Accepted Manuscript

Investigation of chabazitic materials as Cs-137 sorbents from cementitious aqueous solutions

P. Misaelides, S. Sarri, N. Kantiranis, F. Noli, A. Filippidis, B. de Blohouse, A. Maes, E. Breynaert

PII: S1387-1811(18)30113-6

DOI: [10.1016/j.micromeso.2018.02.048](https://doi.org/10.1016/j.micromeso.2018.02.048)

Reference: MICMAT 8811

To appear in: *Microporous and Mesoporous Materials*

Received Date: 23 October 2017

Revised Date: 21 February 2018

Accepted Date: 26 February 2018

Please cite this article as: P. Misaelides, S. Sarri, N. Kantiranis, F. Noli, A. Filippidis, B. de Blohouse, A. Maes, E. Breynaert, Investigation of chabazitic materials as Cs-137 sorbents from cementitious aqueous solutions, *Microporous and Mesoporous Materials* (2018), doi: 10.1016/j.micromeso.2018.02.048.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Graphical abstract

INVESTIGATION OF CHABAZITIC MATERIALS AS Cs-137 SORBENTS FROM CEMENTITIOUS AQUEOUS SOLUTIONS

P. Misaelides ^{1*}, S. Sarri ¹, N. Kantiranis ², F. Noli ¹, A. Filippidis ², B. de Blochouse ³, A.
Maes ⁴, E. Breynaert ⁴

⁽¹⁾ *Department of Chemistry, Aristotle University of Thessaloniki, 54124Thessaloniki,
Greece*

⁽²⁾ *Department of Geology, Aristotle University of Thessaloniki, 54124Thessaloniki,
Greece*

⁽³⁾ *ONDRAF/NIRAS, Kunstlaan 14, 1210 Sint-Joost-ten-Node, Belgium*

⁽⁴⁾ *Centre for Surface Chemistry and Catalysis, K.U. Leuven, Celestijnenlaan 200F- box
2461f, 3001 Leuven, Belgium*

Abstract

The ability of a chabazite-bearing tuff (AT), a synthetic chabazite (SYN) and pure natural chabazite crystals (CHA) to sorb cesium (C_{Cs} : 10^{-9} - 10^{-2} M) from young concrete pore water (YCW), an aqueous medium that can potentially leach from cement-based barriers of radioactive waste disposal facilities, was investigated using a batch technique and $^{137}\text{CsCl}$ -spiked solutions. The sorbents were mineralogically characterized prior and after the sorption tests, whereas their uptake ability was determined by the ammonium acetate saturation (AMAS) method. Two series of experiments were performed using sorbate solutions in pH~13 and pH~7 YCW

(contact time: 14 days and 100 days). The Cs-uptake by the zeolites was determined by counting the 661.6 keV ^{137}Cs γ -rays in the liquid phase. SYN presented the highest Cs-uptake ability followed by CHA and AT. The Cs-uptake, which remained constant between 14 and 100 days, depended on the zeolite content of the sorbents and the Cs-concentration of the solutions. The zeolites remained stable in the YCW environment for the total duration of the experiment. Kinetic experiments, performed for AT at 23, 35 and 50°C using a 10^{-3} M Cs-solution in pH~13 YCW spiked with ^{137}Cs , showed that the equilibrium was established, for all temperatures, in less than 30 min. Cs-leaching tests (duration: 14 days and 100 days) performed using pH ~13 YCW as eluent, indicated that AT was the most sensitive to leaching losing ca. 60% of the sorbed Cs in less than 10 min, whereas SYN and CHA ca. 30%. No further leaching was observed at prolonged contact of the Cs-loaded zeolites with YCW.

Keywords: Cesium; chabazite; young concrete pore water; sorption

1. Introduction

In Belgium low- and intermediate-level short-lived radioactive waste will be permanently disposed of in a near-surface disposal facility located in the northern part of Belgium [1, 2]. To prevent the release of harmful elements from this facility to the environment a multi-barrier approach is adopted. The main retardation barrier for the release of radionuclides is cement-based (i.e. concrete and mortar). Zeolites are being considered in this context as a potential complementary barrier, as they are known for their good mono- and divalent cation sorption selectivity and capacity.

During the lifetime of the disposal facility the zeolites will come into contact with cement-equilibrated water leaching from the cement materials.

Cesium-137 ($T_{1/2} = 30.1$ years) is a uranium fission product exhibiting high fission yield, half-life and long-term environmental importance. It also belongs, along with strontium-90 ($T_{1/2} = 28.8$ years) and long-living isotopes of plutonium and americium, to the main heat generating radionuclides in the repository environment. The Cs-isotopes released in natural waters are primarily found in cationic form.

Ion-exchange using natural and synthetic sorbents, solvent extraction and precipitation were the main processes used for many years for the removal of cesium from aqueous media [3]. Among the natural sorbents the zeolites, possessing high ion-exchange capacity and selectivity, early gained attention and were utilized for nuclear waste treatment and decontamination purposes (e.g., [4-7]).

