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Impact of sulfate and nitrate incorporation on potassium- and sodium-based geopolymers: geopolymerization and materials properties

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Abstract One of the most promising applications of geopolymers is their use as a waste encapsulating matrix. These binders are indeed compatible with aqueous waste streams and capable of activating several chemical and physical immobilization mechanisms for a wide range of inorganic waste species. Several works have investigated the immobilization of cations, mainly heavy metals or radioactive wastes, but very few studies have taken counterions, namely anions, into account. This work is an experimental investigation of the impact of anions with different valences on the material properties in regard to the requirements of an industrial process at ambient or slightly elevated temperature, including the setting time, maximum achievable compressive strength, or resistance to leaching. The modifications caused by the introduction of monovalent and divalent anions, such as sulfate and nitrate, are also evaluated in term of mineralogy, porosity, and microstructure. Their immobilization appears to be related to the progress of the geopolymerization reaction. Moreover, depending on the alkali ions used in the activation solution, the anionic species considered may also enhance the precipitation of some zeolites.

Introduction

Geopolymers are a class of largely X-ray amorphous three-dimensional aluminosilicate binder materials, usually synthesized by reaction of an aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution, cured at ambient or slightly elevated temperature [1]. These low-cost binders, compatible with aqueous waste streams, were largely considered as immobilizing materials for heavy metals or low-level radioactive wastes [2–6]. Geopolymerization is a complex process involving dissolution of solid reactants, hydrolysis of the dissolved species, and condensation of the geopolymer itself [7]. In a geopolymer, the chemistry and nature of the final products are controlled by a number of factors among which the initial mix formulation and curing conditions—i.e. temperature, pressure and duration—are of primary importance. These experimental conditions are also key parameters in the transformation of geopolymers into crystalline materials, mainly zeolites [8–15]. Starting from these observations, some authors suggested that geopolymers may be viewed as amorphous analogs of zeolites [16, 17] or that, from a thermodynamic point of view, geopolymers can be considered metastable with regard to zeolites [18].

The main parameters considered are:

- the nature of the alkali ion. LaRosa et al. [19] reported that, with fly ash starting materials, the formation of zeolite P and zeolite Y are enhanced by sodium activation, unlike potassium activation which did not lead to zeolite crystallization. This corroborates the structure-forming ability of sodium in comparison to the larger structure-breaking cations [20].
- the nature and concentration of alkali activators. It has been shown that alkali silicate activators seem to produce fewer or smaller crystals than alkali hydroxide activators [12]. The concentration of alkali activating solutions also has a significant role. For example, Murayama et al. [10] have shown that the amount of

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zeolite P and hydroxysodalite, formed by sodium activation of coal fly ashes, varies with the sodium concentration in the activating solutions.

- the water content. The amount of water required in the synthesis of zeolite is much greater than necessary for geopolymer formation [21]: amorphous sodium-based geopolymers tend to crystallize into zeolite of the faujasite family when exposed to pure water or even salt-containing solution [13].
- the temperature. Although high temperatures (>100 °C) and pressures are generally considered necessary to form zeolites, some of them may be obtained at lower temperature [21]. Usually the medium-term phase stability of geopolymer systems is studied between 40 [22] and 85 °C [23]. Depending on the mix parameters used, the secondary zeolite formation is detected after few hours to several months [22, 23].

Surprisingly, despite the fact that aqueous waste streams may contain various anionic species [24] and that it is well established that some anionic species like PO_4^{3-}, SO_4^{2-}, or NO_3^- promote the formation of zeolites [25], very few studies have addressed the effects of anions on the formation and evolution of geopolymer systems [26–28] and, to the authors' knowledge, only one from the standpoint of geopolymer/zeolite secondary transformation [29]. These studies focus mainly on the impact of chloride, carbonate, and phosphate anions on early-age and strength properties.

The aim of this work is to investigate the impact of sulfate and nitrate incorporation in alkali-activated metakaolin systems on the setting time and mechanical properties of the binders. The geopolymer systems obtained are also investigated in term of geopolymer/zeolite secondary transformation, and the mineralogical and microstructural evolution of the mixtures. In this study, the chosen variables are the chemical nature of the alkali, and the chemical nature and concentration of the anionic species.

