PHASE TRANSFORMATIONS IN METAKAOLIN-BASED SYSTEMS AT MODERATE TEMPERATURES IN PRESENCE OF NITRATE

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1. Introduction

Alkali-activated pozzolonic materials, also called geopolymers, were suggested as an alternative binder for the OPC (Ordinary Portland Cement) about 60 years ago. The main advantage of geopolymers over OPC matrices is their higher durability under various conditions as sulfates environment (Fernandez-Jimenez et al. 2007), chlorides and carbonates environment (Zhang et al. 2010, Bernal, S.A., et al. 2011), presence of acids (Bakharev 2005), and presence of silicate aggregates (Alkali-Silicate Reactions) (Fernandez-Jimenez et al. 2007). In addition, the geopolymers have high thermal stability and relatively high strength. The high emission levels of CO_2 during OPC manufacturing are another reason to test other binding materials such as geopolymers, as alternative to the conventional cement in construction industry.

Geopolymers are prepared by reacting pozzolanic raw material with an alkaline solution. Under these conditions the pozzolanic materials are hydrolyzed into monomeric or oligomeric silicate and aluminate species, which then condense to form the dense geopolymeric matrix (Komnitsas 2007, Provis 2007). Alkali cations are incorporated into the geopolymer structure as counter ions to the negatively charged aluminate groups. While the initial product is often fully amorphous, crystalline zeolites or similar phases may eventually develop within the amorphous matrix (De- Silva 2009, Fernandez-Jimenez et al. 2008, Brough et al. 2001, Hajimohammadi et al. 2011). A low silica content ($SiO_2:Al_2O_3 \leq 2$), high alkali content and elevated temperatures are all known to promote the formation of crystalline phases. The mechanical properties of the resulting geopolymers can be affected by zeolitic phase formation (Provis et al. 2005).

Although geopolymers are investigated by many research teams, little attention is given to the presence of nitrate, common ion found in several soils and in specific wastewaters. The aim of the current research was to investigate the phase transformations in presence of nitrate in geopolymers generated at ambient temperature.

2. Materials and Methods

Metakaolin (MK, PowerPozz^{TM}) conforming to ASTM C-618, Class N Specifications for Natural and Calcined Pozzolans, was supplied by Advanced Cement Technologies. The chemical composition and physical properties of metakaolin are presented in Table 1 and Table 2, respectively.

Table 1: Chemical composition of raw metakaolin

Metakaolin (MK)	Oxides, weight (%)										
	SiO2	Al2O	Fe2	CaO	TiO2	MgO	Na2O	K2O	P2O5	SO3	LOI[a]
Manufacture data	51-53	42-44	<2.20	<0.2	<3.00	<0.10	<0.05	<0.40	<0.20	<0.50	<0.50

[a] LOI: loss on ignition, 950°C

Table 2: physical characterization of raw metakaolin

		Particle size		
BET [m^2/g]	Density [g/cm^3]	D10]μm[	D50]μm[	D90 [μm]
23.5	2.6	<2	<4.5	<25

2.1. *Preparation of geopolymers*

Table 3: Activation solutions and mix formulations in terms of molar ratios

Sample	Activation solutions			Mix formulations		
	NaO	H2	NaN	Na2O:	H2O:	NO3:Al2O3
no nitrate, *d*=5.50	1	5.50	0	1	11	0
no nitrate, *d*=9.15	1	9.15	0	1	18.3	0
no nitrate, *d*=13.75	1	13.75	0	1	27.5	0
no nitrate, *d*=27.50	1	27.50	0	1	55	0
with nitrate, *d*=5.50	1	5.50	0.25	1.25	8.8	0.5
with nitrate, *d*=9.15	1	9.15	0.25	1.25	14.6	0.5
with nitrate, *d*=13.75	1	13.75	0.25	1.25	22	0.5
with nitrate, *d*=27.50	1	27.50	0.25	1.25	44	0.5

The activating solutions used in this study were prepared by dissolving NaOH and NaNO3, yielding H2O:OH⁻ (=*d*) ratios of 5.50, 9.15, 13.75 and 27.50, while keeping a constant NaNO3 to NaOH (NO3⁻: OH⁻) ratio of 0.25. Geopolymer samples were prepared by activating MK with the appropriate solutions (Table 3). The Na2O:Al2O3 ratio was set to 1.25:1. Reference samples were prepared from NaOH solutions with the same *d* values. The amounts of solution and MK were adjusted to a Na2O:Al2O3 ratio of 1, in order to obtain similar alkalinity as in the nitrate bearing formulations.