The literature about the ion-exchange and adsorption properties of natural zeolites is rather extended because this is the basis of the majority of their applications (e.g. [8, 9]). On the other hand, it is well-known that the zeolitic rocks are mixtures of minerals and therefore the study of their sorptive properties is not as straight forward as in the case of synthetic ones mostly being single phase tailored materials. Even in the case of pure natural zeolite crystals the exact sorptive behaviour for a given Si/Al ratio cannot be accurately predicted on the basis of the present knowledge. This could mainly be attributed to the mineral chemistry (cationic composition) of the material and to symmetry reasons. Exchanged homo-ionic forms of natural zeolites may also present different properties depending on the degree and type of Si- and -Al ordering as well as on the degree of ion-exchange. Not all

cations are accessible and available for exchange. These facts strengthen the opinion that the most of the adsorption and absorption- / ion-exchange data collected only concern specific materials and do not possess a universal validity. The characterization of representative samples from the specific deposit prior the application becomes in this way inevitable.

Although there is sufficient information about the cesium sorption by chabazites (e.g., [5, 6, 10-29]), the number of publications concerning the sorption of cesium from alkaline and hyper-alkaline solutions is limited (e.g., [17, 27, 29]).

This work presents, along with the investigation of the chemical stability of natural chabazite crystals (Wasson's Bluff, Canada), a chabazite-bearing tuff and a synthetic chabazite, results on their ability to selectively sorb cesium from alkaline and hyper-alkaline aqueous solutions and specifically from young concrete pore water (YCW), an aqueous medium that can potentially leach from the cement-based barriers of radioactive waste disposal facilities.

2. Experimental

Three chabazitic materials were studied for the present study, an Italian chabazitic/phillipsitic tuff from Naples region supplied by Apostolico and Tanagro S.N.C (abbreviated as AT), a natural chabazite from Wasson's Bluff, Nova Scotia, Canada (abbreviated as CHA) and synthetic chabazite crystals synthesized at K.U. Leuven (abbreviated as SYN) [30]. The zeolitic materials were mineralogically characterized prior and after their use as sorbents.

Chemical microanalysis of the studied zeolite phases was performed on polished thin sections using a JEOL JSM-840 scanning electron microscope equipped with an Oxford ISIS300 Energy Dispersion analyzer. To minimize volatilization of alkalis in the zeolites framework, the electron beam spot size was enlarged and the counting time decreased. Different minerals (micas, carbonates, feldspars) and pure metals were used as probe standards.

The mineralogical composition of the samples was determined by X-ray powder diffraction (XRPD). XRPD analysis was performed using a Philips diffractometer (PW1710) with Ni-filtered $\text{CuK}\alpha$ radiation on randomly oriented samples (step size: $0.01^\circ 2\theta$, start and end angle: 3° and 63° respectively, scan speed: $0.02^\circ 2\theta/\text{sec}$). The phase identification was carried out using the PDF-4⁺ database and applying the DDView⁺/Sieve⁺ ICDD's viewing/search indexing software [31]. The estimation of the abundance of the mineral phases was derived from the XRPD data using the intensity of certain reflections according to the absorption-diffraction method of Klug and Alexander [32]. The mass absorption coefficient of the individual crystalline phases detected was calculated from its chemical formula measured by SEM-EDS. External standard mixtures of the phases, identified in ratios obtained from the absorption-diffraction method, were scanned under the same conditions and the accuracy of the semi-quantitative results was improved [33]. Finally, corrections were made, using the software MAUD-Material Analysis, using diffraction with full pattern Rietvelt refinement [34]. Applying these successive steps for the calculation of mineralogical composition, precision of $\pm 1\%$ w/w could be achieved [33, 35]. The amorphous material of the studied samples was calculated according to Kantiranis et al. [33].

The uptake ability of the materials was determined using the ammonium acetate saturation (AMAS) method [35, 36].

Batch sorption experiments (S/L-ratio: 50 mg sorbent in 10 mL liquid) were performed using Cs-containing rain-based concrete pore water solutions (Cs-concentration: 10^{-9} to 10^{-2} M) labelled with a small quantity of $^{137}\text{CsCl}$ in 0.1 M HCl supplied by EUROSTANDARD CZ s.r.o..

