due to nitrate sodalite was also observed (661, 730 cm<sup>-1</sup>). The combination of data from both XRD and FTIR supports the proposed transformation from zeolite A to nitrate sodalite and nitrate cancrinite phases.

A comparison of the diffraction patterns of products from geopolymerization at d = 5.50 at different Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios reveals that the formation of both nitrate sodalite and nitrate cancrinite was facilitated by increasing this ratio. Relatively weak X-ray diffraction peaks attributed to nitrate sodalite were obtained after 1 week and 3 months of curing at the lowest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.04 (Fig. 18). Sharper peaks attributed to nitrate sodalite together with some weak peaks attributed to nitrate

![](_page_14_Figure_2.jpeg)

Fig. 18 XRD patterns of geopolymerization products after activation with NaOH and NaNO<sub>3</sub> for different Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios after 1 week and 3 months of curing (*top*: d = 13.75, *bottom*: d = 5.50)

cancrinite appeared at a Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.25 after both curing periods. At the highest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.50, the diffraction pattern of nitrate cancrinite was clearly observed after 1 week of curing, and became more pronounced after 3 months of curing. The increase in the intensity of the diffraction peaks attributed only to nitrate cancrinite at  $2\theta = 24.30^{\circ}$ , 27.48°, 37.00° is significantly higher than the increase observed for the shared peaks. Nevertheless, the diffraction peak at  $2\theta = 60.03^{\circ}$  was still observed after 3 months of curing, indicating that both feldspathoid phases are present within the geopolymeric matrix.

The enhanced formation of nitrate cancrinite at the higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio was also evident from the FTIR results for the samples prepared with d = 5.50 which are presented in Fig. 19. Unlike the XRD measurements, the FTIR spectra show that nitrate cancrinite was formed at all Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios. The SBU signals of geopolymers formed at a lower Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.04 were very unclear after 1 week of curing, indicating low crystallinity of the product at this stage, which is in agreement with the XRD results. After 3 months of curing, the absorbance peaks at 661 and 730 cm<sup>-1</sup> were much better resolved, indicating the presence of nitrate cancrinite (the absorbance at

 $1415 \text{ cm}^{-1}$  in addition to small peaks at 578 and  $624 \text{ cm}^{-1}$ ). The same peaks were also observed at a Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.25, with no detectable change between 1 week and 3 months of curing. At the highest Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.50, the geopolymer formed during 1 week of curing contained both nitrate sodalite and nitrate cancrinite. However, after 3 months of curing, a well-resolved pattern attributed to nitrate cancrinite was obtained, with only very weak absorbance due to nitrate sodalite detected at 730  $\text{cm}^{-1}$ . In addition, the absorbance peak of asymmetric T-O-T stretching vibrations in nitrate sodalite previously was observed at 990  $\text{cm}^{-1}$  shifted to 999  $\text{cm}^{-1}$ , which is attributed to similar asymmetric T-O-T stretching vibrations in nitrate cancrinite. The relative increase in nitrate cancrinite content compared with nitrate sodalite at higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios after 3 months of curing can be seen clearly by comparing the lines of  $Na_2O:Al_2O_3 = 1.25$ and  $Na_2O:Al_2O_3 = 1.50$  in Fig. 19. Needle-like morphology of the nitrate cancrinite phase [43, 44] was detected in SEM images at d = 5.50 (Fig. 20), at a Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.50.

These XRD and FTIR measurements imply that the reorganization of the geopolymer toward nitrate cancrinite is preferred at higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios. In our experimental set-up, higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios were achieved by using a

Fig. 19 FTIR spectra of geopolymerization products after activation with NaOH and NaNO<sub>3</sub> for different Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios (*top*: d = 13.75, *bottom*: d = 5.50)

![](_page_15_Figure_3.jpeg)

higher solution:MK ratio, resulting in a higher water content (H<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio) as well. As suggested in "Activation at higher dilution factors (lower alkali concentrations): d = 9.15, 13.75, 27.50" section, high water content facilitates the reorganization processes, resulting in enhanced nitrate cancrinite formation. In addition, the high nitrate content may also enhance crystalline phase formation in general, as will be discussed in the following chapter.