MK was manually mixed with the activating solution at ambient temperature until reaching homogenous texture of the paste. The mixture was molded in polypropylene containers (50 ml) which were sealed and then subjected to curing at

40°C±3 for curing periods of 1 week, 1 month or 3 months.

2.2 Characterization techniques

The structural evolution of the geopolymeric products was monitored using XRD (Diffractometer D5000, SIEMENS) and FTIR measurements (BRUKER Vector 22). Samples for XRD and FTIR measurements were ground manually using mortar and pestle. FTIR samples were prepared by mixing 2 -5 mg of the ground sample with 100 mg dry KBr, and then pressed into pellets (French Press LCAD cell, BLA, type: C2P1). Samples of the starting materials, metakaolin and $NaNO_3$, were prepared in a similar manner. The FTIR spectra were normalized with respect to the integrated intensity in 900-1300 cm^{-1} range, which is attributed to the asymmetric stretching vibration of T-O-T (T = Al, Si) bonds. Normalization by sample weight was performed as well, and yielded similar results. The XRD spectra were normalized with respect to the quartz diffraction line at $2\theta=25.4°$ which was observed in all diffraction patterns. Quartz is present as an impurity in MK, and remains unaltered throughout the geopolymerization process.

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

SEM images (not presented in this paper) 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 hours and coating with Au.

3. Results & Discussion

The effect of nitrates on the activating process was initially studied in the most alkali environment (d=5.50, $[OH^-]\approx9M$) by comparing nitrate bearing geopolymer mixes to nitrate-free mixes. The evolution of the various phases in the nitrate bearing geopolymers was further studied by using activating solutions of different alkality.

3.1 Activation at a low dilution factor (high alkali concentration) - <u>d=5.50</u>

Activation of MK with highly alkali solutions (d=5.50) yielded geopolymeric matrices which consisted of amorphous and crystalline phases.

Figure 1 presents the diffraction patterns of geopolymers prepared with and without nitrates at d=5.50 after one month of curing at 40ºC. The diffraction pattern of the raw MK is shown as a reference.

The main diffraction peaks in XRD pattern of the nitrate-bearing samples are associated with nitrate-sodalite ($Na_8Al_6(SiO_4)_6(NO_3)_2$ (Powder Diffraction File #04- 009-1879) (Figure 1, trace 3). In addition, signals associated with nitrate-cancrinite ($Na_8Al_6(SiO_4)_6(NO_3)_2 \cdot 4H_2O$, (Powder Diffraction File #00-038-0513) can be noticed as well. The presence of these two phases indicates that nitrate ions were incorporated within the crystalline phases in the geopolymeric matrix. The diffraction pattern of the reference samples, without nitrate, was attributed to zeolite A ($Na_{96}Al_{96}Si_{96}O_{384}\cdot216H_2O$, PDF #00-039-0222) and faujasite ($Na_2Al_2Si_{2.4}O_{8.8}\cdot6.7H_2O$, PDF #00-012-0246) (Figure 1, trace 2).
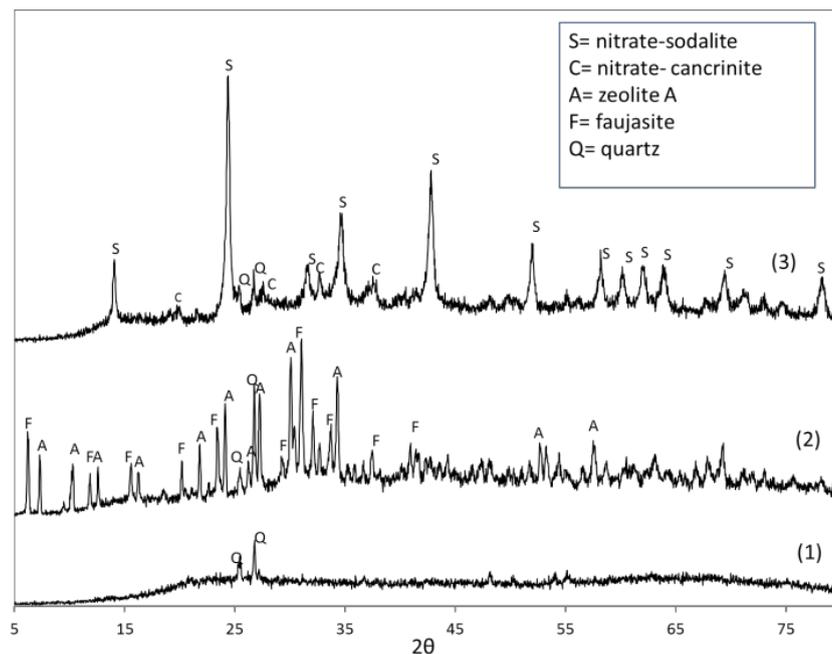
Figure 1: XRD patterns of (1) MK raw material, and geopolymerization products after 1 month of curing with NaOH (*d*=5.50) (2) without NaNO3, and (3) in presence of NaNO3.

