Cesium leaching from γ-irradiated CsA and CsX zeolites

Enrique Lima[a,*], Ilich A. Ibarra[a], Victor Lara[a], Pedro Bosch[b], Silvia Bulbulian[c]

[a] *Universidad Autónoma Metropolitana, Iztapalapa, A. P. 55-532, Av. San Rafael Atlixco No. 186 Col. Vicentina, 09340 México, D.F., Mexico*
[b] *Instituto de Investigaciones en Materiales, A. P. 70-360, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México, D.F., Mexico*
[c] *Instituto Nacional de Investigaciones Nucleares, A.P. 18-1027, Col. Escandón, Delegación Miguel Hidalgo, 11801 México, D.F., Mexico*

ARTICLE INFO

ABSTRACT

The present study discusses the effect of γ-irradiation on Cs^+-exchanged X and A zeolites. The incorporation of Cs^+ ions into A and X zeolites was performed using three different cesium salts (chloride, nitrate or acetate). Cs^+ ions immobilized into the vitrified zeolites by thermal treatment are located in different sites of the zeolite networks. It is found that γ-irradiation favors cesium retention depending on the cesium precursor salt used in the cationic exchange step.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Cesium is one of the most pollutant radionuclides present in radioactive wastes. It may be released from the core of high temperature reactors and interact with the coating graphitic material. Hensel and Hoinkis [1,2] and Hayashi and Fukuda [3] have determined the diffusion coefficients and the corresponding activation energy of cesium in the graphitic matrix. Cesium may contaminate liquids. Then, it has to be retained in a solid matrix. This separation from liquids is usually performed through an ion exchange with clays or zeolites [4]. For instance, clinoptilolite and zeolite A were the exchangers used to trap cesium and strontium in the Chernobyl and the Three Mile Island accidents [5,6]. The vitrification of these materials to immobilize the radionuclides has been widely reported [7–9]. In previous works, the temperature effect on vitrification was studied for natural and synthetic zeolites [7,10]. With temperature well ordered lattices collapse to give rise to a denser and more stable material, for instance a glass.

Furthermore, in high level wastes, ^{137}Cs, a gamma emitter with an energy of 0.661 MeV and a half-life of about 30 years, is a common source of radiation. Radiation damage in host materials can result in swelling, formation of bubbles and other chemical changes.

High energy photons or electrons may, indeed, penetrate deeply and alter the vitrified material. With 200 and 400 keV electrons, analcime, natrolite and zeolite Y are amorphized at room temperature [11,12]. The effects of gamma irradiation have been compared to those due to a thermal treatment. Thus, a primary area of concern is whether radionuclides can leach through those defects after long periods.

Safe retention depends on the location of cesium in the zeolite structure as shown in our previous paper [13]. We found that depending on the anions present in the exchange solution the cesium cations were located in different sites of the zeolite, A or X, network. NMR spectra and radial distribution functions showed that the local environment of cesium is significantly altered with the increase of temperature. Cesium–oxygen distances are, indeed, reduced. In the thermally treated zeolite, non-leaching cesium is most probably occluded in an amorphous aluminosilicate network where it maintains its original electric-field gradient. Cesium leaches preferentially when it is located in the large cavity, site II.

As above-mentioned, cesium radionuclide is a common pollutant in radioactive wastes. Its immobilization can occur through retention in zeolites. Those zeolites, containing radioactive species, can develop structural defects as time goes on. Thus, the aim of the present paper is to study the radiation effects, on the one hand, on cesium-exchanged X and A zeolites and, on the other, on thermally treated cesium-exchanged X and A zeolites.

* Corresponding author. Tel.: +52 5 58044667; fax: +52 5 58044666.
 E-mail address: lima@xanum.uam.mx (E. Lima).

2. Experimental

2.1. Materials

A and X synthetic powdered zeolites in the Na^+ form were utilized to prepare the Cs-exchanged zeolites. The first one (4A), with a framework Si/Al ratio of 1.0, was supplied by Union Carbide with the following composition $Na_{12}Si_{12}Al_{12}O_{48}\cdot xH_2O$. The second one, with a framework Si/Al ratio of 1.2, was supplied by The Sigma Chemical Company with the following composition $Na_{86}(SiO_2)_{106}(AlO_2)_{86}\cdot xH_2O$ and a particle diameter less than $10\,\mu m$.

