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Safe trapping of Cs in heat-treated zeolite matrices ☆

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Abstract

Cesium retention performances of two different natural zeolites (an Italian phillipsite-rich tuff and a Mexican erionite-rich tuff), pre-exchanged in Cs form and heat-treated, are compared. After thermal treatment at 1000 °C both zeolites satisfactorily retain Cs during back-exchange tests with NaCl solution or by a prolonged contact with distilled water. The different mechanisms of Cs encapsulation are elucidated. The Cs-exchanged phillipsite, a less siliceous and less heat-stable zeolite, tends to form pollucite on heating. Pollucite is a naturally occurring mineral phase which contains and irreversibly traps cesium. The Cs-exchanged erionite tends to form an amorphous phase on heating and Cs is immobilized through glass formation.

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1. Introduction

Stabilization of high- to low-level radioactive wastes may be effected using hardened cement matrices as storage media. Cation retention in cement matrices proved, however, to be in general unsatisfactory [1], unless radio-nuclides are previously trapped in a cation exchanger. The decontamination of radioactive waste streams is therefore faced by a two-step procedure: (1) removal of noxious cations by ion exchange and (2) subsequent storage of the spent exchanger in a cement matrix prior to encapsulation in stainless steel drums. The use of organic resins as exchangers turned out unsuitable because of their low radiation and thermal stability [2]. That is why research has focused in recent years on inorganic ion exchangers, especially natural zeolites. These, commonly referred to as zeolitic tuffs, present a series of advantages such as: (a) high ion exchange selectivity and capability for the main cationic contaminants of nuclear wastewaters [3,4]; (b) proven radiation (α, β, γ, *n*) and thermal resistance [5]; (c) compatibility with cement encapsulation (zeolites are materials having pozzolanic activity) [5]; (d) possibility of reuse of recovered radio-nuclides as sources of heat and radiation [6]; (e) low cost. Application of natural zeolites in the decontamination of nuclear wastes has been reviewed recently [7,8].

Cesium (^{137}Cs) is a major component of intermediate-level radioactive wastes. The application of the ion exchange procedure to remove cesium from nuclear waste streams is particularly appropriate, because natural zeolites, especially the most siliceous, present high affinity for this cation [3,9]. This was originally recognized by Ames in the course of his pioneering research on the environmental application of clinoptilolite [10] and has since then been confirmed by other investigators with other zeolite minerals, e.g., erionite [11], phillipsite [12,13] and chabazite [14]. Immobilization of Cs-containing zeolitic tuffs in cement matrices has been the subject of several investigations, which pointed out the safety of the procedure (see, e.g., [15–17]).

An alternative way to safely store radio-nuclides after entrapping them in a zeolite framework is based on a

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thermal treatment that destroys the zeolite structure and blocks the radioactive species into a vitreous lattice or a non-exchanging crystalline phase. Clinoptilolite, among the natural zeolites, is the most frequently used in this type of procedure (see, e.g., [18,19]), but also phillipsite has been successfully tested [20]. The performance of other natural zeolites in this type of procedure would be of interest.

The aim of this paper is therefore to compare the thermal behavior of two Cs-exchanged zeolitic tuffs to check the ability of both materials to entrap cesium and to study the related entrapment mechanisms. The rocks that have been examined are: an erionite-rich tuff from Mexico and an Italian phillipsite/chabazite-rich tuff, that is the most common zeolitic occurrence in Italian zeolite deposits [21].

2. Experimental part

2.1. Materials

Two zeolite-bearing tuffs, coming from Marano (Naples, Italy) and from Agua Prieta (Sonora, Mexico), respectively, were used in this work. Fig. 1 shows the X-ray diffraction (XRD) patterns of these materials, obtained with a Philips PW 1730 instrument (Cu Kα radiation). The Italian rock (Fig. 1(a)), belonging to the huge formation of Neapolitan yellow tuff (NYT) [21], is primarily phillipsitic (Ph) with minor contents of chabazite (C) and analcime (A), whereas the Mexican material (APT) [22] (Fig. 1(b)) is mainly erionitic (E) with minor chabazite (C) and clinoptilolite (Cl). Both samples contain minor amounts of non-zeolitic (non-exchanging) phases, such as feldspar and/or quartz, unreacted original glassy materials and amorphous compounds (e.g., hydrous iron oxides).