The FTIR absorbance spectra were in agreement with the XRD results: Figure 2 shows FTIR spectra of the same geopolymerization products after one month of curing. The asymmetric stretching vibration of T-O-T bonds (T= Si, Al) shifted from a frequency of 1092 cm^{-1} in the raw material (MK) to 990 cm^{-1} in the geopolymeric matrices. This frequency has been associated with the amorphous geopolymeric phase, as well as with zeolites and sodalites (Fernandez-Jimenez et al. 2008, Barnes et al. 1999).

In addition, the symmetric stretching band, which appeared at 798 cm^{-1} in MK, is no longer observed following the geopolymerization process. In the nitrate free sample, four bands were observed in the 500-800 cm^{-1} range which is attributed to symmetric stretching of T-O-T bonds. Two bands at 556 cm^{-1} and 671 cm^{-1} are associated with zeolite A (Demortier et al. 1999), and two bands at 695 cm^{-1} and 746 cm^{-1} are associated with faujasite. In the nitrate-bearing sample, vibration bands at 661 and 730 cm^{-1}, which were previously assigned to the symmetric T-O-T stretching vibrations of the sodalite framework in carbonate-sodalite systems, were observed (Barnes et al. 1999). Based on the XRD results and the relatively high nitrate concentration in this sample we can conclude that the same absorbance bands are due to the framework of nitrate-sodalite.

The absorbance bands at 1383 cm^{-1} and 1415 cm^{-1}, which were observed in the spectrum of the nitrate-bearing geopolymer sample, are due to the symmetric vibration of the nitrate anion (Buhl 1996). The band at 1383 cm^{-1} can also be observed in FTIR spectra of NaNO3, and has been reported in spectra of nitrate sodalite (Buhl 1996). The non-equivalent arrangement of the nitrate anions in the hexagonal channel of the cancrinite framework causes splitting of this band, resulting in an additional absorbance at 1415 cm^{-1} (Buhl et al. 2000(a), Buhl et al. 2000(b)). The appearance of this band in the spectrum of the nitrate-bearing geopolymer sample is a clear indication to the formation of nitrate cancrinite.
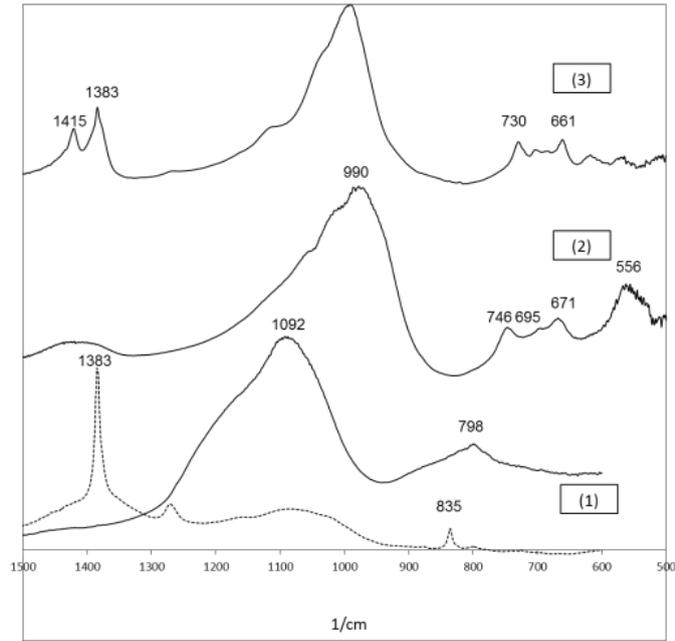
Figure 2: FTIR spectra of (1) raw materials (solid line-MK, dashed line-NaNO3), and geopolymerization products after 1 month curing with NaOH (d=5.50), (2) without NaNO3, and (3) in presence of NaNO3

