Journal of Nuclear Materials 514 (2019) 247-254

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Cesium immobilization in nitrate-bearing metakaolin-based geopolymers



1927

JOURNAL OF

E. Ofer-Rozovsky ^{a, *, 1}, M. Arbel Haddad ^b, G. Bar-Nes ^b, E.J.C. Borojovitz ^b, A. Binyamini ^b, A. Nikolski ^b, A. Katz ^a

^a Faculty of Civil and Environmental Engineering, Technion I.I.T, Haifa, 32000, Israel ^b Chemistry Department, Nuclear Research Centre – Negev, PO Box 9001, Beer-Sheva, 84901, Israel

HIGHLIGHTS

• Mixed CsOH-NaOH low-Si geopolymers containing NaNO3 were prepared from metakaoin

• Curing at moderate temperatures led to the formation of nitrate-bearing feldspathoids

• The formation of nitrate-bearing phases is correlated with enhanced Cs immobilization.

ARTICLE INFO

Article history: Received 4 June 2018 Received in revised form 25 October 2018 Accepted 1 November 2018 Available online 15 November 2018

Keywords: Cesium immobilization Geopolymers Nitrate Nitrate-cancrinite Nitrate-sodalite Zeolite A

ABSTRACT

Low-level nuclear wastes containing radioactive cesium (Cs) are often highly alkaline and rich in sodium nitrate. The goal of the present study was to examine immobilization of cesium in nitrate-bearing geopolymers with low Si/Al ratio (SiO₂:Al₂O₃ < 2.0), which are known to have relatively high crystalline phase content.

Geopolymers were prepared by activating metakaolin with a mixed NaOH-CsOH solution containing NaNO₃ where Cs⁺ ions make up 7% of the total alkali content. Geopolymer samples were cured at 40 ± 3 °C for up to 3 months. The structure of the cured geopolymers after varying curing times was characterized by XRD and FTIR, and the immobilization efficiency for Cs⁺, Na⁺ and NO₃⁻ was determined from leaching tests following the ANSI/ANS-16.1 standard procedure for low and intermediate level nuclear wasteforms.

The first phase crystallized from the amorphous gel was zeolite A. This phase gradually undergoes further transformations to yield the nitrate-bearing feldspathoids, nitrate sodalite and nitrate cancrinite. The leaching curves for Cs⁺, Na⁺ and NO₃ ions were clearly not linear with t^{1/2}, suggesting a change in leaching mechanism after the initial 24 hours of the leaching experiment. The apparent diffusion constants, D_a, as well as leaching indices for Cs⁺ and Na⁺ were therefore calculated separately for the 1st and 2nd time domains of the experiment (t^{1/2} < 1 days^{1/2} and t^{1/2} > 2.65 days^{1/2}, respectively). The leachability indices for Cs⁺ were found to increase with increasing curing time (from 7.4 and 11.2 for the 1st and 2nd time domains after 1 month of curing to 9.6 and 12.6 for the 1st and 2nd time domains after 3 months of curing). The enhanced immobilization of Cs⁺ is correlated with the formation of the nitrate-bearing feldspathoid phases.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Geopolymers are a relatively novel class of materials which are obtained by alkaline activation of various aluminosilicate raw

* Corresponding author.

https://doi.org/10.1016/j.jnucmat.2018.11.003 0022-3115/© 2018 Elsevier B.V. All rights reserved. materials, either calcined clays such as metakaolin, or waste materials such as fly-ash, slag etc. The resulting product is a network of interconnected silicate and aluminate groups. The tetrahedrally bonded aluminate groups are negatively charged, and may therefore serve as cation binding sites. The properties of the geopolymeric product vary depending on the composition of the aluminosilicate source material [1–6], the nature of activation solution [7–9] and the curing conditions [10,11]. High-Si



E-mail address: elyaofer@technion.ac.il (E. Ofer-Rozovsky).

¹ Present address: Ariel University, Department of Civil Engineering, Ariel, Israel.

compositions form a glass-like porous amorphous matrix [4,12], whereas low-Si compositions (SiO₂:Al₂O₃ molar ratio < 2.0) result in the formation of a composite structure, with crystalline domains imbedded within the amorphous matrix [13–16]. The crystalline domains are often zeolites or similar structures [16–19].

Due to their cation-binding sites combined with chemical resistance to acidic media as well as good mechanical properties. geopolymers have been considered as candidates for waste immobilization applications, including nuclear waste [20–26]. In this context, special attention has been given to the possibility of immobilizing ¹³⁷Cs, a radionuclide often found in nuclear waste streams. The immobilization of cesium is especially challenging due to its high solubility in both alkaline and acidic media [27-29]. Mineral additives such as fly ash, slag and silica fume are often included in Portland cement based matrices which are used for the conditioning of low-level radioactive waste. These additives, which can undergo alkaline activation within Portland cement based matirces, yielding products which are chemically similar to those found in geopolymers, have been shown to improve overall wasteform performance, and more specifically Cs⁺ immobilization [29–31]. Therefore, geopolymers which are produced by alkaline activation of these and similar pozzolonic materials, are also expected to immobilize waste species efficiently.

In a recent study we have shown that the enhanced immobilization of Cs⁺ in a low-Si geopolymer may be correlated with the formation of a specific Cs⁺-bearing zeolite phase, namely zeolite F [32]. However, Cs⁺-bearing nuclear waste streams often contain high concentrations of nitrate ions. Previous studies reported in the literature described changes in the geopolymerization process due to the introduction of nitrates into the reaction mixture, which were manifested as delayed setting times [33,34] enhanced zeolite formation upon heat-treatment [34], and enhanced leaching of cations [34]. However, all of the above mentioned studies employed high-Si formulations (SiO₂:Al₂O₃ molar ratio \geq 3.6). A previous study carried out in this laboratory has shown that the addition of nitrate ions into NaOH activation solutions of low-Si MK-based geopolymers (SiO₂:Al₂O₃ molar ratio < 2.0) leads to the formation of specific nitrate bearing crystalline phases, namely nitrate sodalite and nitrate cancrinite [16]. In the current study, the incorporation and immobilization of Cs⁺ by nitrate-bearing low-Si geopolymers was investigated.