Experimental methods

Materials

In order to focus on a model system and avoid the precipitation of calcium silicate hydrate phases mixed with geopolymeric materials [30], the choice was made to synthesize metakaolin-based geopolymer paste. This product was purchased under the brand name of Pieri Premix MK from Grace Construction Products. The chemical composition of metakaolin determined by X-ray Fluorescence (XRF) can be found in Table 1. X-ray Diffraction (XRD) analysis showed that the metakaolin contained anatase, kaolinite, and quartz as impurities. The Brunauer–Emmet–Teller (BET) specific surface area was 19.9 m^2/g and the mean particle size (d50) determined by laser granulometry was 5.9 µm.

Table 1 Chemical composition of metakaolin used in this study

	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	K_2O	Na_2O	MgO	L.o.I[a]
Weight %	54.4	38.4	0.10	1.27	1.6	0.62	<0.2	<0.2	1.90

[a] Loss on ignition

Alkali hydroxide activating solutions were prepared by dissolving NaOH, KOH (Prolabo, Rectapur, 98%) pellets in Milli-Q water, with all containers kept sealed to minimize contamination by atmospheric carbonation. Amorphous silica provided by Rhodia (Tixosil 331) with a mean particle size of 9.19 µm was added to the mix. Sulfate and nitrate ions were mixed in the activating solution starting from potassium nitrate, potassium sulfate, sodium nitrate, or sodium sulfate pellets (Prolabo, Rectapur, 98%).

Geopolymer synthesis and hydrothermal treatment

The five series of mixtures prepared are summarized in Table 2 in terms of molar ratios. Each set incorporates the same SiO_2, Al_2O_3, and M_2O content with $SiO_2/Al_2O_3 = 3.6$, $Al_2O_3/M_2O = 1$, which is a typical composition for metakaolin geopolymers reported in the literature. The Al_2O_3/M_2O ratio was adjusted to 1 to maximize the geopolymerization reactions [31] and mechanical properties [32]. This geopolymer composition is also known to be composed of a stable amorphous phase with no tendency toward phase transformation at moderate curing temperatures during 6 months [22]. The water content varies among the formulation mix in order to reach good fluidity of the geopolymer immediately after casting and to avoid bleeding after setting, but remains low enough to be representative of geopolymer materials: sodium-based geopolymers were therefore mixed with $H_2O/M_2O = 12$ and potassium-based geopolymers with $H_2O/M_2O = 10$.

Mixing was performed in two steps. First, alkali silicate solutions were prepared by dissolving and mixing amorphous silica in alkali solution for 30 min. The alkali solutions were prepared by dissolution of appropriate pellets (alkali hydroxide, alkali sulfate or alkali nitrate) in Milli-Q water. During the second step, geopolymer samples were prepared by mixing metakaolin and alkali solution. Mixing was performed at low speed for 1 min and at high speed for 2 min in a standard laboratory mixer (European Standard EN 196-1). The material was then transferred to 4 × 4 × 16 cm PTFE molds, vibrated for a few seconds, and sealed from the atmosphere. Samples

Table 2 Mix formulations used in this study in term of molar ratios

Sample	Chemical nature of alkali used	SiO_2/Al_2O_3	M_2O/Al_2O_3	H_2O/M_2O	MOH/M_2SO_4	MOH/MNO_3
Na ref	Na	3.6	1	12	–	–
K ref	K	3.6	1	10	–	–
Na S 60	Na	3.6	1	12	60	–
Na S 30	Na	3.6	1	12	30	–
Na S 10	Na	3.6	1	12	10	–
K S 60	K	3.6	1	10	60	–
K S 30	K	3.6	1	10	30	–
K S 10	K	3.6	1	10	10	–
Na N 20	Na	3.6	1	12	–	20
Na N 6	Na	3.6	1	12	–	6
K N 20	K	3.6	1	10	–	20
K N 6	K	3.6	1	10	–	6

were cured for 1 day at 20 °C and at atmospheric pressure before removal from the mold and stored in an airtight bag at room temperature and pressure for 28 days. After this period, the samples were divided into two parts: one dedicated to mechanical and leaching tests, the other one dedicated to the hydrothermal treatment, consisting of placing the samples in sealed conditions in an oven at 90 °C for a given period. Some samples are removed after 5 days for testing, while the remaining samples were tested after 10 days of hydrothermal treatment.

Analytical methods

The setting time was measured with a Vicat needle as per European standard EN 196 3. Compressive strength measurements were conducted as per European standard EN 196 1 on samples of geopolymer paste, using a 3R testing machine.