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 nitrate-free 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 3 shows that the increase in compressive strength was more rapid in the presence of nitrate compared with the corresponding nitrate-free samples. The compressive strength of nitrate-bearing samples reached a value of 9.0±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 nitrate-free 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 (**Error! Reference source not found.**). However, due to the addition of NaNO3 to the activation solution, the Na2O:Al2O3 ratio in the nitrate-bearing samples was higher than in the corresponding nitrate-free samples. The Na2O:Al2O3 ratio may influence geopolymerization kinetics and product distribution
(Ofer-Rozovsky et. al, 2016). Moreover, nitrate anions (NO_3^-) are known to have a structure forming ability, which may also enhance the reactions rates (Kumar et al. 1996, Desbats-Le Chequer C, Frizon F, 2011). Thus, the higher rate of strength development in the nitrate-bearing system is 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.
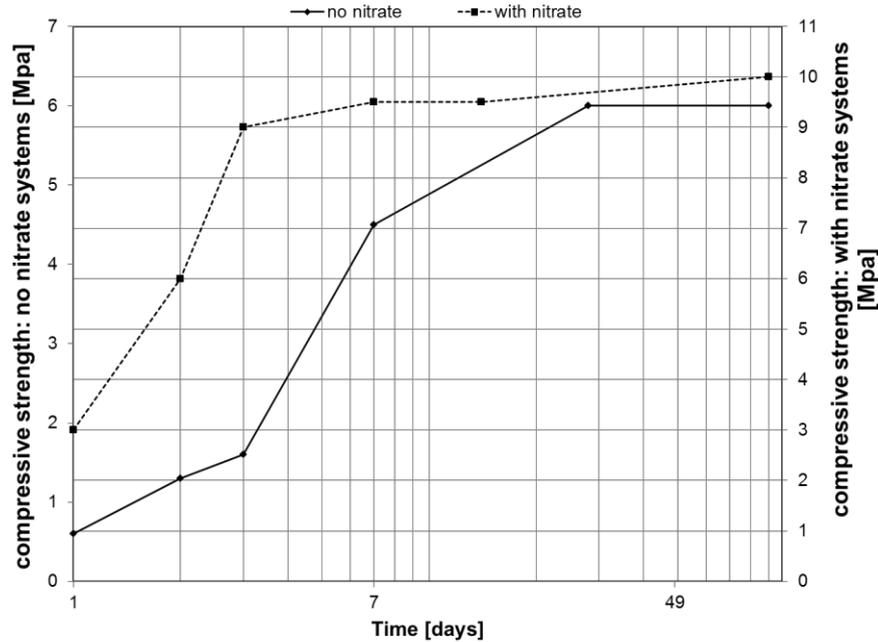
Figure 3: Development of compressive strength of geopolymers activated at *d*=5.50 without nitrate (solid line, left vertical axis) vs. geopolymers activated in presence of nitrate (dashed line, right vertical axis) presented in logarithmic scale (base 10).