2. Experimental

2.1. Sample preparation

Metakaolin (MK, PowerPozzTM, supplied by Advanced Cement Technologies, Blaine, WA, USA) conforming to ASTM C-618, Class N Specifications for Natural and Calcined Pozzolans, was used as the sole alumino-silicate source for geopolymer preparation. The chemical composition and physical properties of MK as supplied by the producer are presented in Tables 1 and 2.

Activation solutions were prepared by dissolution of NaOH (Frutarom, chemically pure), NaNO₃ (Loba Chemie, extra pure) and CsOH monohydrate (Aldrich, high purity, >99.5%) in deionized water (2 μ mho/cm at 25 °C), to yield solutions where Cs⁺ makes up 7% (by mole) of the total alkali content, with a H₂O:OH⁻ molar ratio

Table 1						
Chemical	com	position	of 1	aw	metakaoli	'n.

Table 1

Table 2

Physical characterization of raw metakaolin.

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

of 12.75, (corresponding to $[OH^-] \approx 3.8 \text{ M}$), and a $NO_3^-:OH^-$ molar ratio of 0.35 ($[NO_3^-] \approx 1.5 \text{ M}$).

MK was mixed manually with the activating solution at ambient temperature to yield a homogenous paste. The MK:solution ratios were adjusted to obtain a M₂O:Al₂O₃ ratio ($M = Na^++Cs^+$) of 1, assuming Al₂O₃ content of 44% in MK. The resulting pastes were cast into sealed polypropylene containers (50 ml) and cured at 40±3 °C for periods of 1 week, 1 month and 3 months.

2.2. XRD measurements

Samples for XRD measurements were prepared by manual grinding (mortar and pestle). XRD data were collected from $2\theta = 5^{\circ}$ to $2\theta = 80^{\circ}$ using a SIEMENS D5000 diffractometer with CuK_α radiation at 20 kV, 5 mA, and a scanning rate of 0.36° min⁻¹. Diffraction peaks due to quartz and anatase, which were present as impurities in MK and remain unaltered throughout the geopolymerization process, were used as internal standards. The XRD spectra are presented after background subtraction and normalization with respect to the $2\theta = 25.68^{\circ}$ diffraction peak of anatase.

2.3. FTIR measurements

FTIR samples were prepared by pressing a mixture of 2-5 mg ground sample (see above) with 100 mg dry KBr (French Press LCAD cell, BLA, type: C2P1). Samples of metakaolin and NaNO₃ were prepared in a similar manner. FTIR spectra of samples cured for either 1 week or 1 month were measured using BRUKER Vector 22 (500-1500 cm⁻¹). Due to technical failure of the latter spectrometer, samples cured for 3 months were measured using Bruker Tensor 27 FTIR spectrometer (850-1500 cm⁻¹). Transmittance mode was used in both cases.

FTIR spectra were normalized with respect to the integrated intensity in the 900-1300 cm⁻¹ range, which is attributed to the asymmetric stretching vibration of T-O-T (T=Al, Si) bonds. Normalization using sample weight was also performed, yielding similar results.

2.4. Leaching tests

Samples cured at 40 °C for either 1 month or 3 months were stored at room temperature for an additional period of 1 or 3 months, respectively, before being submitted to the leaching test. The leaching test was performed according to the American Nuclear Society standard procedure for low-level waste ANSI/ANS-16.1, 2003 [35]. The leaching test was conducted in closed vessels under static conditions using cylindrical samples (26.5 mm diameter, height ranging from 34 to 37 mm). Deionized water was used as

Oxides, weight (%)										LOI ^a
SiO ₂ 51-53	$\begin{array}{c} Al_2O_3\\ 42-44\end{array}$	Fe ₂ O ₃ <2.20	CaO <0.2	TiO ₂ <3.00	MgO <0.10	Na ₂ O <0.05	K ₂ O <0.40	P ₂ O ₅ <0.20	SO ₃ <0.50	<0.50%

^a LOI: loss on ignition, 950 °C.

leachant. The leachant was replaced 11 times during the 90 day test. Cs^+ , NO_3^- and Na^+ concentrations in the leachant were determined by Ion Chromatography using Dionex DX-5000 equipped with a conductivity detector and with a 50 µL injection loop. An IonPack CS12 column with 20-mM methanesulphonic acid mobile phase (flow rate 1 ml/min) was used for determining concentrations of the cations. An IonPack AS4A-SC column with solution of NaHCO₃ (1.7 mM) and Na₂CO₃ (1.8 mM) mobile phase (flow rate 2 ml/min) was used for determining NO_3^- concentrations.

The results of the leaching experiments indicated selectivity for Cs⁺ immobilization within the geopolymer. The degree of selectivity (SL) was estimated for each sampling interval by calculating the ratio SL=Na_f/Cs_f, where Na_f and Cs_f are the fractions of Na⁺ or Cs⁺ leached during that interval.

The incremental apparent diffusion coefficients, D_a , were calculated for Cs⁺ and Na⁺ using equation (1), which is derived from the solution to Fick's second law of diffusion for semi-infinite media [35]:

$$D_a = \pi \left[\frac{(a_n/A_o)}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T \tag{1}$$

where D_a – the apparent diffusion coefficient [cm²/s], a_n – the amount released from the sample during leaching interval n [mg], A_0 – total content in the sample prior to leaching [mg], $(\Delta t)_n$ – duration of the nth leaching interval [s], V – volume of the sample [cm³], S – geometric surface area of the sample [cm²], T –the mean time of the nth leaching interval [s] given by equation (2):

$$T = \left[\frac{t_n^{1/2} + t_{n-1}^{1/2}}{2}\right]^2 \tag{2}$$

where t_n , t_{n-1} , are the sampling times [s] for the n^{th} sampling period and the preceding sampling period, respectively. Equation (1) is not valid in cases in which the cumulative fraction exceeds 20%. In such cases D_a should be calculated from the specific solution of the mass transport equations using a tabular method given by Ref. [35].