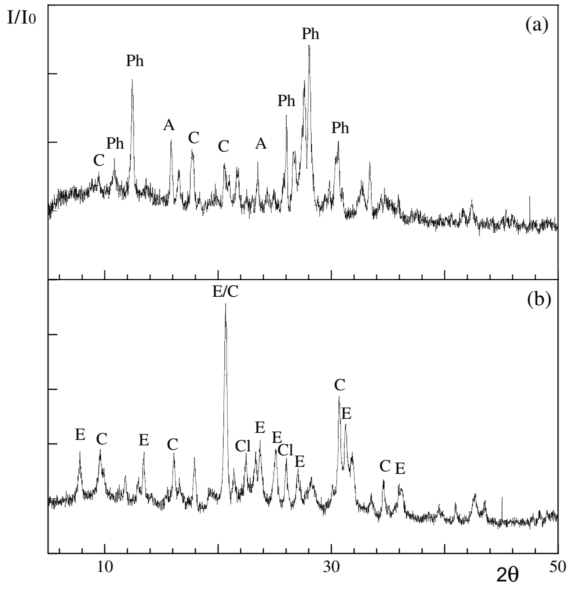

Fig. 1. X-ray powder diffraction patterns of (a) Neapolitan yellow tuff and (b) Agua Prieta tuff. A: Analcime; C: chabazite; Cl: clinoptilolite; E: erionite; Ph: phillipsite. Only the main reflections are indicated.

Table 1
Chemical composition (wt%) on anhydrous basis of the two zeolite-rich tuff samples examined

Oxide	NYT	APT
SiO_2	58.82	69.48
Al_2O_3	19.10	16.34
Fe_2O_3	4.60	2.42
TiO_2	0.53	n.d.
CaO	3.10	2.87
MgO	1.11	1.93
Na_2O	3.44	3.73
K_2O	9.39	3.22
Si/Al[a]	2.62	3.61

[a] In mole.

The results of the chemical analysis on anhydrous basis (silica content was obtained gravimetrically, the other constituents, after suitable acid attack, were determined by atomic absorption spectrophotometry, AAS, Perkin Elmer AAnalyst 1000 instrument), are reported in Table 1. It is to be pointed out that the Si/Al ratio, that is an important parameter in directing the evolution of both materials as a function of temperature, is markedly different in the NYT and APT samples (see Table 1), reflecting essentially the different 'acidity' of the zeolites present in both tuffs [4].

2.2. Methods

Both tuffs were ground to a fineness of <170 mesh. Tuff powders were subjected to ion exchange with Cs^+. In order to enhance the thermal effects, zeolites were loaded with cesium exhaustively, up to their maximum exchange capacity. Accordingly, samples of 100 mg of the powdered rocks were put into contact with 50 ml of a 0.1 M CsCl solution (made from reagent grade Aldrich cesium chloride 99%) under agitation for 24 h. Solution was then replaced after centrifugation and the process repeated until the content of Ca, Mg, Na and K in the contact solution, was at ppm level, which happened roughly after ten exchange steps. Cation concentration in solution was monitored by AAS. Cation exchange capacity (CEC), measured by summing up the amounts of the cations displaced from the tuffs, was equal to 2.47 and 2.15 meq/g for the NYT and APT tuffs, respectively. Comparing these values to the CEC values of the single zeolite phases present in the two tuff samples [8], a rough zeolite content of 70% and 80%, respectively, was worked out.

At the end of the exchange procedure, Cs-exchanged tuff samples were washed with distilled water and dried at 60 °C before thermal treatments. Original powdered tuff materials were also heat-treated for reference.