## Discussion

The development of low-silica (Si:Al = 1.4) metakaolinbased geopolymers with and without nitrates at ambient temperature was followed over a period of 3 months. Special attention was given to the reorganization of the geopolymer matrix and the formation of crystalline zeolites and feldspathoids, as these were recognized as potential

![](_page_16_Picture_1.jpeg)

Fig. 20 SEM images of MK-based geopolymers after alkali-activation with NaOH (d = 5.50) and NaNO<sub>3</sub>

immobilization agents for hazardous or radioactive species present in industrial or nuclear waste streams [15, 23, 24, 27, 45, 46].

It appears that several parameters, acting simultaneously in these systems, control the dissolution, condensation, and reorganization of the various species into amorphous and crystalline phases: alkalinity of the activation solution, transient SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio, Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio, and the presence of nitrate ions. These parameters are discussed in the following paragraphs. While temperature is also known to affect the same processes, this study intentionally examined all samples at a constant temperature of 40 °C, as close as possible to ambient temperature while allowing reasonable rate of progress within the timescale of the experimental program.

The alkalinity of the activation solution is well known to have a major effect on the rate of the geopolymerization processes. High alkalinity accelerates the dissolution of the raw material as well as the condensation and reorganization within the geopolymer matrix, while lower alkalinity slows these processes. The results presented here suggest that while the kinetics of the process is affected by the increased dilution or the reduced alkalinity of the activation solution, the sequence of the geopolymerization reactions taking place is not altered.

The use of activation solutions of lower alkalinity allowed better insight into the transformations taking place in the early stages of geopolymerization. Two main zeolite phases were identified in the low-Si geopolymeric systems prepared in the absence of nitrate: zeolite A and zeolite X. At the temperature studied (40 °C), both zeolite A and zeolite X were detected after 2 days of curing at the highest alkalinity used (d = 5.50), whereas the formation of both zeolites was delayed at lower alkalinities. Zeolite A was the first crystalline phase formed, followed by formation of zeolite X at later times. Similar results, namely early formation of zeolite A followed by zeolite X formation at later stages, were previously reported by Purnomo et al. during zeolite preparation at 90 °C [33]. These authors suggested that the crystallization rate of zeolite X is lower than that of zeolite A due to a higher activation energy which they related to the higher complexity of the repeating unit in the zeolite X structure. However, these authors and others have noted that the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio has an effect on the nature of the zeolites formed [32, 33].

Although the initial SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio in each geopolymer formulation is fixed, the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio of dissolved species may vary considerably throughout the geopolymerization process. It is well established that the dissolution of the aluminum species from aluminosilicate materials is faster than that of silicon species [7], resulting in a solution with a relatively low SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio. Under such conditions, the crystallization of zeolite A from the amorphous gel is favored [32, 33]. Variations in the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio due to further raw material dissolution on the one hand, and faster alumina than silica uptake on the other hand, may eventually lead to higher SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratios in solution, which were claimed to favor zeolite X formation [47].

The extent of zeolite X formation is also highly dependent upon Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio. Our results showed that higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios promoted reorganization within the geopolymer and formation of crystalline phases, and increase in the relative amount of zeolite X formation, while lower Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratios inhibited the reorganization process, with only slight amounts of zeolite X detected. These findings are in agreement with previous reports claiming that increasing the Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio enhances the extent of reaction, as well as the formation of crystalline products [26]. Several authors considered the sodium ion to be a structure-directing agent [6, 48]. The structure forming ability of sodium ion is related to its high hydration energy, which results in partial dehydration of the aluminosilicate monomers and oligomers, as well as their association with the charged hydrated ion, both of which facilitate condensation reactions.