Two series of sorption experiments were performed using pulverized zeolitic materials of particle size between 5 and 50 μm and sorbate solutions of pH ~ 13 (K-rich solution simulating the young concrete pore water (YCW) of state I) as well as its more neutral-pH counterpart (pH ~ 7 approaching the conditions of state IV pore water) [29, 30]. The young concrete pore water (State I, pH ~ 13) was prepared by adding in a 1L volumetric flask 500 mL doubly distilled water, 0.0296 g of $\text{Ca}(\text{OH})_2$ [4×10^{-4} mole], 10 mL of a 10^{-2} M Na_2CO_3 solution, 180 mL of a 1M KOH solution, 70 mL of a 1M NaOH solution and 0.189 g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [1.1×10^{-3} moles]. After complete dissolution of all components the total volume was made up to 1 L by addition of bi-distilled water, followed immediately by a transfer of the solution to a closed 1L polypropylene bottle. The moderate-pH counterpart of the State I concrete pore water was prepared in a 1L volumetric flask by dissolving 0.189g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1.1×10^{-3} mole) and 0.0945 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 500 mL of bi-distilled water, followed by addition of 10 mL of a 10^{-2} M NaHCO_3 solution, 180 mL of a 1M KNO_3 solution, 70 mL of a 1M NaNO_3 solution. After complete dissolution of all components the total volume was made up to 1L by addition of bi-distilled water,

immediately followed by a transfer of the solution to a closed 1L polypropylene bottle.

The contact times applied for the sorption experiments were 14 days and 100 days. The determination of the Cs-uptake by the zeolites was performed by counting the 661.6 keV γ -rays emitted by ^{137}Cs in the liquid phase by means of Canberra Reverse Electrode Ge-detector (Efficiency: 23%, Energy resolution: 2.1 keV for the 1332 keV ^{60}Co gamma-energy) in a low-background shield. The EG&G MAESTRO software was used for the data collection and analysis.

Kinetic experiments were performed only for the chabazite/phillipsite tuff (AT) using a 10^{-3} M spiked Cs-solutions in State I YCW (pH ~ 13). After sampling in predetermined time intervals (up to 120 min), the cesium in the separated liquid phase was determined by gamma-ray spectroscopy. Kinetics experiments were performed at 23, 35 and 50°C.

CHA, SYN and AT preloaded with cesium by contacting them with a 10^{-2} M Cs YCW-solution for 2 weeks were subjected to leaching tests also using YCW State I as eluent. The total duration of the leaching tests was 100 days. At the end of the contact time and after separation of the liquid from the solid phase, the maximum Cs-uptake by the individual zeolitic materials was determined, as previously described, in the liquid phase by gamma-ray spectroscopy. The initial Cs-loading was 0.049, 0.058 and 0.015 mmol Cs in 50 mg of CHA, SYN and AT, respectively.

3. Results and Discussion

3.1. Mineral chemical and mineralogical characterization

The mineral chemistry of the zeolite phases contained in the studied natural samples was investigated by SEM-EDS. The chemical formula of chabazite contained in the Apostolico & Tanagro zeolitic tuff (AT) was found to be $\text{Ca}_{1.0}\text{K}_{0.7}\text{Na}_{0.2}\text{Al}_{3.0}\text{Si}_{8.9}\text{O}_{24}\cdot 12\text{H}_2\text{O}$, while that of the phillipsite $\text{K}_{2.0}\text{Ca}_{0.7}\text{Na}_{0.4}\text{Al}_{3.8}\text{Si}_{12.1}\text{O}_{32}\cdot 12\text{H}_2\text{O}$. The chemical formula measured for the pure Wasson's Bluff chabazite crystal (CHA) was $\text{Ca}_{1.5}\text{Na}_{0.2}\text{K}_{0.2}\text{Sr}_{0.1}\text{Al}_{3.1}\text{Si}_{8.8}\text{O}_{24}\cdot 12\text{H}_2\text{O}$.

The mineralogical composition (wt%) of the Apostolico & Tanagro zeolitic tuff, as well as its solid residues after 100 days in State I YCW (pH ~13) and its moderate-pH counterpart (pH ~7) are shown in Table 1. The mineralogical composition of the Wasson's Bluff chabazite crystals and its solid residues after treatment for one week in KOH solution of pH ~8, KOH + 500 mg/L Cs, State I YCW in absence and presence of 500 mg/L Cs as well as for 100 days in State I YCW and its moderate pH counterpart are given in Table 2.

Table 1. Mineralogical composition of the Apostolico & Tanagro tuff (AT) and its solid residues after treatment for 100 days treatment with State I YCW (pH ~13) and its moderate-pH counterpart (pH ~7).

Mineral	Untreated AT	AT + YCW (pH ~13) (100 days)	AT + moderate-pH YCW (pH ~7) (100 days)
Chabazite	39	38	40
Phillipsite	18	18	20
Amorphous	12	9	9
Calcite	1	13	1

Micas	3	2	4
Clay minerals	1	1	1
Feldspars	22	17	21
Pyroxene	3	2	4
Amphibole	1	-	-
Total	100	100	100

Table 2. Mineralogical composition of the pure chabazite crystal and its solid residues under various experimental conditions.