Thermal stability of zeolites depends on their nature and chemistry, especially on type and amount of extra-framework cations, usually Na, K, Ca and Mg. Most zeolites are stable over 600 °C, e.g., erionite, clinoptilolite and analcime [23]. Phillipsite framework, on the contrary is rather weak, as it breaks within the range 250–360 °C to form feldspar [24]. The chabazite framework is maintained up to about 400 °C, after which it starts to collapse [25]. For all the above reasons and considering the mineralogical compositions of the examined tuffs, the chosen treatment temperatures in air were 60 (dried original samples), 400, 800 and 1000 °C. Time was fixed at 6 h.

Changes in mineral composition of the various samples after thermal treatments were monitored by XRD.

To test the safety of cesium trapping, two procedures were used:

(a) tuff samples were treated with a Na^+ solution, in order to evaluate the amount of back-exchangeable Cs^+. Accordingly, 100 mg of thermally treated Cs-exchanged tuff samples were stirred for 24 h with 50 ml of a 1 M NaCl solution. Cs content in the final solution was analyzed by AAS.

(b) tuff samples were subjected to the so-called ‘availability test’, which measures, at room temperature, the fraction of an element that is not tied up in poorly soluble mineral phases and can potentially be released into environment [26]. In this case Cs^+ release was estimated by contacting the ground samples with distilled water (solid-to-liquid ratio by weight equal to 1/50). In a first stage, which lasted 3 h, the pH of the contact solution was kept constant at 7.0 by adding suitable amounts of a 1 M HNO_3 solution. The treatment was then renewed on the same solid, after separation from solution, in the same conditions as above, except pH which was fixed at 4.0.

3. Results and discussion

3.1. Neapolitan yellow tuff

Table 2 summarizes the results of the X-ray diffraction analysis of the heat-treated original NYT samples and heat-treated Cs-exchanged NYT samples. Mineral phases reported are limited to zeolite phases or their transformation products by heating, that is non-exchanging ancillary phases present in the original samples are not reported.

The Cs-exchanged NYT, treated at 60 °C, showed reduced phillipsite peaks not recovered after back-exchange with a 1 M NaCl aqueous solution. This was probably due to the reduced presence or lack of K, which is reported to be essential for the stability of the framework [13].

In the samples treated at 400 °C, the difference between the Cs-exchanged material and the original material was in the content of amorphous compounds (higher in the exchanged sample), showing that Cs-exchange further destabilizes the crystalline lattice promoting the formation of amorphous phases upon heating.

After treatment at 800 °C, a feldspar, presumably a K-feldspar, $(K,Na)AlSi_3O_8$, appeared in the original sample, besides residual analcime (small amount) and the usual amorphous phases. At 1000 °C a higher amount of alkali feldspar formed, the amorphous compounds being still present. Analcime was no longer observed (Fig. 2(a)).

Instead, in the Cs-containing NYT treated at 800 °C, the amorphous compound was the main constituent, although some minor feldspar and analcime (or pollucite) were found. At 1000 °C, in substantial agreement with previous research [20], the Cs-exchanged sample was mostly a well crystallized pollucite, $CsAlSi_2O_6$, belonging to the family of analcime (Fig. 2(b)), with a limited amount of amorphous phase. As pollucite does not possess exchange properties [27], this should ensure

Table 2
Mineral phases present in the Neapolitan yellow tuff (NYT) in the original form or in its Cs-exchanged form as a function of the treatment temperature[a]

Temperature (°C)	NYT	Cs-exchanged NYT
60	PHI, ANA, CHA, Am	PHI (reduced), ANA, CHA, Am
400	PHI (low), ANA, CHA, Am	PHI (low), ANA, CHA, Am (high)
800	FEL, ANA (low), Am	FEL, ANA? (low), Am (high)
1000	FEL, Am	POL, Am

[a] PHI: Phillipsite; ANA: Analcime; CHA: Chabazite; FEL: K-feldspar; POL: Pollucite; Am: Amorphous; (high), (low) = high, low content.