Leachability indices, L, were calculated from the apparent diffusion constants according to the guidelines given by the ANSI/ANS-16.1 standard (Equation (3)):

$$L = \frac{1}{n} \sum_{i=0}^{n} \log\left(\frac{\beta}{D_a}\right) \tag{3}$$

where n is the number of D_a values used for the calculation, and β is a constant (1.0 cm²/s).

3. Results

3.1. Structural characterization

3.1.1. X-ray diffraction

X-ray diffraction patterns of geopolymer samples cured for 1 week, one month or 3 months at 40 °C are presented in Fig. 1. The diffraction pattern obtained from a sample cured for one week has a wide hump centered at $2\theta \sim 30^\circ$, indicating the formation of an amorphous geopolymer gel. This hump is superimposed by diffraction peaks due to zeolite A. Diffraction peaks due to zeolite A are also dominant in the diffraction pattern obtained after 1 month of curing. However, the relative contribution of the amorphous peak is lower than after 1 week of curing, indicating that rearrangements leading to higher crystalline phase content had taken place during this time. In addition, two diffraction peaks at $2\theta = 24.30^{\circ}$ and 27.48° , were the first indications for the formation of the nitrate-bearing feldspathoid phases, nitrate sodalite and nitrate cancrinite. Diffraction lines due to both nitrate sodalite and nitrate cancrinite are clearly observed in the diffraction pattern obtained after a 3 month curing period, together with lines due to zeolite A. Moreover, the relative intensity of zeolite A diffraction lines after 3 months of curing is lower than in the earlier diffraction



Fig. 1. XRD patterns of MK based geopolymer activated by NaOH-CsOH solution in presence of NaNO₃ as a function of curing time. The diffraction pattern of raw MK is added as a reference.



Fig. 2. FTIR spectra of MK based geopolymer activated by NaOH-CsOH solution in presence of nitrate as a function of curing times. The spectra for MK and $NaNO_3$ are added as a reference.

pattern (1 month), indicating a transformation of zeolite A to nitrate sodalite and nitrate cancrinite. Zeolite A is known to be a precursor of nitrate sodalite and nitrate cancrinite in hydrothermal processes [36,37]. A similar series of transformations from the amorphous phase to zeolite A \rightarrow nitrate sodalite \rightarrow nitrate cancrinite was previously observed in low-Si MK-based nitrate bearing geopolymers without Cs⁺ [16].

3.1.2. FTIR spectroscopy

FTIR data, which are presented in Fig. 2, support the conclusions drawn from XRD measurements. The main IR absorbance band of aluminosilicate materials, which is attributed to asymmetric stretching of the T-O-T bonds (T = Si, Al), appears between 900 and 1200 cm⁻¹. The maximal intensity of this band, which appears at 1092 cm^{-1} in the raw material (MK), had shifted to 1002 cm^{-1} within 1 week of curing at 40 °C. This shift is due to the incorporation of Al within the aluminosilicate framework of the geopolymer, which results in a higher average T-O-T angle and consequently lower bond energies and lower frequencies [38]. A further decrease in the frequency of this band is observed after curing for 3 months, indicating further rearrangements within the geopolymer matrix throughout this period. The bands at 835 cm⁻¹ and 873 cm⁻¹ observed after a week of curing are assigned to T-OH terminal groups, which are known to be present during the rearrangement process [15,16,39].

The 500-800 cm⁻¹ region in the FTIR spectrum is assigned to T-O-T symmetric stretching modes. Metakaolin exhibits a single band in this region of the spectrum, at 798 cm⁻¹, which is assigned to the symmetric stretching of either Al-O-Al [15,40] or Si-O-Si [41]. This band is no longer observed after 1 week of curing, indicating rapid dissolution of the raw material. Specific absorbance bands associated with the secondary building blocks (SBUs) of zeolites and related crystalline structures may be observed in the spectra

measured after a 1 week or 1 month curing period. A band at 556 cm^{-1} , which is assigned to the double ring unit of zeolite A (D4R), is clearly observed after 1 week of curing together with a smaller band at 671 cm⁻¹, which had also been assigned to zeolite A [40]. The identification of these bands with zeolite A is in agreement with the XRD data. Unfortunately data for the SBU region for the sample cured for 3 months are not available, so that the spectral bands which were previously reported for nitrate sodalite (660 cm⁻¹, 730 cm⁻¹) [15,42] or nitrate cancrinite (575 cm⁻¹, 622 cm⁻¹ and 682 cm⁻¹) [15,43] are not observed.

The absorbance bands in the $1380-1440 \text{ cm}^{-1}$ region are attributed to N-O symmetric stretching modes of nitrate ions [36]. The precise position of these bands is highly dependent on the chemical environment of the nitrate ion. A single band at 1383 cm^{-1} is observed for nitrate ion in aqueous environment, as well as crystalline NaNO₃ or the nitrate sodalite phase [36], whereas nitrate cancrinite is characterized by 3 absorption bands in this region, at 1425 cm^{-1} , 1435 cm^{-1} and 1440 cm^{-1} [43,44]. The shift of the N-O symmetric stretching modes to higher wavenumbers is due to intercalation of nitrate ions within the cancrinite structure, resulting in distortion of the nitrate ions over 3 non-equivalent positions within this structure [43,44].