Mineral	Untreated CHA	CHA (500 mg/L) + KOH solution of pH 8 (1 week)	CHA + YCW (1 week)	CHA + Cs (500 mg/L) + YCW (1 week)	CHA + YCW (pH ~13) (100 days)	CHA + moderate-pH YCW (pH ~7) (100 days)
Chabazite	92	93	83	75	69	91
Amorphous	8	7	12	22	14	5
Calcite	-	-	5	3	17	4
Total	100	100	100	100	100	100

As shown in Table 2, the pure chabazite crystal consisted of 92 wt% chabazite and 8 wt% amorphous material. The presence of amorphous material in the pure chabazite crystal powder is due to the pulverization. After treating the crystal with KOH solution of pH 8 for 1 week, no significant change was observed, and its solid

residue consisted of 93 wt% chabazite and 7 wt% amorphous material. The treatment of the crystal with YCW of pH ~13 for 1 week decreased zeolite content to 83 wt% and increased the amorphous material (12 wt%). At the same time, the formation of calcite (5 wt%) was obvious. The presence of 500 mg/L Cs in the YCW solution caused a further decrease of the chabazite content (75 wt%) and simultaneously an increase of the amorphous material (22 wt%). The calcite content remained almost the same (3 wt%).

After 100 days treatment in the moderate-pH YCW counterpart (pH ~7), the pure chabazite crystal showed no significant change concerning its zeolite content (91 wt%), while a slight decrease in amorphous material (5 wt%) and formation of calcite (4 wt%) were observed. After 100 days in YCW (pH ~13) significant changes were observed. More specifically, the chabazite content was reduced from 92 to 69 wt%, the content in amorphous material almost doubled (from 8 to 14 wt%) and a remarkable formation of calcite (17 wt%) was observed.

The mineralogical composition of the synthetic chabazite (SYN) and its solid residues after 100 days treatment in YCW and its moderate-pH counterpart are given in Table 3. SYN mainly consisted of chabazite (91 wt%) and small amount of amorphous material (7 wt%). Small amounts of erionite (1 wt. %) and levyne (1 wt%) were also found. Chabazite, erionite and levyne belong to the same zeolitic group named “zeolites with six-member rings” [37-39]. Erionite and levyne are very frequently found associated with chabazite in the nature.

After 100 days in YCW at pH ~7 and at pH ~13 significant changes were observed. In particular, after 100 days in YCW at pH ~7 the amount of chabazite

decreased from 91 to 84 wt%, the amount of amorphous material slightly increased from 7 to 10 wt%, while the formation of calcite (4 wt%) is obvious. After 100 days in YCW at pH ~13 a further decrease in the amount of chabazite (81 wt%) was observed, the amount of amorphous materials remained unchanged, while the calcite reaches the value of 7 wt%.

Table 3. Mineralogical composition (wt%) of the synthetic chabazite and its solid residues after 100 days in YCW at pH ~13 and its moderate-pH counterpart of pH ~7.

Mineral	Untreated SYN	SYN + YCW (pH ~13) (100 days)	SYN + moderate-pH YCW (pH ~7) (100 days)
Chabazite	91	81	84
Erionite	1	1	1
Levyne	1	1	1
Calcite	-	7	4
Amorphous	7	10	10
Total	100	100	100

The uptake ability of AT, CHA and SYN determined using the AMAS method was respectively found to be 214, 341 and 356 meq/100g. The uptake ability shows a strong positive correlation with the total zeolite content of the studied materials,

which means that the main procedure which takes place, during sorption, is the ion exchange.

3.2 Sorption study

Figure 1 presents the experimental distribution coefficient values (K_d) for the Cs-sorption from State I YCW (upper diagram) and its low-pH counterpart (lower diagram) by the AT, CHA and SYN. The K_d represents the ratio the sorbate concentration in the solid phase (sorbent) in mg/g over its equilibrium concentration in the liquid one (aqueous solution) in mol/L. For the specific case of cesium K_d is given by ratio $[Cs]_s/[Cs]_{aq}$.

Fig. 1: Distribution coefficients (K_d) for the Cs-sorption by CHA, SYN and AT (Upper: 14-day experiments; Lower: 100-day experiments).

The synthetic chabazite (SYN) studied during this work showed the best Cs-sorption performance followed by the pure natural chabazite crystals (CHA). The Apostolico and Tanagro tuff (AT) showed the lowest Cs-uptake ability both in experiments of 14 days and 100 days duration. The difference between in the Cs-uptake between SYN and CHA could be assigned to the different mineral chemistry of the two materials. CHA is a natural material containing a number of potentially exchangeable cations whereas SYN is synthetic (practically homo-ionic) material.

The sorption capacity of AT is not only due to chabazite but also to the phillipsite present in the tuff and at a very low percentage in the amorphous + micas + clay-minerals [37-40].

Borai et al. [27] indicated that the pretreatment of the natural zeolites with Na-containing aqueous solutions considerably increases their reactivity and sorption potential. On the other hand, it is also known that the presence of Na-ions in the solution reduces the K_d of the chabazite towards Cs but increases its selectivity [17]. Mimura et al. [23] also found out that the distribution coefficient value (K_d) of Cs^+ and Sr^{2+} onto zeolites decreases with increasing concentration of monovalent cations in the solution. Harjula and Lehto [41] observed, studying the Cs-sorption by synthetic chabazite (Linde AW-500) and mordenite (Zeolon 900) in the presence of Na and K in the pH region 6-13, that the absorption of cesium is inversely proportional to their concentrations in the solution. High concentrations of sodium and especially potassium ions greatly prevent retention of cesium on zeolites. Finally, Barrer et al. [11] observed that Cs does not completely exchange with Na in chabazite (exchange 0.84 of the CEC).