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

The formation of crystalline phases within the nitrate bearing geopolymers prepared by highly alkali activating solutions (*d*=5.50) was very rapid. At this concentration, diffraction lines indicating the presence of crystalline phases were observed already after one day at 40^OC. The diffraction pattern obtained after 1 week of curing was very

similar to the one obtained after three months (Figure 4), indicating that little change had occurred during this period. Activation of MK by solutions having lower alkality and higher water content (i.e. *d* values of 9.15, 13.75, 27.50), both of which are known to retard the geopolymerization process (Swaddle 2001, Rahier et al. 2007), was investigated in order to follow the reaction steps and to elucidate the structural evolution, mainly in nitrate bearing geopolymers.

The diffraction patterns of nitrate-bearing samples prepared using activation solutions of intermediate alkality (*d* = 9.15, 13.75, (Figure 4)) indicated the formation of zeolite A in addition to an amorphous phase (wide hump centered around $2\theta=30^O$) after one week of curing. When an activating solution of *d*=9.15 was used, faujasite and nitrate sodalite were also detected after 1 month of curing. A clear indication of nitrate cancrinate formation was only observed after 3 months of curing. At lower alkality (*d* = 13.75), the first indications of nitrate sodalite formation were observed at a later time, after 3 months of curing. Nitrate cancrinate formation was not yet detected by XRD at this stage. Zeolite A was the only crystalline phase observed at the least alkali environment (*d*= 27.50), even after 3 months of curing at 40°C. The absence of nitrate-bearing crystalline phases was most probably due to the relatively low dissolution-condensation rate at these conditions ([OH^-]=2M) and the relatively low concentration of nitrate ([NO3]=0.5M).
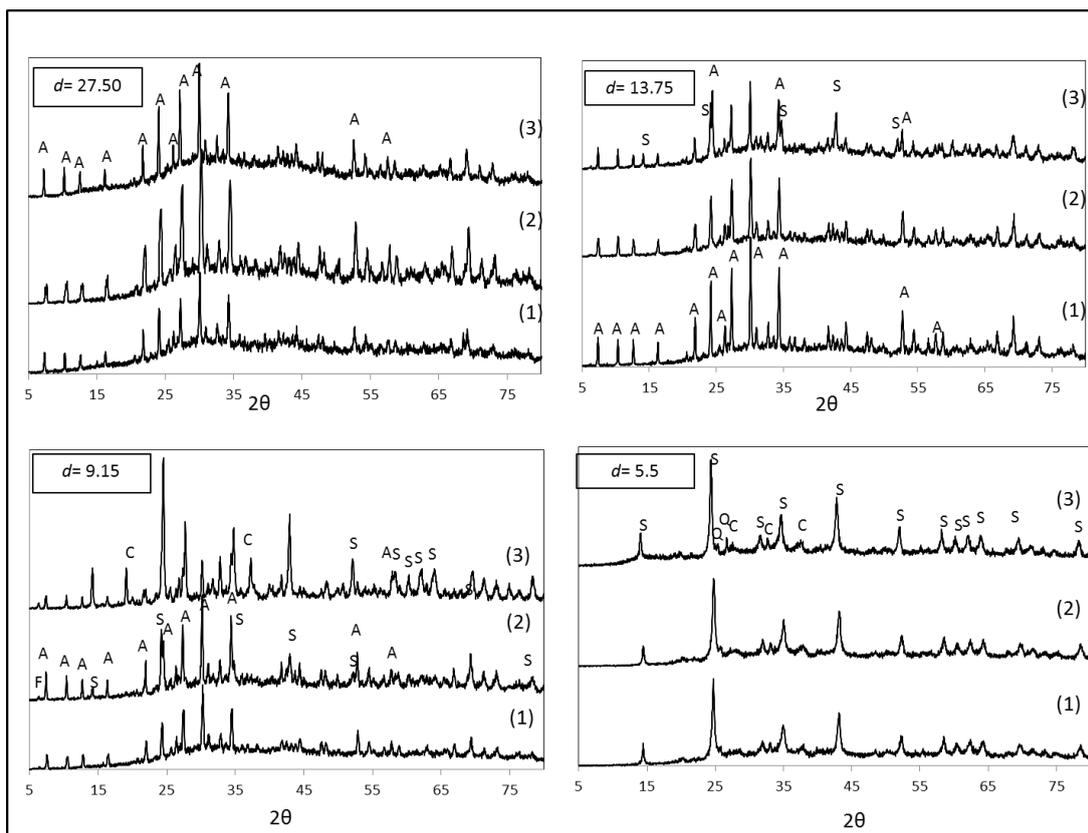
Figure 4: XRD patterns of geopolymerization products after activation with NaOH in presence of NaNO3 (d=27.50, 13.75, 9.15 and 5.50) after curing period of (1) one week, (2) one month and (3) three months. A- zeolite A, F- faujasite, S- nitrate sodalite, C-nitrate cancrinite, Q- quartz.