The absorbance band at 1383 cm^{-1} was observed in the FTIR spectra of samples cured for either 1 week, 1 month or 3 months. In addition, The band at 1425 cm^{-1} which is due to the formation of nitrate cancrinite is initially observed in samples cured for 1 month, and is clearly observed after 3 months of curing together with the bands at 1435 cm^{-1} and 1440 cm^{-1} . These results are well correlated with XRD data, which show a substantial increase in nitrate cancrinite content within the geopolymer matrix within this timeframe.

3.2. Leaching experiments

Samples cured for either 1 month or 3 months were stored at room temperature for additional periods of 1 or 3 months, respectively, before being submitted to the leaching test. The results of the leaching test, which are presented in Fig. 3, show a substantial influence of the curing period on the extent of leaching. The cumulative fractions of Cs⁺ leached during the 90 day leaching test were 0.12 for samples cured for 1 month, and less than 0.02 for samples cured for 3 months. Na⁺ leaching had also undergone a substantial decrease following a longer curing period, changing from 0.24 after 1 month of curing to 0.16 after a 3 months curing period. In a similar manner, NO₃ leaching, which was much higher than for the two cations, reaching cumulative values of 0.65 for samples cured for 1 month, decreased to 0.39 for samples cured for 3 months.

The leaching curves obtained for Cs⁺, Na⁺ and NO₃⁻ (Fig. 3) do not conform to the expected trend for diffusion controlled processes, which is characterized by a linear dependence between the cumulative fraction leached and the square root of time (t^{1/2}). Inspection of the cumulative leaching curves shows that more than 60% of the overall leaching during the 90 day leaching experiment had occurred during the initial 24 h (1 day). Linear dependence was observed for the initial sampling points (t < 1 day or t^{1/2} < 1) as well as for the late data points (t > 7 days or t^{1/2} > 2.65), suggesting that two diffusion controlled processes, with very different time constants, contribute to the overall leaching of both cations and anions. A similar interpretation was recently suggested for the cumulative leaching curves of Cs⁺ and Na⁺ from nitrate-free geopolymers [32].

Following this interpretation of the data, the average apparent diffusion constants, D_a , for Cs^+ and Na^+ ions were determined separately for $t^{1/2} < 1$ (1st time domain) and $t^{1/2} > 2.65$ (2nd time



Fig. 3. Cumulative fraction of Cs^+ , Na^+ and NO_3^- leaching from MK based geopolymer activated by NaOH-CsOH solution in presence of nitrate.

domain). These are summarized in Table 3. Although the calculation of incremental D_a values according to Equation (1) is limited to cases where the cumulative leaching fraction is lower than 0.20, an exception was made in the case of Na⁺ ion leaching from samples cured for 1 month. In this case the cumulative fraction leached at the end of the 90-day leaching experiment was 0.25. This exception seems to be justified in this specific case due to the fact that the observed slopes of the Na⁺ cumulative leaching curves in the 2nd time domain are similar for the two curing periods studied.

Inspection of the values presented in Table 3 show that the 1st time domain D_a values for the both Cs⁺ and Na⁺ ions are several orders of magnitude higher than 2nd time domain values. This finding is valid for both curing periods. We propose that the initial 24 hours of the leaching experiment were dominated by leaching of ions from the open pore network within the amorphous geopolymer phase. The cumulative fractions of nitrate ions leached during the initial 24 hour of the leaching experiment were 0.57 for samples cured for 1 month and 0.30 for samples cured for 3 months (Fig. 3). Leaching of the positively charged Cs⁺ and Na⁺ ions was impeded due to interaction with aluminate groups whereas nitrate ions, which do not bind to the negatively charged aluminate groups within the amorphous phase, diffuse rapidly. The cumulative fractions of Na⁺ ions leached during the initial 24 hours were ~0.18 and 0.10 for samples cured for 1 month and 3 months, respectively. The cumulative fractions of Cs⁺ ions leached were yet lower with values of 0.10 and 0.008 obtained for samples cured for the same periods. The average D_a values calculated for Na^+ for this time domain ($t^{1/2} < 1$ day), which are 1.18×10^{-7} cm²/s and 4.17×10^{-8} cm²/s for 1 month and 3 months curing, respectively, are similar to previously reported values for Na⁺ during the initial leaching period $(t^{1/2} < 1 \text{ day})$ from low-Si NO₃-free geopolymers (3.68*10⁻⁸ cm²/s) [32] as well as from a high-Si amorphous geopolymer $(3.95*10^{-7} \text{ cm}^2/\text{s})$ [45]. The 1st domain D_a value for Cs⁺ after 1 month of curing, $4.29*10^{-8}$ cm²/s, is also within the same range.

As the pore water is depleted of ions, ion exchange gradually becomes the rate determining step for further leaching, resulting in lower leaching rates as indicated by the lower slope of the leaching curves in the 2nd time domain ($t^{1/2} > 1$ day). It is interesting to note that the D_a values obtained for both Cs^+ and Na^+ in this time domain are in the same range as literature values for intracrystalline diffusion in crystalline zeolite or feldspathoid phases $(2*10^{-9} \text{ to } 5*10^{-13} \text{ cm}^2/\text{s})$ [46,47]. Differences in sample composition and experimental conditions, as well as different assumptions concerning sample surface area, contribute to discrepancies of several orders of magnitude between D_a values obtained in the different studies [46]. Nevertheless, the 2nd time domain values obtained for the two cations in the current study are within this range, suggesting that ion-exchange between the crystalline phases and the pore water, a process which involves intra-crystalline diffusion, is in fact the rate-limiting process during the 2nd time domain.

The extent of leaching during the 1st time domain was strongly dependent on curing time, and was clearly lower for samples cured for 3 months. This may be correlated with the formation of the

Table 3

Leaching selectivity, average apparent diffusion coefficients and leachability indices for Cs⁺ and Na⁺ ions as calculated from leaching data. Values in parentheses are estimated errors.