There is no especially significant difference in the Cs-uptake data obtained from the interaction of AT, CHA and SYN with State I YCW and its moderate-pH counterpart. This was also observed by Van Tendeloo et al. [29], who comparing data obtained in alkaline with corresponding ones from near-neutral media, demonstrated that the cation exchange selectivity of the zeolites remains unaffected by the increased hydroxyl concentration.

No significant difference in the Cs-uptake data obtained with 14 days and 100 days contact time was observed. The K_d -values are somehow more sensitive to the low Cs-concentrations involved.

The kinetics of the Cs-uptake by AT were very fast. The sorption process was practically terminated in less than 30 minutes although some authors provide longer equilibration times. No considerable effect of the temperature (up to 50 °C) on the sorption kinetics was observed. This agrees with the findings of Dyer and Zubair [26], who also observed that the changes in temperature had little effect on the sorption isotherms. The fast uptake did not allow the reliable modelling of the kinetic data and the determination of thermodynamic parameters of the sorption process.

The experimental results for the investigated zeolitic materials were fitted by the Langmuir, Freundlich and Dubinin-Radushkevich isotherm equations (e.g. [42-45]).

The Langmuir (L) and the Freundlich (F) models are widely used to describe the equilibrium characteristic of the adsorption on a solid phase. The Langmuir model assumes a localized monolayer adsorption on a fixed number of adsorption sites of equal energy.

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

K_L is a constant related to the sorption/desorption energy (L/mg), and $q_{\max}$ is the maximal uptake upon complete saturation of the sorbent surface (mg/g).

On the other side, the Freundlich model additionally takes into account the surface heterogeneity in the sense that the adsorption energy is distributed.

$$q_e = K_F C_e^{(1/n)} \quad (2)$$

K_F is the Freundlich constant indicating the sorption capacity and n the surface heterogeneity factor of the sorbent. Sites having the same adsorption energy are grouped together leading to a patch-type surface topography. The Freundlich model, in contrast to the Langmuir one, does not reach a limited sorption capacity.

Opposed to layer-by-layer adsorption, the Polanyi theory is based on the adsorption by micropore volume filling. It assumes, for a given adsorbate, the existence at any point in the neighborhood of an adsorbent surface of a potential ϵ depending on the proximity to the surface and its nature:

$$q_e / Q_{\max} = f(\epsilon) \quad (3)$$

ϵ is an arbitrary function, which differs in various applications of the Polanyi theory. Generally, the formation of a heterogeneous adsorption surface is governed by the distribution of adsorption centers. The adsorption energy of these centers can be expressed as a local adsorption isotherm in the form of the Dubinin-Radushkevich (DR) equation

$$\ln q_e = \ln Q_{\max} - K_{DR} \epsilon^2 \quad (4)$$

q_e is the amount of the ion adsorbed at the equilibrium, K a constant related to the adsorption energy, $q_{\max}$ the theoretical saturation capacity, ϵ , the Polanyi potential, is equal to $RT \ln(1 + 1/C_e)$. The slope and the intercept of the plot of $\ln q_e$ versus ϵ^2 give K_{DR} (mol^2/kJ^2) and the sorption capacity $Q_{\max}$.

The experimental sorption capacities for 14 and 100 days contact time could be better reproduced by the Freundlich equation. However, all these equations

provide a mathematical description of the experimental data rather than direct information about the sorption mechanism.

The values of the parameters of the Freundlich and Langmuir equations for the three investigated zeolites are presented in Table 4 whereas those of the Dubinin - Radushkevich model in Table 5. All these equations provide a mathematical description of the experimental data rather than direct information about the sorption mechanism. The experimental sorption capacity for the 14 and 100 days contact time could be better reproduced by the Freundlich equation rather by the Langmuir and Dubinin-Radushkevich ones.

Table 4. Calculated Freundlich and Langmuir parameters along with corresponding R^2 values.

			Freundlich			Langmuir		
			K _F (L/g)	n	R ²	Q _{max} (mmol/g)	K _L (L/mol)	R ²
14 days	YCW (pH 13)	CHA	0.233	1.03	0.999	2.265	155.047	0.944
		SYN	0.322	1.02	0.999	3.603	117.403	0.870
		AT	0.035	1.11	0.997	0.361	427.417	0.9
	Mod.- pH	CHA	0.247	1.02	0.999	2.475	133.462	0.905
		SYN	0.289	1.01	0.999	2.997	125.311	0.913
		AT	0.033	1.11	0.992	0.241	667.133	0.990
100 days	YCW (pH 13)	CHA	0.320	1.01	0.999	4.065	92.527	0.768
		SYN	0.382	1.01	0.999	4.221	112.718	0.908
		AT	0.039	1.11	0.997	0.391	427.318	0.942
	Mod.- pH	CHA	0.298	1.01	0.999	3.688	99.231	0.902
		SYN	0.354	1.01	0.999	4.413	97.383	0.884
		AT	0.038	1.11	0.997	0.369	441.402	0.947

Table 5. Calculated Dubinin-Radushkevich parameters along with their R^2 -values.