The FTIR absorbance spectra of the samples generated at d=9.15, 13.75 and 27.50 after 3 months of curing are presented in Figure 5. The main absorbance peak which is due to the T-O-T asymmetric stretching is observed at 990 cm^{-1} for the three samples, as was observed at the more alkaline conditions (Figure 2). The features in the 500-800 cm^{-1} range of the spectra, which is attributed to the symmetric stretching of T-O-T groups, correlate well with the XRD data. The absorbance bands observed for the sample prepared at the least alkali conditions (d= 27.50) at 556, 671 cm^{-1} indeed belong to zeolite A. The sample prepared at d= 13.75 had absorbance bands due to zeolite A at the same frequencies, as well as bands at 661, 730 cm^{-1} due to nitrate-sodalite. In addition, a small shoulder at 1425 cm^{-1} appeared indicating the formation of nitrate cancrinite, although this phase was not yet clearly identified from XRD data. The absorbance band at 1420 cm^{-1} is more pronounced in the spectrum of sample prepared at d=9.15, in agreement with the clear identification of diffraction lines due to this phase in the XRD data. The presence of nitrate cancrinate in this sample is also indicated by a set of bands at 575-578 cm^{-1}, 622-624 cm^{-1}, 682 cm^{-1}, and 820 cm^{-1} (Buhl et al. 2000). In the asymmetric stretching region, bands with the maxima at 1037 cm^{-1} and 1123 cm^{-1} assigned with nitrate-cancrinite appeared besides (Buhl et al. 2000).
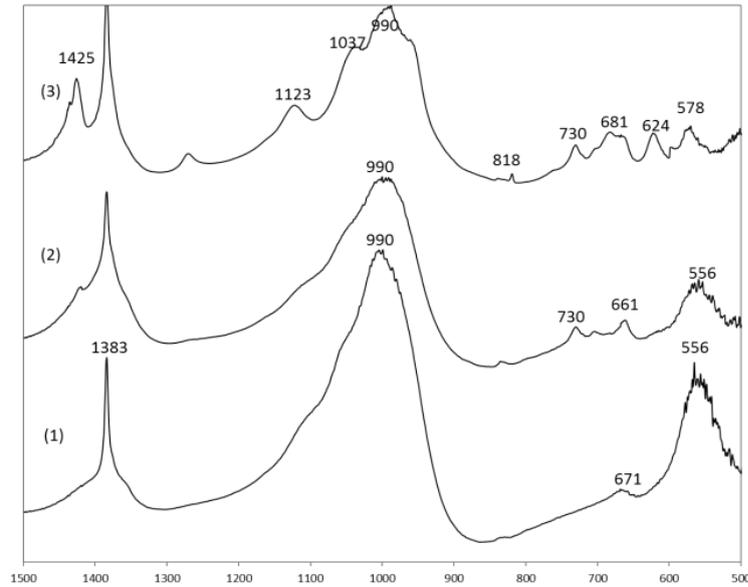
Figure 5: FTIR spectra of geopolymerization products after activation with NaOH in presence of NaNO3 after three months of curing at different *d*; (1) *d*=27.50, (2) *d*= 13.75, (3) *d*= 9.15.