Curing time	Selectivity		Da [cm ² /s] (x10 ⁻¹⁰)				Leachability index			
	1 st domain	2 nd domain	Cs ⁺		Na ⁺		Cs ⁺		Na ⁺	
			1 st domain	2 nd domain	1 st domain	2 nd domain	1 st domain	2 nd domain	1 st domain	2 nd domain
1 month + 1 month @RT 3 months + 3months @RT	1.69 (0.20) 12.16 (0.14)	2.84 (0.35) 15.98 (2.20)	429.8 (205.7) 2.8 (0.6)	0.085 (0.071) 0.004 (0.004)	1185.4 (504.1) 416.7 (86.82)	0.678 (0.581) 0.889 (0.776)	7.4 (0.3) 9.6 (0.2)	11.2 (0.4) 12.6 (0.5)	7.0 (0.3) 7.4 (0.2)	10.3 (0.4) 10.2 (0.4)



Fig. 4. Diffusion coefficients of $\mathsf{C}\mathsf{s}^+$ and $\mathsf{N}\mathsf{a}^+$ at the two time domains and two curing periods.

nitrate bearing phases, nitrate sodalite and nitrate cancrinite, and the decrease in zeolite A content in the geopolymer matrix, as indicated by XRD and FTIR. This correlation is most clearly understood in the case of NO_3^- ion leaching, where incorporation of $NO_3^$ ions within the neo-formed phases decreases the amount of nonbound NO_3^- ions within the geopolymer pore system, and consequently reduces the driving force for leaching. However one should also note that nitrate sodalite and nitrate cancrinite incorporate salt molecules in excess of the charge balancing cations. Therefore, the lower leaching of non-bound Cs⁺ and Na⁺ cations may also be correlated to the formation of nitrate sodalite and nitrate cancrinite.

The 1st domain D_a value obtained for Na^+ after 3 months of curing (4.17*10⁻⁸ cm²/s) is approximately three times lower than the value obtained after a 1 month curing period (1.18*10⁻⁷ cm²/s). In the case of Cs⁺ the effect of curing time is even more pronounced. The 1st time domain D_a value for Cs⁺ from samples cured for 3 months, 2.8*10⁻¹⁰ cm²/s, is two orders of magnitude lower than the value obtained from samples cured for 1 month, 4.29*10⁻⁸ cm²/s (Fig. 4). The affinity of Cs⁺ to cancrinite and so-dalite phases was reported to be higher than its affinity to zeolite A [47,48]. Selective uptake of Cs⁺ during the transformation of the initial zeolite A structure to the feldspathoid phases may be the reason for the exceptionally marked decrease of the 1st domain Da value for Cs⁺ after 3 months of curing.

The high affinity of Cs⁺ to the feldspathoid phases may also be the cause for the decrease in 2nd time domain D_a values for Cs⁺ with curing time (Fig. 4). In contrast, the 2nd time domain values for Na⁺ were essentially the same for both curing periods $(6.7*10^{-11} \text{ cm}^2/\text{s} \text{ and } 8.89*10^{-11} \text{ cm}^2/\text{s} \text{ for Na}^+)$. These changes are also manifested in the selectivity values obtained (Table 3). Whereas selectivity for Cs⁺ was already observed after 1 month of curing (selectivity values of 1.69 ± 0.20 and 2.84 ± 0.35 for the 1st and 2nd time domains, respectively) after 3 months the selectivity was significantly higher, as indicated by selectivity values of 12.16 ± 0.14 and 15.98 ± 2.20 .

Leachability indices for Na⁺ and Cs⁺ were calculated using the incremental D_a values for the two time domains (Table 3). The indices obtained for Cs⁺ and Na⁺ in both time domains are well above the minimum value of 6 recommended by the NRC for low-level nuclear waste [49,50].

4. Discussion

The aim of the study reported here was to estimate the efficiency of Cs⁺ immobilization in low-Si geopolymers prepared in the presence of nitrate, an anion often present in low-level nuclear waste streams. The samples for this study were prepared by activating metakaolin (MK) with a mixed CsOH-NaOH solution containing sodium nitrate. Due to the low solubility of CsNO₃, the fraction of Cs in the activation solution was limited to 7% of the total alkalis (Cs₂O:M₂O = 0.07, where $M = Cs^+ + Na^+$). This, however, was not a drawback, as Cs⁺ content in actual nuclear waste streams is several orders of magnitude lower than that of either Na⁺ or nitrate. In addition, the geopolymer formulation was similar to that of nitrate bearing geopolymers prepared with no Cs⁺ addition studied previously [16], allowing us to probe the influence of Cs⁺ on the geopolymerization process as well as product properties.

The presence of nitrate directed the rearrangements within the geopolymer matrix towards the formation of the nitrate-bearing feldspathoid phases, nitrate sodalite and nitrate cancrinite, as observed for the parallel Cs-free geopolymers [16]. In a previous study we have shown that the presence of 7% Cs^+ in the activating solution of a nitrate-free geopolymer was sufficient in order to induce the formation of the Cs-bearing zeolite F (also called zeolite D in earlier publications) [32]. This phase was not observed in the current case, despite the similar Cs₂O:M₂O molar ratio. It should be noted that the presence of nitrate ions does not preclude the formation of zeolite F. Deng et al. reported the precipitation of zeolite F from an aluminosilicate solution containing 1.0 M NaOH and 0.5 M C_{sNO_3} ($C_{s_2O:M_2O}$ and $NO_3^-:OH^-$ ratios of 0.33) [48]. In the current study the nitrate concentration was higher ($\sim 1.5 \text{ M NO}_3$) than that used by Deng et al., while the Cs₂O:M₂O ratio was considerably lower. At these conditions the role of the nitrate ion as structuredirecting agent was more dominant than that of cesium ion, leading to the formation of nitrate sodalite and nitrate cancrinite. Similar geopolymer matrices containing nitrate cancrinite and nitrate sodalite as the predominant crystalline phases are therefore expected to form upon activation of MK with low-level nuclear waste solutions, as the concentration of Cs⁺ in low-level nuclear wastes is roughly 3 orders of magnitude lower than that of nitrate 51.52