			Dubinin-Radushkevich		
			$Q_{\max}$ (mmol/g)	K_{DR} (mol ² /kJ ²)	R^2
14 days	YCW (pH 13)	CHA	0.939	6.E-09	0.975
		SYN	1.135	6.E-09	0.975
		AT	0.294	6.E-09	0.986
	Mod.- pH	CHA	0.971	6.E-09	0.976
		SYN	1.078	6.E-09	0.977
		AT	0.296	6.E-09	0.989
100 days	YCW (pH 13)	CHA	1.113	6.E-09	0.975
		SYN	1.250	6.E-09	0.975
		AT	0.323	6.E-09	0.983
	Mod.- pH	CHA	1.078	6.E-09	0.976
		SYN	1.208	6.E-09	0.977
		AT	0.308	6.E-09	0.981

The results of the leaching tests performed using YCW (State I, pH 13) as eluent indicated the Cs-leaching was very fast. The CHA, SYN and AT lost in the first 10 min of elution 29, 30 and 62 % of their Cs-load. The situation then remained stable

and no considerable further Cs- loss was observed during the 100 days of the duration of the test. The leaching measurements are not absolute measurements because are totally dependent upon the leaching conditions (e.g. composition and pH of the eluent, temperature) [46].

4. Conclusions

SYN presented the highest Cs-uptake ability followed by CHA and finally by AT. The uptake ability and, consequently, the corresponding distribution coefficient (K_d) values strongly depend on the zeolite content and the mineral chemistry of the microporous minerals contained in sorbents as well as on the Cs-concentration of the solutions. The Cs-uptake from State I YCW solutions is somehow, but not considerably, higher than this from its low-pH counterpart. The Cs-uptake remained constant between 14 and 100 days indicating that the ion exchange equilibrium was established within 14 days and the zeolite remained almost stable in the hyper-alkaline YCW environment for the total duration of the experiment (100 days).

The sorption kinetics at all studied temperatures were very fast. Equilibrium was established in all cases in less than 30 min. The AT was the most sensitive to leaching losing about 60% of the sorbed Cs in less than 10 min, whereas SYN and CHA about 30%. No further leaching was observed at prolonged contact (14 and 100 days) of the Cs-loaded zeolitic materials with the YCW.

5. Acknowledgements

The CHA/PHI-tuff used for this work was kindly supplied by Apostolico and Tanagro S.A. The close collaboration with and the financial support by ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and Fissile Materials, are thankfully acknowledged.

6. References

- [1] Niras/Ondraf *The cAt project in Dessel: A long-term solution for Belgian category A waste*; NIROND 2010- 02 E March, Brussels, 2010.
- [2] ONDRAF/NIRAS, Waste Plan for the long-term management of conditioned high-level and/or long-lived radioactive waste and overview of related issues, report NIROND 2011-02 E, 2011.
- [3] P. Misaelides, in: M. Václavíková, K. Vitale, G.P. Gallios, L. Ivaničová (Eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*, NATO Science for Peace and Security Series C: Environmental Security, Springer, Dordrecht, 2009, pp. 183-191.
- [4] L. L. Jr. Ames, *Am. Mineral.* 45 (1960) 689-700.
- [5] L. L. Jr. Ames, *Am. Mineral.* 42 (1961) 1120-1131.
- [6] L. L. Jr. Ames, Removal of cesium by sorption from aqueous solutions, U.S. Patent No 30,017,242, Jan.16, 1962.
- [7] Use of local minerals in the treatment of radioactive wastes. Technical Report Series v. 136, International Atomic Energy Agency, Vienna, 1972.

http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/04/059/4059411.pdf

f (accessed 20.02.2018).