Laboratory X-ray powder diffraction (XRPD) patterns were recorded in a Bragg–Brentano X'Pert Pro diffractometer (PANanalytical) using a copper anode: $\lambda K\alpha 1 = 1.54056$ Å generated at 40 mA and 40 kV. Samples were scanned from 5° to 60° 2θ, in continuous mode. The step size was 0.017° with a time per step of 200 s and a scan speed of 0.01°/s.

Leaching behavior was studied on material suspensions prepared by mixing crushed non hydrothermally treated geopolymer paste samples (<100 µm) with ultrapure water (liquid to solid ratio: 9 mL g^{-1}) and stirring for 24 h, 7 days, and 28 days. In some experiments, complete solution renewal was performed at the end of these periods. Ionic concentrations were determined by ion chromatography on a Dionex DX 500.

Microstructure evolution was investigated using a Philips XL PW6631/01 scanning electron microscope (SEM) equipped with an energy-dispersive analyzer (EDS). These observations were conducted using a secondary electron detector on fracture surfaces which had been carbon coated to prevent charging.

Results and discussion

Setting time

The impact of the chemical nature of the alkali used and of the chemical nature and concentration of anionic species on the setting time are summarized in Table 3. Tests were repeated twice and values indicated are the mean values.

The results clearly show that the setting time of a geopolymer material is dependent on the alkali used for its synthesis. For each given activation solution composition, the greater the basicity of the alkali hydroxide, the slower the setting. This is in agreement with previous work [5], for example.

The impact of the anionic species varies with the alkali considered:

– Although sulfate ions appear to have almost no impact on sodium-based geopolymers, the setting time of

Table 3 Setting time measurements conducted on Vicat apparatus as function of anions and alkalis used for geopolymer synthesis

Sample	Na ref	Na S 60	Na S 30	Na S 10	Na N 20	Na N 6
Setting time (h)	3h12	3h03	3h05	3h48	4h19	5h24
Sample	K ref	K S 60	K S 30	K S 10	K N 20	K N 6
Setting time (h)	12h30	7h14	5h58	6h57	5h23	5h52

The reported result is the min value of two samples with an experimental error of ±15 min potassium-based geopolymers is reduced by 5–6 h. No clear effect of sulfate concentration was noted.

- In the case of sodium-based geopolymers, nitrate ions act as retarders: the higher the concentration, the slower the setting. When added to potassium-based geopolymers, nitrates accelerate the setting, with few variations induced by their concentration.

As previously noted [27], increasing the solution ionic strength through inorganic salts, which is known to enhance or exert no influence on the dissolution of aluminosilicates, should be expected to accelerate or have no effect on the geopolymeric gel formation, i.e. setting time. This was not always the case here: the solidification process is controlled not only by the kinetics of mineral dissolution, but also by polycondensation steps. As sodium-based geopolymers appear to be less disturbed by the presence of anionic species than potassium-based geopolymers, the results indicate that the structure-making ability of smaller cations in comparison to larger ones [33] should also be taken into account. In other words, large alkalis that require higher concentration for activation are more susceptible to the presence of alkalis.

Mechanical properties

The compressive strengths of the five series of geopolymers prepared are plotted in Fig. 1. The results highlight several trends. First, whatever the anions considered, the potassium-based geopolymers exhibit globally better mechanical properties than sodium-based samples and these properties improve with time. Second, after 28 days of curing the introduction of anions in the activating solutions seems to increase the compressive strength of the geopolymers in comparison to the reference materials. This point is more marked for potassium-based materials. Concerning sulfate ions, a larger amount in sodium-based geopolymers slightly increases the strength of the material, while in potassium-based geopolymers the behavior was exactly the opposite. For nitrate ions, the global behavior is less clear. In sodium-based geopolymers, the mechanical properties seem to be diminished by increasing nitrate concentration. In potassium-based geopolymers, this drop is detected after 7 days of curing, but the compressive strengths reached after 28 days of curing for nitrate containing materials are similar to those of reference material without anions. In every case, the microstructure was dense (Fig. 2) and no crystalline phases were detected either during SEM observation nor by XRD.

Leaching experiments

The results of the leaching experiments are presented in Table 4 in terms of the percentage of initial species introduced during the geopolymer synthesis.