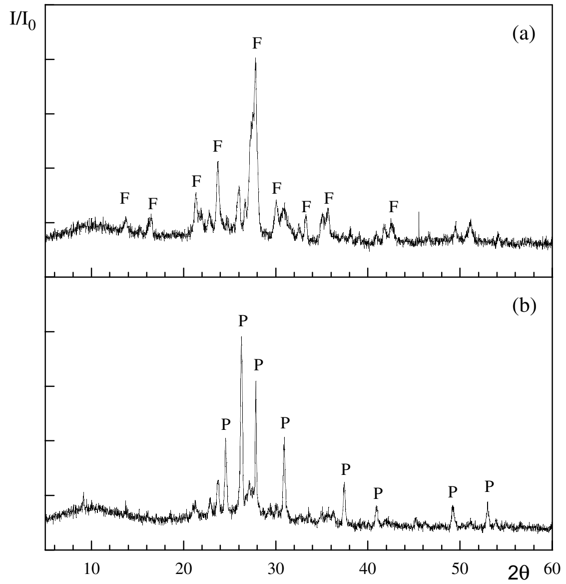

Fig. 2. Comparison of the X-ray diffraction patterns of the Neapolitan yellow tuff treated at 1000 °C: (a) original sample and (b) Cs-exchanged sample. F: K-feldspar; P: pollucite.

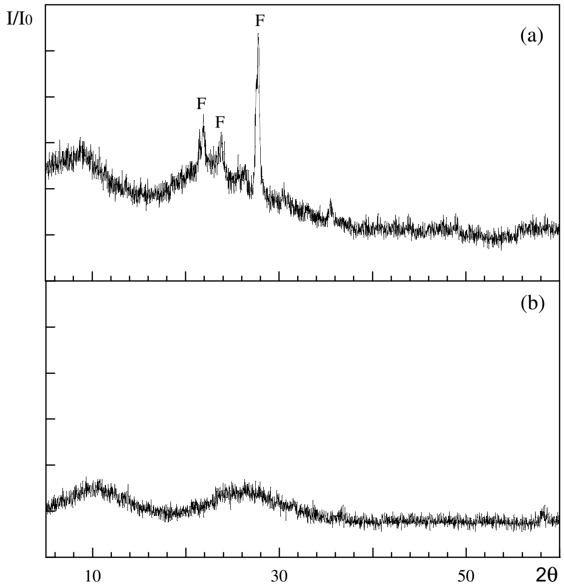

Fig. 3. Comparison of the X-ray diffraction patterns of the Agua Prieta tuff treated at 1000 °C: (a) original sample and (b) Cs-exchanged sample. F: alkali feldspar and/or plagioclase.

that cesium atoms are safely trapped in a crystalline lattice.

3.2. Agua Prieta tuff

Table 3 summarizes the results of the X-ray diffraction analysis of the heat-treated APT samples, analogous to Table 2 with NYT.

No particular changes were observed in the original sample treated at 60 °C. After 400 and 800 °C thermal treatments, the relative content of erionite decreased and, simultaneously, the percentage of amorphous material increased. At 1000 °C the amorphous compounds began to crystallize as feldspar, possibly an alkali feldspar and/or a plagioclase, $(Ca_x,Na_{1-x})Al_{1+x}Si_{3-x}O_8$ (Fig. 3(a)).

The Cs-loaded APT sample presented after treatment, at the lower temperatures, the same compounds as the not exchanged sample, only the ratio of amorphous compounds to zeolite was higher. No cesium compounds were observed. Cesium, most likely, destabilized the network and propitiated its collapse with temperature. At 1000 °C the Cs-exchanged erionite-rich tuff was constituted only by amorphous (possibly vitreous) material (Fig. 3(b)). Pollucite was expected to appear, but presumably the higher Si/Al ratio of the APT sample, compared to the NYT sample (see Table 1), disfavored the conversion of the non-crystalline compounds into pollucite. It is to note, however, that the formation of pollucite is reported in the literature also starting from Cs-exchanged siliceous zeolites, e.g., clinoptilolite [19].

3.3. Back-exchange of the heat-treated samples

Fig. 4 compares the extent of cesium release by the Cs-exchanged NYT and APT samples further to back-

Table 3
Mineral phases present in the Agua Prieta tuff (APT) in the original form or in its Cs-exchanged form as a function of the treatment temperature[a]

Temperature (°C)	APT	Cs-exchanged APT
60	ERI, CHA, CLI, Am (low)	ERI, CHA, CLI, Am (high)
400	ERI, CHA, CLI, Am (low)	ERI, CHA, CLI, Am (high)
800	ERI (low), CLI, Am (high)	ERI (low), Am (high)
1000	FEL, Am (high)	Am

[a] ERI: Erionite; CHA: Chabazite; CLI: Clinoptilolite; FEL: Alkali feldspar and/or plagioclase; Am: Amorphous; (high), (low) = high, low content.