The formation of the nitrate bearing feldspathoid phases is correlated with decrease in D_a values for Cs⁺, as well as increase in selectivity for Cs⁺. The leachability indices of Cs⁺ after a 3 months curing period are well above value of 6 which is considered as acceptable for radioactive waste immobilization [49,50]. The selectivity of zeolites, as well as other ion-exchange materials towards Cs⁺, is a well-known phenomenon, which was demonstrated in ion exchange experiments as well as in self-diffusion studies [32,46,53–56]. Moreover, selective uptake of Cs⁺ was reported to occur during hydrothermal synthesis of nitrate cancrinite and nitrate sodalite [47,48], and was also observed in geopolymer synthesis from a mixed NaOH-CsOH activating solution [32]. Although steric effects due to the large ionic radius of Cs⁺ are often mentioned as the cause for the efficient retention of Cs⁺ within crystalline structures, these do not explain its efficient uptake from solution during synthesis, or its ability to exchange for the smaller alkali cations [53]. The higher ionic radius of Cs⁺ does however result in a smaller effective charge, and consequently in a hydration shell which is more loosely-bound and labile when compared to that of Na⁺ [57]. Cs ions may therefore dehydrate more readily than Na ions, and bind more efficiently to the charged aluminate groups either within the zeolite structure or in the amorphous phase of the geopolymer matrix. Nevertheless, the enhanced selectivity provided by nitrate cancrinite and nitrate sodalite is not well understood. A detailed study of the Na-Cs ion exchange process and identification of the specific sites occupied by Cs⁺ in mixed Cs-Na systems is needed in order to clarify the structural features which control this enhanced selectivity.

The series of structural transformations starting from an

amorphous aluminoslicate and leading to the formation of thermodynamically favoured nitrate cancrinite (amorphous phase \rightarrow zeolite A \rightarrow nitrate sodalite \rightarrow nitrate cancrinite) was previously observed during hydrothermal synthesis of the feldspathoid phases [37] as well as in low-Si MK-based geopolymers [16]. While the transformations are accelerated at elevated temperatures, the data presented here has shown that they may occur at the relatively moderate temperature of 40 °C. Our experience with similar geopolymer formulations shows that the thermodynamically favoured product is obtained even at room temperature when sufficient time is allowed. It is therefore expected that the nitrate cancrinite content within the geopolymer matrix will increase with prolonged aging, resulting in yet lower D_a values and higher leachability indices for Cs⁺, which is highly favorable for the long-term performance of radioactive wasteforms.

5. Conclusions

The results presented in this paper show that a nitrate bearing geopolymer containing a sufficient amount of nitrate cancrinite and nitrate sodalite may serve as an efficient immobilization matrix for cesium ions. The structural data indicate that the presence of Cs⁺ ions did not alter the sequence of rearrangements previously observed during the curing of MK-based nitrate-bearing geopolymers, leading from an amorphous structure to crystalline products (amorphous phase \rightarrow zeolite A \rightarrow nitrate sodalite \rightarrow nitrate cancrinite). Moreover, the leachability indices for Cs⁺ which were found to conform with the guidelines given by NRC for low-level nuclear waste, were shown to increase with the progress of this series of transformations within the geopolymer matrix.

These findings are very promising in the context of nuclear waste management, as they suggests that metakaolin activated by low level wastes containing sodium nitrate and trace amounts of radioactive cesium may yield similar matrices. Moreover, the naturally occurring series of transformations starting from an amorphous aluminosilicate matrix and ending in the thermodynamically stable nitrate cancrinite, which is induced by the presence of nitrate, is expected to result in the enhancement of Cs⁺ immobilization with time.

Funding sources

This work was supported by the Technion and Pazy Foundation (Research No.162).

Data availability statement

The raw data required to reproduce these findings are available in the experimental section of this manuscript and in the PhD thesis of Dr. Ela Ofer-Rozovsky.

Acknowledgements

Ela Ofer-Rozovsky would to like to acknowledge a scholarship from the Rieger Foundation-Jewish National Fund Program for Environment Studies and Dr. Vladimir Rozovsky for his help in XRD measurements.

References

- H. Xu, J.S.J. van Deventer, The geopolymerisation of aluminosilicate minerals, Int. J. Miner. Process. 59 (3) (2000) 247–266.
- [2] H. Xu, J.S.J. van Deventer, Microstructural characterisation of geopolymers synthesized from kaolinite/stilbite mixtures using XRD, MAS-NMR, SEM/EDX, TEM/EDX and HREM, Cement Concr. Res. 32 (2002) 1705–1716.
- [3] K. Komnitsas, D. Zaharaki, Geopolymerisation: a review and prospects for the

minerals industry, Miner. Eng. 20 (14) (2007) 1261-1277.