At these concentrations, the introduction of anions in the activating solutions leads to an increase in alkali leaching, the larger the amount of anions added, the greater the leaching. This means that alkalis ions are less incorporated in the material in presence of anions species. This could be related to a modification in the raw materials dissolution step or in the gel solidification step process, which is also consistent with the modification of setting time. Furthermore, the amount of anions released during this experiment was quite stable around 14.1% for sulfate ions for both alkalis, and slightly less for nitrate ions (14.2% and 12.7% for sodium and potassium, respectively).

Geopolymer/zeolite secondary transformation

From a thermodynamic standpoint, geopolymers can be considered as metastable with regard to zeolites [18]. The initial mix formulation and curing conditions are of primary importance for the chemistry and nature of the final products as well as for the transformation of geopolymers into crystalline materials [8]. In this study, no changes in the geopolymers' structure are detected between samples when they were not hydrothermally treated: Fig. 3 shows diffraction patterns of sodium and potassium-based geopolymers after storage for 28 days in an airtight bag at room temperature. Two major features may be observed on these diffraction diagrams. First, a broad hump, centered around $2\theta = 27–29°$, is observed for all the materials

Fig. 1 Compressive strengths of geopolymers after 7 and 28 days of curing in airtight bag under atmospheric conditions. Three different measurements were realized and experimental dispersion is indicated on the graph

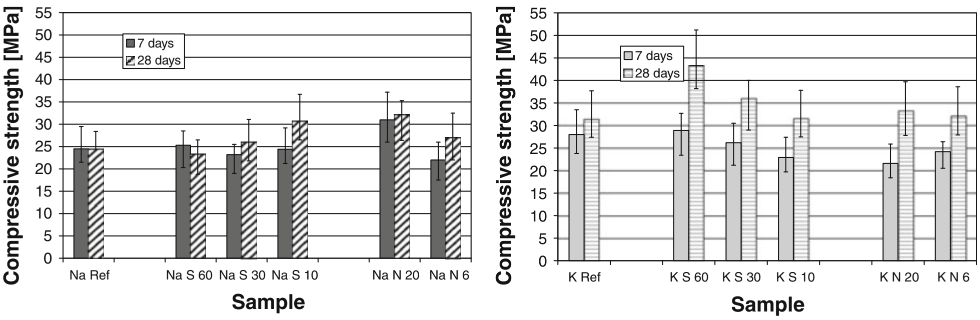
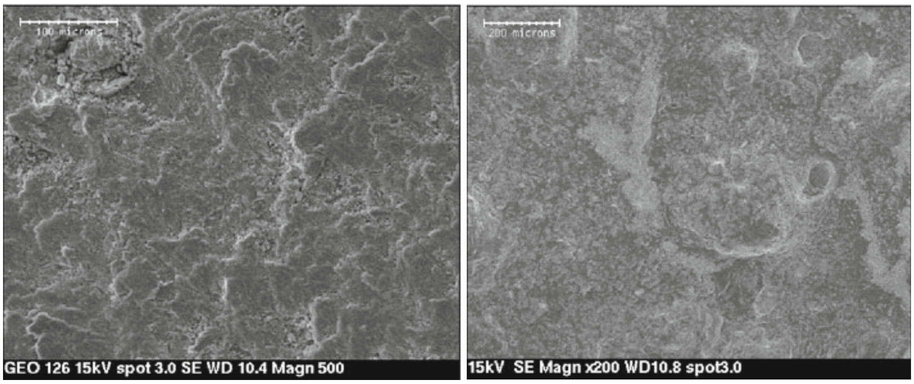


Fig. 2 SEM images of geopolymers containing anions after 28 days of curing in airtight bag. K S 30 sample after 28 days of curing. N S 6 sample after 28 days of curing



K S 30 sample after 28 days of curing N S 6 sample after 28 days of curing

Table 4 Leaching results on geopolymers after curing for 28 days. The relative accuracy of each measurement is 15%

Sample	Anions leached (%)		Cations leached (%)	
	SO_4^{2-}	NO_3^-	Na^+	K^+
Na ref	–	–	3.27	–
K ref	–	–	–	1.85
Na S 30	13	–	4.2	–
Na S 10	14.9	–	6	–
K S 30	14.4	–	–	2.2
K S 10	14.3	–	–	4.3
Na N 20	–	14.7	4.1	–
Na N 6	–	13.7	5.5	–
K N 20	–	12.8	–	2.2
K N 6	–	12.6	–	3.7

whether they are containing anions or not. That indicates a glassy or amorphous material and can be attributed to potential residual metakaolin and to geopolymers. Second, it appears from these results that the crystalline impurities within the metakaolin have not fully reacted since some quartz (JCPDS 00-046-1045), anatase (JCPDS 00-021-1272), and andalusite (JCPDS 01-083-1511) remain in the material after curing period. Potassium sulfate (JCPDS 01-072-0354) is also detected for high sulfate concentrations (K S 10). Nitrate or sulfate containing geopolymer present similar structure and mineralogy after the curing period.