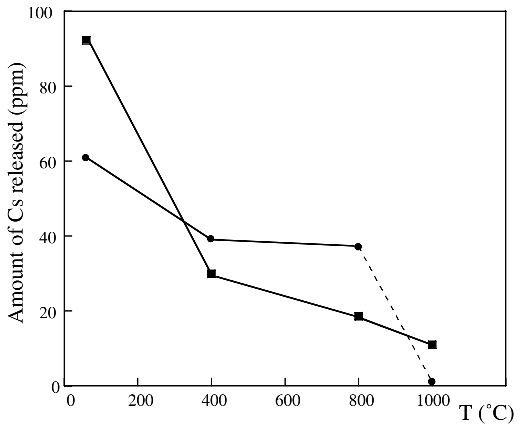

Fig. 4. Amount of cesium released by 100 mg of Cs-exchanged NYT (circles) and APT (squares) samples contacted with 50 ml of a 1 M NaCl solution for 24 h, as function of the treatment temperature.

exchange with NaCl, as a function of temperature. The amount of cesium released evidently reflects zeolite nature and treatment temperature of the exchanged samples. In the materials treated at low temperature (60 °C) cesium was retained more efficiently by the NYT sample, compared to the APT sample, most likely because of the higher Cs affinity for phillipsite than for erionite.

With stronger thermal treatments, the amount of back-exchanged cesium decreases more rapidly for APT than for NYT, possibly because of the different nature of the amorphous material formed, e.g., glassy material versus collapsed zeolite phase, respectively. It may also be speculated that different amounts of vitreous material formed in the two instances. At 1000 °C the trend was reversed. Although cesium was rather safely trapped in the glassy compound reported for the Agua Prieta tuff, the retention of the cation in the heat-treated Neapolitan yellow tuff was much more effective (some ten times higher), because of the formation of pollucite, a non-exchanging cesium alumino-silicate, that definitely inhibits cesium release. Obviously crystalline bonds established in a compound as pollucite are expected to be stronger and more stable than those between occluded cesium and the amorphous (vitreous) silicate lattice.

3.4. Availability test

This test confirms even more convincingly the outcomes of the back-exchange (Table 4). The percent amounts of Cs leached from the NYT and APT samples treated at 800 °C (4.2% and 4.8%, respectively) and especially at 1000 °C (only 0.01% and 0.09%, respectively) are really very small. In addition, it should be kept in mind that the above figures are the maximum amounts of cation that can potentially be released into environment, at room temperature, in the most unfavorable conditions, not the effective extent of leaching in the case of accidental contact with water.

Table 4
Cesium leached by the Cs-bearing tuff samples in the 'availability test'

Treatment temperature (°C)	Total leached Cs, mg/g		Leached Cs, %	
	NYT	APT	NYT	APT
800	13.81	13.71	4.2	4.8
1000	0.05	0.24	0.01	0.09

4. Conclusion

It has been shown that the thermal behavior of two phillipsite-rich or erionite-rich Cs-exchanged tuffs strongly differs from the thermal behavior of the corresponding not exchanged materials. The Cs-containing zeolites, after a thermal treatment of 1000 °C, retain cesium through different mechanisms: the Neapolitan yellow tuff ends up as pollucite, whereas the Agua Prieta tuff forms a vitreous compound. The formation of such compounds determines the leaching behavior of the samples. The Neapolitan yellow tuff is a more efficient cesium encapsulator if treated at 1000 °C than the Agua Prieta tuff. Hence the differences in zeolite structure and composition determine the final safety of the Cs retention.

This conclusion seems to point towards the use of natural materials containing zeolites with a low thermal stability and a lower Si/Al ratio, which likely crystallize as a ceramic compound incorporating cesium.

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