- [4] P. Duxson, A. Fernandez-Jimenez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer, Geopolymer technology: the current state of the art, J. Mater. Sci. 42 (9) (2007) 2917–2933.
- [5] E.I. Diaz, E.N. Allouche, S. Eklund, Factors affecting the suitability of fly ash as source material for geopolymers, Fuel 89 (5) (2010) 992–996.
- [6] J. Davidovits, "Geopolymer Green Chemistry and Sustainable Development, in: World Congress Geopolymer, 2005, p. 236, 2005.
- [7] A. Fernández-Jiménez, A. Palomo, Composition and microstructure of alkali activated fly ash binder: effect of the activator, Cement Concr. Res. 35 (10) (2005) 1984–1992.
- [8] P.S. Singh, T. Bastow, M. Trigg, Structural studies of geopolymers by 29Si and 27Al MAS-NMR, J. Mater. Sci. 40 (15) (2005) 3951–3961.
- [9] R. Aiello, F. Crea, A. Nastro, B. Subotic, F. Testa, Influence of cations on the physicochemical and structural properties of aluminosilicate gel precursors . Chemical and thermal properties, Zeolites 11 (1991) 767–775.
- [10] P. Rovnaník, Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer, Construct. Build. Mater. 24 (7) (2010) 1176–1183.
- [11] Y.M. Liew, C.Y. Heah, A.B. Mohd Mustafa, H. Kamarudin, Structure and properties of clay-based geopolymer cements: a review, Prog. Mater. Sci. 83 (2016) 596–629.
- [12] M. Soutsos, A.P. Boyle, R. Vinai, A. Hadjierakleous, S.J. Barnett, Factors influencing the compressive strength of fly ash based geopolymers, Construct. Build. Mater. 110 (2016) 355–368.
- [13] J.L. Provis, G.C. Lukey, J.S.J. van Deventer, Do geopolymers actually contain nanocrystalline zeolites? a reexamination of existing results, Chem. Mater. 17 (12) (2005) 3075–3085.
- [14] P. Silva, K. Sagoecrenstil, V. Sirivivatnanon, Kinetics of geopolymerization: role of Al2O3 and SiO2, Cement Concr. Res. 37 (4) (Apr. 2007) 512–518.
- [15] A. Fernández-Jiménez, M. Monzo, M. Vicent, A. Barba, A. Palomo, Alkaline activation of metakaolin-fly ash mixtures: obtain of Zeoceramics and Zeocements, Microporous Mesoporous Mater. 108 (1–3) (2008) 41–49.
- [16] E. Ofer-Rozovsky, M. Arbel Haddad, G. Bar-Nes, A. Katz, The formation of crystalline phases in metakaolin-based geopolymers in the presence of sodium nitrate, J. Mater. Sci. 51 (10) (2016), 4975–4814.
- [17] B. Zhang, K.J.D. MacKenzie, I.W.M. Brown, Crystalline phase formation in metakaolinite geopolymers activated with NaOH and sodium silicate, J. Mater. Sci. 44 (17) (2009) 4668–4676.
- [18] T. Bakharev, Resistance of geopolymer materials to acid attack, Cement Concr. Res. 35 (4) (2005) 658–670.
- [19] S. Chen, M. Wu, S. Zhang, Mineral phases and properties of alkali-activated metakaolin-slag hydroceramics for a disposal of simulated highly-alkaline wastes, J. Nucl. Mater. 402 (2–3) (2010) 173–178.
- [20] M.Y. Khalil, E. Merz, Immobilization of intermediate-level wastes in geopolymers, J. Nucl. Mater. 211 (2) (1994) 141–148.
- [21] A.D. Chervonnyi, N.A. Chervonnaya, Geopolymeric agent for immobilization of radioactive ashes after biomass burning, Radiochemistry 45 (2) (2003) 182–188.
- [22] Y. Bao, S. Kwan, D.D. Siemer, M.W. Grutzeck, Binders for radioactive waste forms made from pretreated calcined sodium bearing waste, J. Mater. Sci. 39 (2) (2004) 481–488.
- [23] D. Perera, E. Vance, S. Kiyama, Z. Aly, P. Yee, Geopolymers as candidates for the immobilization of low-and intermediate-level waste, in: Materials Research Society Symposium Proceedings vol 985, 2007, pp. 361–366.
- [24] S. Berger, F. Frizon, C. Joussot-Dubien, Formulation of caesium based and caesium containing geopolymers, Adv. Appl. Ceram. 108 (7) (2009) 412–417.
- [25] C. Chlique, D. Lambertin, P. Antonucci, F. Frizon, P. Deniard, XRD analysis of the role of cesium in sodium-based geopolymer, J. Am. Ceram. Soc. 98 (4) (2015) 1308–1313.
- [26] J. Melar, G. Renaudin, F. Leroux, A. Hardy-dessources, J. marie Nedelec, C. Taviot-gueho, E. Petit, P. Steins, A. Poulesquen, F. Frizon, The porous network and its interface inside geopolymers as a function of alkali cation and aging, J. Phys. Chem. C (2015) 17619–17632.
- [27] S. Bagosi, LJ. Csetényi, Caesium immobilisation in hydrated calcium-silicatealuminate systems, Cement Concr. Res. 28 (12) (1998) 1753–1759.
- [28] R.W. Crawford, C. McCulloch, M. Angus, F.P. Glasser, A.A. Rahman, Instrinsic sorption potential of cement components for 134Cs, Cement Concr. Res. 14 (4) (1984) 595–599.
- [29] G. Bar-nes, A. Katz, Y. Peled, Y. Zeiri, The mechanism of cesium immobilization in densified silica-fume blended cement pastes, Cement Concr. Res. 38 (2008) 667–674.
- [30] M.I. Ojovan, W.E. Lee, An Introduction to Nuclear Waste Immobilisation, second ed., Elsevier, Amsterdam, 2014, p. 376.
- [31] IAEA-TECDOC-1701, The Behaviours of Cementitious Materials in Long Term Storage and Disposal of Radioactive WasteThe Behaviours of Cementitious Materials in Long Term Storage and Disposal of Radioactive Waste: Results of a Coordinated Research Project, IAEA, Vienna, 2013.
- [32] M. Arbel Haddad, E. Ofer-Rozovsky, G. Bar-Nes, E.J.C. Borojovich, A. Nikolski, D. Mogiliansky, A. Katz, Formation of zeolites in metakaolin-based geopolymers and their potential application for Cs immobilization, J. Nucl. Mater. 493 (2017) 168–179.
- [33] J.L. Provis, P. Walls, J.S.J. van Deventer, Geopolymerisation kinetics. 3. Effects of Cs and Sr salts, Chem. Eng. Sci. 63 (18) (2008) 4480–4489.
- [34] C. Desbats-Le Chequer, F. Frizon, Impact of sulfate and nitrate incorporation

on potassium- and sodium-based geopolymers: geopolymerization and materials properties, J. Mater. Sci. 46 (17) (2011) 5657–5664.