2.2. Exchange procedure

Cation exchange with $CsCl$, $CsNO_3$ or $CsOOC_2H_3$ was performed as described elsewhere [13]. The exchanged zeolites with the CsCl solution are referred in this paper as CsX-1 or CsA-1, the samples exchanged with the $CsNO_3$ solution are labeled as CsX-2 or CsA-2 and finally, the solids denoted as CsX-3 or CsA-3, correspond to samples exchanged with the $CsOOC_2H_3$ solution. The neutron activation analysis of Cs showed that under these experimental conditions, the cesium contents in the cesium zeolites were $1.10 \pm 0.05\,Cs^+$ mequiv./g CsA-1, $1.09 \pm 0.04\,Cs^+\,Cs^+$ mequiv./g CsA-2, $1.07 \pm 0.05\,Cs^+$ mequiv./g CsA-3, $1.10 \pm 0.05\,Cs^+$ mequiv./g CsX-1, $1.20 \pm 0.06\,Cs^+\,Cs^+$ mequiv./g CsX-2 and finally $1.25 \pm 0.06\,Cs^+$ mequiv./g CsX-3.

2.3. pH measurements

The pH was measured with a potentiometer, LPH430T (Tacuseel Electronique). The exchange solutions $CsCl$, $CsNO_3$ and $CsCOOC_2H_3$ were evaluated before and after the contact with the zeolite.

2.4. Thermal treatment

Zeolite**s** A samples were heated at 673 and 1073 K and the X samples at 673 and 973 K for 12 h. In previous works [7,14] we found that sodium or cobalt A zeolites treated at 1073 K recrystallized as nepheline and carnegeite. Instead, sodium and cobalt X zeolites are stable at temperatures of 973 K. We chose these temperatures to study, first, the behavior of a recrystallized zeolite, zeolite A. In cobalt-exchanged X zeolite we found that with irradiation and thermal treatment (973 K) the Co leaching was reduced 20%. Therefore local vitrification seems to have started at this temperature. Our purpose was to study the performance of this same zeolite exchanged with cesium and to compare it, on the one hand, to the cobalt zeolite and, on the other, to the carnegeite–nepheline mixture.

2.5. γ-Irradiation

The samples were γ-irradiated in a ^{60}Co γ-beam at 6 MGy as this dose is known to be high enough to modify zeolite structures [7].

2.6. Characterization

2.6.1. Neutron activation analysis

The Cs content was determined by neutron activation analysis. Aliquots of 1 mL of the cesium solutions were neutron irradiated in a Triga Mark III nuclear reactor for 15 min with an approximate neutron flux of 10^{13} n/cm² s. The 0.605 MeV photo-peak from ^{134}Cs, produced by the nuclear reaction ^{133}Cs (n, γ) ^{134}Cs, was utilized to determine the Cs radioactivity with a gamma spectrometer that was set up with a Ge/hyperpure solid-state detector coupled to a computerized 4096-channel pulse analyser. The amounts of Cs lixiviated from the solids were determined expressing them as the ratio between the obtained activity and the activity of a standard solution. Cs exchange was calculated in milliequivalents of Cs^+ ion per gram of zeolite. No corrections for the decay of ^{134}Cs were made.

2.6.2. X-ray diffraction

X-ray powder diffraction patterns were obtained using a Siemens D5000 powder diffractometer with a copper anode tube. The Kα radiation ($\lambda = 1.54186$ Å) was selected with a diffracted beam monochromator.

2.6.3. NMR spectroscopy

^{27}Al and ^{133}Cs MAS NMR spectra were acquired operating a Bruker ASX 300 spectrometer at frequencies of 78.21 and 39.37 MHz, respectively. To collect the NMR spectrum data, the heated samples were immediately placed in a glove-box under dry N_2 and were packed in ZrO_2 rotors. The time for recording one NMR spectrum was not longer than 10 min.

The ^{27}Al MAS NMR spectra were acquired with short single pulses ($\pi/6$) and repetition times of $2\,\mu s$. The samples were spun at 10 kHz, and the chemical shifts were referenced to a 1 M $Al(Cl)_3$ solution.

The ^{133}Cs MAS NMR spectra were obtained with sample spinning rates of 5 kHz. The single exciting pulse was of $2\,\mu s$ with a repetition time of 2 s. The chemical shifts were referenced to a 1.0 M aqueous solution of CsCl.