However, the materials' behavior is quite different after hydrothermal treatment. Although high temperatures (>100 °C) and pressures may also be considered, the medium-term phase stability of geopolymer systems is generally studied at moderate temperature, usually in the range 80–90 °C [22, 23]. In agreement with previous findings, metakaolin systems with SiO_2/Al_2O_3 molar ratios of around 3.6 (with $M_2O/Al_2O_3 = 1$) are stable materials with no tendency—or at a least very low tendency—toward the amorphous/crystalline transformation [22] (Fig. 4). When anions are added to the system, this property changes depending on the chemical nature of the alkalis and anions used: zeolites can be formed even under moderate hydrothermal conditions (Table 5; Fig. 4). The overall behavior of geopolymers and of the zeolites formed strongly depends on the material compositions.

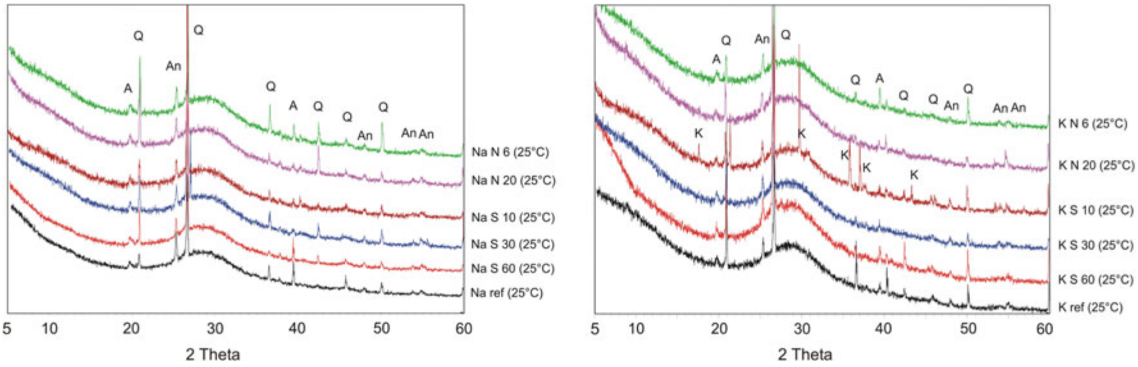


Fig. 3 Diffractograms of the four systems studied 28 days of curing in airtight bad at room temperature. Q quartz, An anatase, A andalusite, K potassium sulfate