- [8] C. Colella, *Miner. Deposita* 31 (1996) 554-562.
- [9] S. Zaidi, in: D. Inamuddin, M. Luqman (Eds.), *Ion Exchange Technology II: Applications*, Springer, Dordrecht, 2012, pp. 183-215.
- [10] L. L. Jr. Ames, *Am. Mineral.* 49 (1964) 127-145.
- [11] R. M. Barrer, J. A. Davies, L. V. C. Rees, *J. Inorg. Nucl. Chem.* 31 (1969) 219-232.
- [12] J. W. Roddy, A survey: Utilization of zeolites for the removal of radioactivity from liquid waste streams, ORNL/TM -7782, 1981.
- [13] S. Komarneni, R. Roy, *Nucl. Chem. Waste Man.* 2 (1981) 259-264.
- [14] S. Komarneni, G.L. Palau, K.K.S. Pillay, *Nucl. Chem. Waste Man.* 4 (1983) 335-338.
- [15] S. Komarneni, D.M. Roy, *Clay Clay Miner.* 31 (1983) 383-391.
- [16] E. D. Collins, D. O. Campbell, L. J. King, J. B. Knauer, *AIChE Symp. Ser.* 78 (213) (1982) 9-15.
- [17] H. Mimura, T. Kanno, *J. Nucl. Sci. Technol.* 22 (1985) 284-291.
- [18] S. M. Robinson, J. R. Jr. Parrott, Pilot-Scale demonstration of process wastewater decontamination using chahazite zeolites, ORNL/TM- 10836, 1989.
- [19] S. M. Robinson, T. E. Kent, W. D. Arnold, J. R. Jr. Parrott, The development of a zeolite system for upgrade of the process waste treatment plant, ORNL/TM-12063 1993.
- [20] S. M. Robinson, T. E. Kent, W. D. Arnold, in: D. W. Ming, F. A. Mumpton (Eds.), *Natural Zeolites '93: Occurrence, Properties, Use*, International Committee on Natural Zeolites, Brockport, New York, 1995, pp. 579-586.

- [21] J. J. Perona, *AIChE* 39 (1993) 1716-1720.
- [22] D. T. Bostick, W. D. Jr. Arnold, P. A. Taylor, D. A. Mc Taggart, M. W. Burgess, B. Guo, Evaluation of improved techniques for the removal of ^{90}Sr and ^{137}Cs from process wastewater and groundwater: Chabazite zeolite baseline study, ORNL/TM-12903, 1995.
- [23] H. Mimura, T. Kobayashi, K. Akiba, *J. Nucl. Sci. Technol.* 32 (1995) 60-67.
- [24] S. M. De Paoli, J. J. Perona, *AIChE* 42 (1996) 3434-3441.
- [25] D. T. Bostick, S. M. DePaoli, B. Guo, A comparative evaluation of ionsiv[®] IE-911 and chabazite zeolite for the removal of radiostrontium and cesium from wastewater, ORNL/CP-99431, 1998.
- [26] A. Dyer, M. Zubair, *Micropor. Mesopor. Mat.* 22 (1998) 135-150.
- [27] E.H. Borai, R. Harjula, L. Malinen, A. Paajanen, *J. Hazard. Mater.* 172 (2009) 416-422.
- [28] D. Li, D. I. Kaplan, A. S. Knox, K. P. Crapse, D. P. Diprete, *J. Environ. Radioactiv.* 136 (2014) 56-63.
- [29] L. Van Tendeloo, B. de Blohouse, D. Dom, J. Vancluysen, R. Snellings, J.A. Martens, C. E. A. Kirschhock, A. Maes, E. Breynaert, *Environ. Sci. Technol.* 49 (2015) 1729-1737.
- [30] L. Van Tendeloo, W. Wangermez, M. Kurttepel, B. de Blohouse, S. Bals, G. Van Tendeloo, J.A. Martens, A. Maes, C. E. A. Kirschhock, E. Breynaert, *Environ. Sci. Technol.* 49 (2015) 2358-2365.

- [31] The International Centre for Diffraction Data, <http://www.icdd.com/products/pdf4.htm> (accessed 20.02.2018).
- [32] H. P. Klug, L. E. Alexander, X-ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, second ed., John Wiley, New York, 1959, pp. 251.
- [33] N. Kantiranis, A. Stergiou, A. Filippidis, A. Drakoulis, Bull. Geol. Soc. Greece 36(1) (2004) 446-453.
- [34] L. Lutterotti, M. Bortolotti, G. Ischia, I. Lonardelli, H.-R. Wenk, Z. Kristallogr. Suppl. 26 (2007) 125-130.
- [35] N. Kantiranis, K. Sikalidis, A. Godelitsas, C. Squires, G. Papastergios, A. Filippidis, J. Environ. Manage. 92 (2011) 1569-1576.
- [36] C. Bain, L. Smith, in: M. Wilson (Ed.), A handbook of determinative methods in clay mineralogy, Blackie, Glasgow, 1987, pp. 248-274.
- [37] R. M. Barrer, B. M. Munday, J. Chem. Soc. A (1971) 2904-2909.
- [38] S. Komarneni, Clay Clay Miner. 33 (1985) 145-151.
- [39] M. Adabbo, D. Caputo, B. de Gennaro, M. Pansini, C. Colella, Micropor. Mesopor. Mat. 28 (1999) 315-324.
- [40] A.F. Gualtieri, D. Caputo, C. Colella, Micropor. Mesopor. Mat. 32 (1999) 319-329.
- [41] R. Harjula, J. Lehto, Nucl. Chem. Waste Man. 6 (1986) 133-137.
- [42] G. Limousin, J.-P. Gaudet, L. Charlet, S. Szenknect, V. Barthès, M. Krimissa, Appl. Geochem. 22 (2007) 249-275.
- [43] K.Y. Foo, B.H. Hameed, Chem. Eng. J. 156 (2010) 2-10.
- [44] V.J. Inglezakis, Micropor. Mesopor. Mat. 103 (2007) 72-81.
- [45] E. Malkoc, J. Hazard. Mater. B137 (2006) 899-908.