The results obtained for samples prepared at low and intermediate alkalinity clearly demonstrate the evolution of crystalline phases in nitrate bearing geopolymers. The first phase to crystallize from the amorphous geopolymer gel is zeolite A, which is followed by the appearance of faujasite, as reported for nitrate-free geopolymers as well (Hajimohammadi et al. 2011). The presence of nitrate ions induces further transformation of these zeolites to form nitrate-bearing phases, first nitrate-sodalite and then nitrate-cancrinite. This sequence of phase evolution in geopolymers, which is presented in Figure 6, is in agreement with the phase sequence suggested for nitrate cancrinate formation at hydrothermal conditions (Liu 2007).
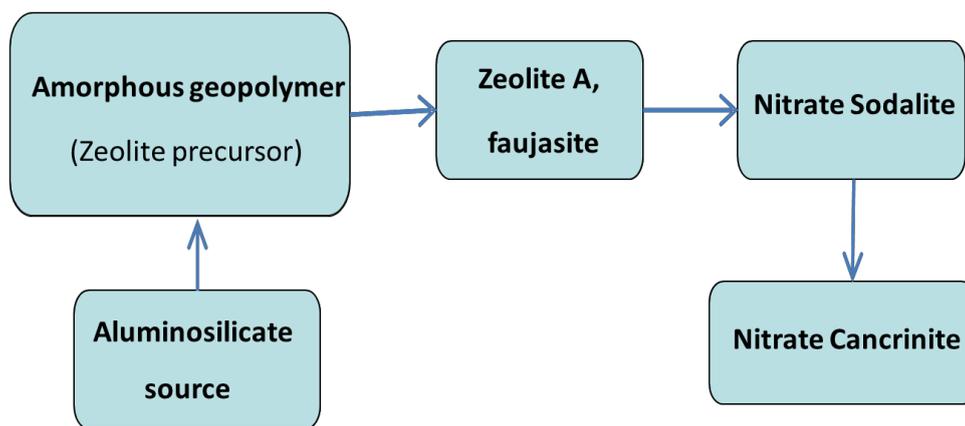

Figure 6: Phases development during geopolymerization at moderate temperatures in the presence of nitrate anion

4. Conclusions

The presence of nitrate has a noticeable effect on the composition and phase distribution of low-silica geopolymers. While in nitrate-free systems zeolite A and faujasite were crystallized from the amorphous geopolymer, two nitrate-bearing feldspathoids, nitrate sodalite and nitrate cancrinite, were formed in the geopolymers generated in the presence of nitrate anion. These crystalline phases are promising candidates for the immobilization of hazardous species from waste streams containing nitrate salts, such as nuclear waste streams.

References

BAKHAREV, T., 2005. *Resistance of geopolymer materials to acid attack.* Cement and Concrete Research, **35**(4): p. 658-670

BARNES, M., ADDAI-MENSAH, J. and GERSON, A., 1999. *A methodology for quantifying sodalite and cancrinite phase mixtures and the kinetics of the sodalite to cancrinite phase transformation.* Microporous and Mesoporous Materials, **31**(3), pp. 303-319.

BERNAL, S.A., et al., , 2011. *Effect of binder content on the performance of alkali-activated slag concretes.* Cement and Concrete Research. **41**(1): p. 1-8.

BROUGH, A., KATZ, A., SUN, G., STRUBLE, L., KIRKPATRICK, R. and YOUNG, J., 2001.
Adiabatically cured, alkali-activated cement-based wasteforms containing high levels of fly ash - Formation of zeolites and Al-substituted C-S-H. Cement and Concrete Research, **31**(10), pp. 1437- 1447.

BUHL, J. and LONS, J., 1996. *Synthesis and crystal structure of nitrate enclathrated sodalite Na- 8[AlSiO4](6)(NO3)(2).* Journal of Alloys and Compounds, **235**(1), pp. 41-47.

BUHL, J., STIEF, F., FECHTELKORD, M., GESING, T., TAPHORN, U. and TAAKE, C., 2000(a).
Synthesis, X-ray diffraction and MAS NMR characteristics of nitrate cancrinite Na-7.6[AlSiO4](6)(NO3)(1.6)(H2O)(2). Journal of Alloys and Compounds, **305**(1-2), pp. 93-102.