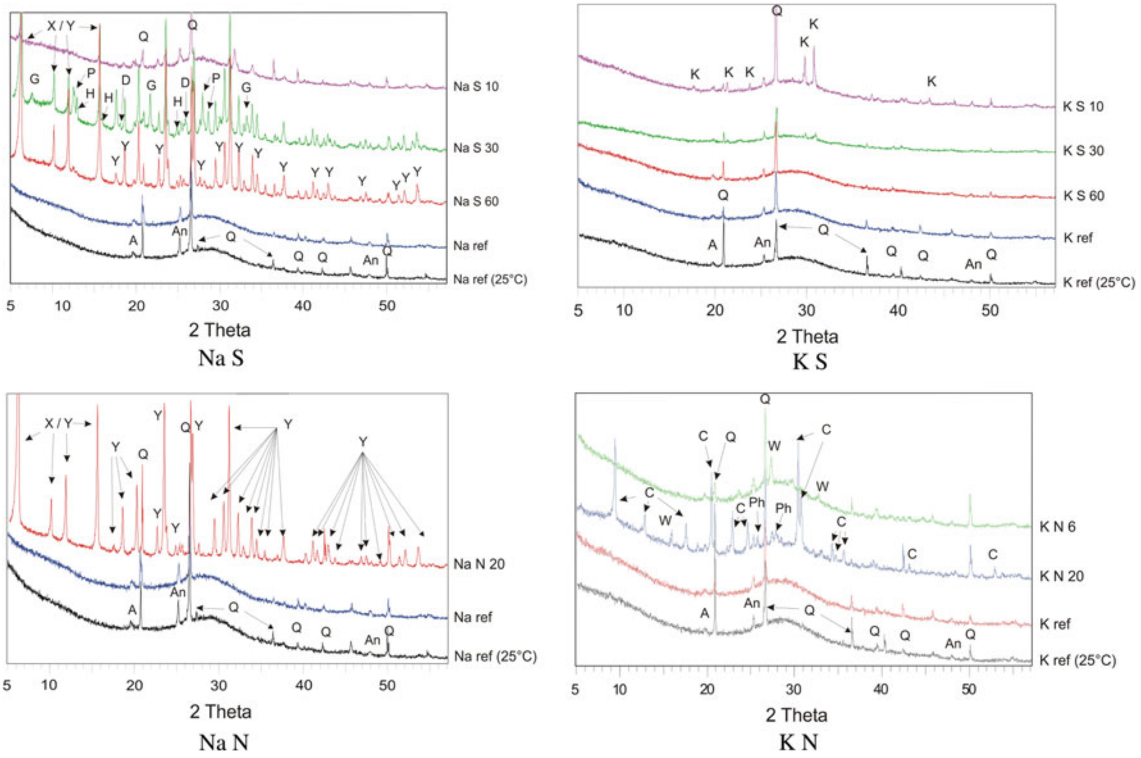


Fig. 4 Diffractograms of the four systems studied after 10 days under hydrothermal treatment at 90 °C in sealed conditions. *Q* quartz, *An* anatase, *A* andalusite, *C* chabazite, *Ph* philipsite, *W* zeolite W, *K* potassium sulfate, *X* zeolite X, *Y* zeolite Y, *G* gmelinite, *H* herschelite, *D* dachiardite, *P* zeolite P

Sodium-based geopolymers

The zeolites formed starting with sodium based geopolymers are:

- in sulfate materials (Fig. 5): zeolite X (JCPDS 01-072-2422), zeolite Y (JCPDS 00-038-0240), Gmelinite (JCPDS 00-038-0435), Hershelite (JCPDS 00-019-1178), Dachiardite (JCPDS 00-030-1149) and zeolite P (JCPDS 00-034-0524),
- in nitrate materials: zeolite X (JCPDS 01-072-2422) and zeolite Y (JCPDS 00-038-0240).

Table 5 Zeolites obtained from geopolymer samples under hydrothermal treatment at 90 °C in sealed conditions and identified by XRD experiments

Sample	Zeolites obtained at 90 °C	
	After 5 days	After 10 days
Na ref	None	None
K ref	None	None
Na S 60	X–Y	X–Y
Na S 30	X–Y-Gmelinite-Herschelite	X–Y-Gmelinite-Herschelite-Dachiardite
Na S 10	X–Y	X–Y
K S 60	None	None
K S 30	None	None
K S 10	None	None
Na N 20	X–Y	X–Y
K N 20	W-Chabazite-Phillipsite	W-Chabazite-Phillipsite
K N 6	W	W

In these systems, the introduction of anions enhances the geopolymer/zeolite secondary transformation, while the reference geopolymers remain stable. Sulfate ions produce a wider variety of zeolites than nitrate ions. This result can be explained in two ways. First, sulfate ions are better promoters of crystalline structure than nitrate ions [34]: due to the much higher hydration energy of sulfates, these anions can more effectively dehydrate the hydration layer of silicates, aluminates, and alkalis, then enhance the direct interactions between the monomers leading to more crystalline phases or a wider variety of crystalline phases. Second, a tertiary zeolite/zeolite transformation may also occur: zeolite X, for example, is known to be metastable with regard to zeolite P [21]: the nucleation of secondary zeolite phases occurs as the result of the arrangement and decomposition of the primary crystal lattice.

Geopolymer systems containing a very large amount of anions, such as Na S 10, for example, however, tend less to promote the formation of zeolites than lower concentrations. In fact, if external hydrated promoter species are