[46] IAEA-TECDOC-1397: Long term behaviour of low and intermediate level waste packages under repository conditions, IAEA Vienna, June 2004.

Tables

Table 1. Mineralogical composition of the Apostolico & Tanagro tuff (AT) and its solid residues after treatment for 100 days treatment with State I YCW (pH ~13) and its moderate-pH counterpart (pH ~7).

Mineral	Untreated	AT + YCW (pH ~13)	AT + moderate-pH YCW
	AT	(100 days)	(pH ~7) (100 days)
Chabazite	39	38	40
Phillipsite	18	18	20
Amorphous	12	9	9
Calcite	1	13	1
Micas	3	2	4
Clay minerals	1	1	1
Feldspars	22	17	21
Pyroxene	3	2	4
Amphibole	1	-	-
Total	100	100	100

Table 2. Mineralogical composition of the pure chabazite crystal and its solid residues under various experimental conditions.

Mineral	Untreated CHA	CHA (500 mg/L) + KOH solution of pH 8 (1 week)	CHA + YCW (1 week)	CHA + Cs (500 mg/L) + YCW (1 week)	CHA + YCW (pH ~13) (100 days)	CHA + moderate-pH YCW (pH ~7) (100 days)
Chabazite	92	93	83	75	69	91
Amorphous	8	7	12	22	14	5
Calcite	-	-	5	3	17	4
Total	100	100	100	100	100	100

Table 3. Mineralogical composition (wt%) of the synthetic chabazite and its solid residues after 100 days in YCW at pH ~13 and its moderate-pH counterpart of pH ~7.

Mineral	Untreated SYN	SYN + YCW (pH ~13) (100 days)	SYN + moderate-pH YCW (pH ~7) (100 days)
Chabazite	91	81	84
Erionite	1	1	1
Levyne	1	1	1
Calcite	-	7	4
Amorphous	7	10	10
Total	100	100	100

Table 4. Calculated Freundlich and Langmuir parameters along with corresponding R^2 values.

			Freundlich			Langmuir		
			K _F (L/g)	n	R ²	Q _{max} (mmol/g)	K _L (L/mol)	R ²
14 days	YCW (pH 13)	CHA	0.233	1.03	0.999	2.265	155.047	0.944
		SYN	0.322	1.02	0.999	3.603	117.403	0.870
		AT	0.035	1.11	0.997	0.361	427.417	0.9
	Mod.- pH	CHA	0.247	1.02	0.999	2.475	133.462	0.905
		SYN	0.289	1.01	0.999	2.997	125.311	0.913
		AT	0.033	1.11	0.992	0.241	667.133	0.990
100 days	YCW (pH 13)	CHA	0.320	1.01	0.999	4.065	92.527	0.768
		SYN	0.382	1.01	0.999	4.221	112.718	0.908
		AT	0.039	1.11	0.997	0.391	427.318	0.942
	Mod.- pH	CHA	0.298	1.01	0.999	3.688	99.231	0.902
		SYN	0.354	1.01	0.999	4.413	97.383	0.884
		AT	0.038	1.11	0.997	0.369	441.402	0.947

Table 5. Calculated Dubinin-Radushkevich parameters along with their R^2 -values.

			Dubinin-Radushkevich		
			$Q_{\max}$ (mmol/g)	K_{DR} (mol ² /kJ ²)	R^2
14 days	YCW (pH 13)	CHA	0.939	6.E-09	0.975
		SYN	1.135	6.E-09	0.975
		AT	0.294	6.E-09	0.986
	Mod.- pH	CHA	0.971	6.E-09	0.976
		SYN	1.078	6.E-09	0.977
		AT	0.296	6.E-09	0.989
100 days	YCW (pH 13)	CHA	1.113	6.E-09	0.975
		SYN	1.250	6.E-09	0.975
		AT	0.323	6.E-09	0.983
	Mod.- pH	CHA	1.078	6.E-09	0.976
		SYN	1.208	6.E-09	0.977
		AT	0.308	6.E-09	0.981

Figure captions

Fig. 1: Distribution coefficients (K_d) for the Cs-sorption by CHA, SYN and AT (Upper: 14-day experiments; Lower: 100-day experiments).

Figures

Fig. 1

Highlights:

- Chabazitic materials are effective cesium sorbents from cementitious aqueous solutions
- The kinetics of Cs-sorption by chabazites are, at temperatures 23 to 50 °C, very fast
- Natural and synthetic chabazitic materials were stable in alkaline cementitious solutions
- The studied chabazitic tuff was sensitive to leaching by pH13 cementitious solutions.
- Chabazitic materials can be applied as barriers in radioactive waste disposal facilities