BUHL, J., TAAKE, C., STIEF, F. and FECHTELKORD, M., 2000(b). *The crystallisation kinetics of nitrate cancrinite Na-7.6[AlSiO4](6)(NO3)(1.6) (H2O2)(2) under low temperature hydrothermal conditions.* Reaction Kinetics and Catalysis Letters, **69**(1), pp. 15-21.

DEMORTIER, A., GOBELTZ, N., LELIEUR, J. and DUHAYON, C., 1999. *Infrared evidence for the formation of an intermediate compound during the synthesis of*

zeolite Na–A from metakaolin . International Journal of Inorganic Materials, **1**, pp. 129-134.

Desbats-Le Chequer C, Frizon F, 2011. *Impact of sulfate and nitrate incorporation on potassium- and sodium-based geopolymers: Geopolymerization and materials properties.* J Mater Sci 46:5657–5664. doi: 10.1007/s10853-011-5516-6

DE-SILVA, P. and SAGOE-CRENSTIL, K., 2009. *The Role of Al2O3, SiO2 and Na2O on the Amorphous to Crystalline Phase Transformation in Geopolymeric Systems.* Journal of the Australian Ceramic Society, **45**(1), pp. 63-71.

FERNANDEZ-JIMENEZ, A., I. GARCIA-LODEIRO, and PALOMO, A., 2007, *Durability of alkali-activated fly ash cementitious materials.* Journal of Materials Science. **42**(9): p. 3055-3065.

FERNANDEZ-JIMENEZ, A., MONZO, M., VICENT, M., BARBA, A. and PALOMO, A., 2008. *Alkaline activation of metakaolin-fly ash mixtures: Obtain of Zeoceramics and Zeocements.* Microporous and Mesoporous Materials, **108**(1-3), pp. 41-49.

HAJIMOHAMMADI, A., PROVIS, J.L. and VAN DEVENTER, J.S.J., 2011. T*ime-resolved and spatially-resolved infrared spectroscopic observation of seeded nucleation controlling geopolymer gel formation.* Journal of colloid and interface science, **357**(2), pp. 384-392.

KOMNITSAS, K. and ZAHARAKI, D., 2007. *Geopolymerisation: A review and prospects for the minerals industry.* Minerals Engineering, **20**(14), pp. 1261-1277.

Kumar, R., Bhaumik A, Ahedi RK, Genapathy S , 1996. *Promoter-induced enhancement of the crystallization rate of zeolites and related molecular sieves.* Nature 381:298.

LIU, Q. and NAVROTSKY, A., 2007. *Synthesis of nitrate sodalite: An in situ scanning calorimetric study.* Geochimica et Cosmochimica Acta, **71**(8), pp. 2072-2078.

Ofer-Rozovsky, E., Arbel Haddad, M. Bar Nes, G. Katz, A. 2016. T*he formation of crystalline phases in metakaolin-based geopolymers in the presence of sodium nitrate*, J. Mater. Sci. 51 (2016) 4795– 4814. doi:10.1007/s10853-016-9767-0.

PROVIS, J.L., LUKEY, G.C. and VAN DEVENTER, J. S. J., 2005. D*o Geopolymers Actually Contain Nanocrystalline Zeolites? A Reexamination of Existing Results.* Chemistry of Materials, **17**(12), pp. 3075-3085.

PROVIS, J.L. and VAN DEVENTER, J.S.J., 2007. *Geopolymerisation kinetics. 2. Reaction kinetic modelling.* Chemical Engineering Science, **62**(9), pp. 2318-2329.

RAHIER, H., WASTIELS, J., BIESEMANS, M., WILLLEM, R., VAN ASSCHE, G. and VAN
MELE, B., 2007. *Reaction mechanism, kinetics and high temperature transformations of geopolymers* Journal of Materials Science, **42**, pp. 2982-2996.

SWADDLE, T.W., 2001. *Silicate complexes of aluminum(III) in aqueous systems.* Coordination Chemistry Review, **219**, pp. 665-685.

Zuhua Zhang, Xiao Yao , and H. Zhu, , 2010. *Potential application of geopolymers as protection coatings for marine concrete II. Microstructure and anticorrosion mechanism.* Applied Clay Science. **49**: p. 7-12.