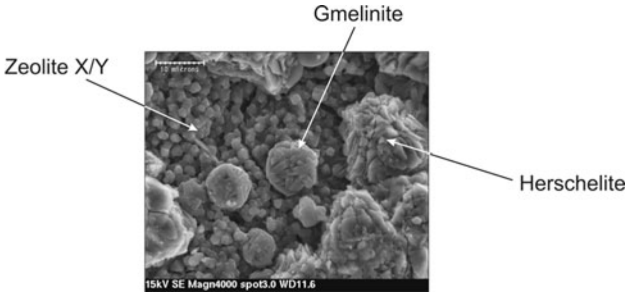


Fig. 5 SEM images of Na S 30 geopolymer after 10 days under hydrothermal treatment at 90 °C in sealed conditions

present in excessive quantities, the amount and size of hydrated ions may obstruct the self-assembly interactions between monomers [34]. As the size of the hydrated sulfate anion is larger than that of nitrate, the obstruction probably occurs at lower concentrations in systems containing sulfate than in systems containing nitrate. In other terms, sulfate ions are more effective in favoring the geopolymer/zeolite transformation than nitrate ions, but the range of effectiveness is narrower.

Potassium-based geopolymers

In sulfate systems, no zeolites are detected and potassium sulfate is even observed for high sulfate concentrations (K S 30 and higher). This result indicates that the threshold concentration above which hydrated anions may obstruct the geopolymerization reaction depends on the alkali. This can be explained in three ways:

- the structure-making ability of potassium, weaker than for sodium in silicate systems [33], is not high enough to compensate the perturbation induced by the addition of sulfate and to lead to zeolite formation.
- Sulfate anions are more easily hydrated in potassium-based geopolymers. First, the hydration sphere of potassium contains eight water molecules, which are less strongly bound than the 6–7 water molecules in the primary hydration sphere of sodium [35]. Second, water molecules, which are released as condensation of aluminosilicate oligomers proceeds during setting, will migrate into the ion hydration spheres. During this process, it will be more energetically favorable for sulfates to adsorb the released water molecules and for potassium to remain closely associated with oligomers or be incorporated into the geopolymeric binder. In other words, sulfate oxyanions are more easily hydrated in potassium-based systems and therefore more easily obstruct interactions between silicate and potassium anions at lower concentration.

In nitrate systems, some zeolites are formed, namely zeolite W (JCPDS 01-086-1110), Chabazite (JCPDS 01-085-0976), and Phillipsite (JCPDS 00-046-1427), but amorphous geopolymer always remains in the material. This result is in good agreement with the proposed mechanism. Nitrate anions exhibit lower hydration energy and are smaller than sulfates: this species is thus less sensitive to the nature of the alkali regarding their geopolymer/zeolites transformation-promoting ability. This ability is not sufficient to fully compensate the weak structure-making ability of potassium, however, and amorphous geopolymer remains in the materials. When the nitrate concentration increases significantly, fewer zeolites are formed, but zeolite W is always detected in the sample even for very high nitrate concentrations.

Conclusions

Anions that can commonly be found in aqueous waste streams, such as nitrates and sulfates, modify the properties of geopolymers. The setting time and mechanical properties vary slightly, although their evolutions suggest a change in geopolymerization reactions, probably related to the hydration energy of the anions introduced. Their leaching behavior is also changed and more alkalis are released from the materials when these anions are added to the system. The proportion of sulfates and nitrates leached remains stable over the composition range investigated in this study.

The major changes are related to the secondary transformation of geopolymers into zeolites under moderate hydrothermal treatment: the direct addition of anions such as sulfate and nitrate to the synthesis of geopolymer enhances this transformation. This result is attributed to the dehydration action of these anions and to their affinity for water molecules: the higher the hydration energy of the anion, the more the geopolymer/zeolite transformation is enhanced. However, threshold behavior appears to exist since a high anion concentration may obstruct the interactions between alkalis, silicates, and aluminates. The overall effect of anions in these systems cannot be described without taking the alkali into account.

Furthermore, the secondary geopolymer/zeolite transformation suggests that these geopolymeric systems are metastable with regard to some zeolites, depending on the mix formulation, treatment temperature and possibly time. Such a change has to be taken into account prior to any use of geopolymers as waste encapsulating materials: zeolites are indeed well known for their ion-exchange abilities.

These geopolymeric systems should be further investigated in several ways. First, the evolution of geopolymeric systems over time should be considered: are these zeolites representative of the natural evolution of the materials? Are they the thermodynamically stable phases or is the system still in evolution? Second, these transformations may induce some changes in mechanical properties that have to be assessed. Third, leaching behavior of the zeolites formed must be evaluated to guarantee that these transformations are not deleterious on this property, which is crucial for immobilizing materials. More generally, geopolymerization reactions in presence of oxyanions should be investigated in greater detail and the role of the hydration spheres of alkalis and anions during these reactions should also be clarified.

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