The addition of sodium nitrate to highly alkaline activation solutions led to the rapid appearance of nitratebearing crystalline phases, namely nitrate sodalite and nitrate cancrinite. The formulations containing sodium nitrate have an inherently higher Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio, which was shown above to enhance the reorganization of geopolymers into crystalline phases. Moreover, the nitrate anion is also highly hydrated, and was claimed to have a structure-directing ability similar to that of the sodium ion [28, 40]. It is not possible to determine which of the ions, sodium or nitrate, had more dominant impact on the kinetics of geopolymer formation and rearrangement. However, it is obvious that the development of strength values was faster in the presence of sodium nitrate than in its absence, as were the strength values of final products.

Here again, using activation solutions of varying alkalinities allowed us to demonstrate the sequence of reactions leading to the formation of the nitrate-bearing phases, nitrate sodalite and nitrate cancrinite. Zeolite A was the first crystalline phase formed at intermediate alkalinities studied (d = 13.75, d = 9.15), followed by the appearance of zeolite X and nitrate sodalite, while nitrate cancrinite was detected only at later stages of the geopolymerization process. At these intermediate alkalinities, the generation of nitrate-bearing phases was observed to be at the expense of zeolite A. No nitrate-bearing phases were observed throughout the 3 months of curing at 40 °C in samples prepared in the least alkaline environment (d = 27.50). Zeolite A was the only crystalline phase obtained in these samples, as in the nitrate-free geopolymers prepared using an activation solution of similar alkalinity. Nitrate-bearing phases were also absent at d = 13.75 in samples with a low Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio of 1.04, in which the alkalinity as well as sodium and nitrate concentrations were relatively low.

It is interesting to note that zeolite A and zeolite X were the first crystalline phases to be formed in geopolymerization reactions in presence of nitrate as well as in its absence. Both zeolite A and zeolite X are known from previous works to be precursors for the generation of nitrate sodalite and nitrate cancrinite, which were shown to be more thermodynamically stable phases relative to the zeolites [37, 39, 41, 49]. Indeed nitrate sodalite was formed in presence of sufficient alkalinity and concentration of nitrate. In relatively high Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>, this phase further reacted and nitrate cancrinite was established. This series of transformations has been previously proposed for the formation of feldspathoid phases at elevated temperatures (90-105 °C) in the presence of either carbonate or nitrate ions [36, 41]. The results presented here demonstrate that the same sequence may take place at a temperature of 40 °C in metakaolin-based geopolymeric systems. Therefore, based on all these data, it can be concluded that higher alkaline concentration, higher sodium and nitrate content as well as higher temperatures enhance the kinetics of phase transformation toward the most thermodynamically stable phase in this sequence, nitrate cancrinite.

These findings are of special interest since zeolites and feldspathoids are known for their immobilizing potential. Thus, for example, structural data for nitrate sodalite and nitrate cancrinite show these are promising candidates for the immobilization of cesium and strontium cations, which are common radioactive species found in nuclear waste streams [24, 43, 50]. In fact, the formation of nitrate sodalite and nitrate cancrinite within weathered aluminosilicate sediments exposed to simulated nuclear waste solutions was

correlated with increased retention of both cesium and strontium cations in the solution [51–53]. Based on the abovementioned data, it is reasonable to expect that geopolymers containing these phases will serve as efficient immobilization matrices for the same radionuclides.

# Summary and conclusions

- The development of low-silica (Si:Al = 1.4) metakaolin-based geopolymers with and without nitrates at near-ambient temperature (40 °C) was studied in the present work.
- The dissolution of the raw material, as well as condensation and reorganization within the geopolymer matrix, was very rapid at high alkalinity. Lower alkalinity slowed these processes considerably, and provided better insight into the transformations taking place during the early stages of geopolymerization.
- The alkalinity of the system as well as Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio was found to affect whether zeolite A or zeolite X are formed.
- High Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> ratio as well as the presence of nitrate enhance the rate of geopolymerization reactions and phase transformations in these systems.
- The sequence of geopolymerization products observed in nitrate-free formulations was as follows: amorphous gel → zeolite A/X. In the presence of nitrate, zeolites A/X further transform to → nitrate sodalite → nitrate cancrinite.
- The crystalline phases formed in these geopolymers in the presence of nitrate at near-ambient temperature are promising candidates for the immobilization of hazardous species from waste streams containing nitrate salts, such as nuclear waste streams.

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