- [35] American Nuclear Society, American National Standard Measurement of the Leachability of Solidified Low-level Radioactive Wastes by a Short-term Test Procedure, ANSI/ANS-16.1, 2003.
- [36] J.C. Buhl, J. Lons, Synthesis and crystal structure of nitrate enclathrated sodalite Na-8[AlSiO4](6)(NO3)(2), J. Alloy. Comp. 235 (1) (1996) 41–47.
- [37] Q. Liu, A. Navrotsky, Synthesis of nitrate sodalite: an in situ scanning calorimetric study. Geochim. Cosmochim. Acta 71 (8) (2007) 2072–2078.
- [38] A. Fernández-Jiménez, A. Palomo, Mid-infrared spectroscopic studies of alkaliactivated fly ash structure, Microporous Mesoporous Mater. 86 (1–3) (2005) 207–214.
- [39] H. Rahier, J. Wastiels, M. Biesemans, R. Willlem, G. Assche, B. Mele, G. Van Assche, B. Van Mele, Reaction mechanism, kinetics and high temperature transformations of geopolymers, J. Mater. Sci. 42 (9) (2006) 2982–2996.
- [40] A. Demortier, N. Gobeltz, J.P. Lelieur, C. Duhayon, "Infrared evidence for the formation of an intermediate compound during the synthesis of zeolite Na–A from metakaolin, Int. J. Inorg. Mater. 1 (2) (1999) 129–134.
- [41] W.K. Lee, J.S.J. van Deventer, The effects of inorganic salt contamination on the strength and durability of geopolymers, Colloids Surfaces A Physicochem. Eng. Asp. 211 (2–3) (2002) 115–126.
- Asp. 211 (2–3) (2002) 115–126.
 [42] M.C. Barnes, J. Addai-Mensah, A.R. Gerson, A methodology for quantifying sodalite and cancrinite phase mixtures and the kinetics of the sodalite to cancrinite phase transformation, Microporous Mesoporous Mater. 31 (1999) 303–319.
- [43] J.C. Buhl, C. Taake, F. Stief, M. Fechtelkord, The crystallisation kinetics of nitrate cancrinite Na-7.6[AlSiO4](6)(NO3)(1.6) (H2O2)(2) under low temperature hydrothermal conditions, React. Kinet. Catal. Lett. 69 (1) (2000) 15–21.
- [44] J.C. Buhl, F. Stief, M. Fechtelkord, T.M. Gesing, U. Taphorn, C. Taake, Synthesis, X-ray diffraction and MAS NMR characteristics of nitrate cancrinite Na-7.6 [AlSiO4](6)(NO3)(1.6)(H2O)(2), J. Alloy. Comp. 305 (1–2) (2000) 93–102.
- [45] N. Ukrainczyk, O. Vogt, E.A.B. Koenders, Reactive transport numerical model for durability of geopolymer materials, Adv. Chem. Eng. Sci. 6 (4) (2016)

355-363.

- [46] R.M. Barrer, R.F. Bartholomew, L.V.C. Rees, Ion exchange in porous crystals part I. Self- and exchange-diffusion of ions in chabazites, J. Phys. Chem. Solid. 24 (1) (1963) 51–62.
- [47] J. Mon, Y. Deng, M. Flury, J.B. Harsh, Cesium incorporation and diffusion in cancrinite, sodalite, zeolite, and allophane, Microporous Mesoporous Mater. 86 (1–3) (2005) 277–286.
- [48] Y. Deng, M. Flury, J. Harsh, a Felmy, O. Qafoku, Cancrinite and sodalite formation in the presence of cesium, potassium, magnesium, calcium and strontium in Hanford tank waste simulants, Appl. Geochem. 21 (12) (2006) 2049–2063.
- [49] Nuclear Regulatory Comission, Wasteform Technical Position, Revision 1, U.S. Government Printing Office, Washington DC, 1991.
- [50] B. Siskind, M.G. Cowgill, Technical Justification for the Tests and Criteria in the Wasteform Tehnical Position Appendix on Cement Stabilization, Waste Management conference at Tucson, AZ, USA, 1992.
- [51] J.P. Mckinley, C.J. Zeissler, J.M. Zachara, R. Jeffrey Serne, R.M. Lindstrom, H.T. Schaef, R.D. Orr, Distribution and retention of 137Cs in sediments at the hanford site, Washington, Environ. Sci. Technol. 35 (17) (2001) 3433–3441.
- [52] Y. Bao, M.W. Grutzeck, C.M. Jantzen, Preparation and properties of hydroceramic waste forms made with simulated hanford low-activity waste, J. Am. Ceram. Soc. 88 (12) (2005) 3287–3302.
- [53] C. Colella, lon exchange equilibria in zeolite minerals, Miner. Deposits 31 (6) (1996) 554–562.
- [54] K. Benyamin, Self-diffusion of sodium and cesium ions in hydrous titanium oxide, Solid State Ionics 73 (3–4) (1994) 303–308.
- [55] M.R. El-Naggar, M.I. El-Dessouky, H.F. Aly, Self-diffusion and ionic transport of sodium and cesium ions in particles of hydrous zirconia, Solid State Ionics 57 (1992) 339–343.
- [56] M. Tsuji, S. Komarneni, Alkali metal ion exchange selectivity of Al-substituted tobermorite, J. Mater. Res. 4 (3) (1989) 698–703.
- [57] I. Persson, Hydrated metal ions in aqueous solution: how regular are their structures? Pure Appl. Chem. 82 (10) (2010) 1901–1917.