2.6.4. X-ray photoelectron spectrometry (XPS)

XPS studies were made with a VG-Scientific Microtech Multilab ESCA2000 coupled to a detector CLAM4 MCD and a source of Al (Kα = 1486.6 eV). The energy step was 50 eV in an ultra-high vacuum chamber which was first operated at 1×10^{-7} mb. In such conditions, the analysis corresponds to a depth close to 40 Å. Then the sample was eroded by ion sputtering for 5 min, the vacuum was then 1×10^{-8} mb.

2.7. Cesium leaching

Cesium-exchanged zeolites were tested for Cs^+ leaching shaking them with a 1N NaCl solution for 2 h. Solids and liquids were then separated by centrifugation, and the desorbed Cs^+ present in the NaCl solution was determined by neutron activation analyses.

3. Results

3.1. Solution pH values

Table 1 shows that, in all samples, after cesium exchange, the reached pH value is 10.4, instead the initial pH values of the standard Cs^+ solutions were different. As expected the acetate solution presents a higher pH than the other two preparations. pH is, indeed, determined by an acid–base equilibrium which depends on acetate anions while the other two salts fully dissociate.

Table 1
pH values of exchange solutions, before and after exchanging step

Sample	pH values of exchange solutions	
	Before exchange	After exchange
CsX-1	7.81	10.43
CsX-2	6.95	10.43
CsX-3	9.31	10.43
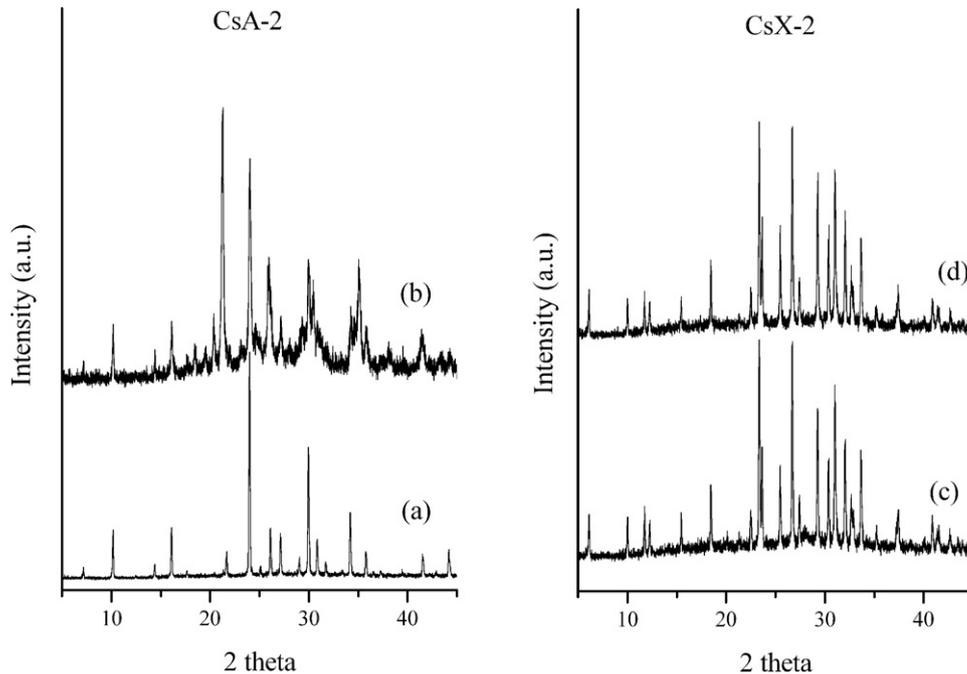
Fig. 1. X-ray diffraction patterns of gamma-irradiated zeolites: (a) and (b) zeolite CsA-2 unheated and heated at 1073 K, respectively; (c) and (d) zeolite CsX-2 unheated and heated at 973 K, respectively.

3.2. X-ray diffraction

As described in our previous work [13], the framework of zeolite A heated at 1073 K is partially destroyed. A high amount of amorphous material is present. The superposed X-ray diffraction peaks can be attributed to zeolite A, nepheline, carnegeite and quartz. In cesium-exchanged zeolite X, the structure is maintained up to 973 K and no other crystalline compounds are detected.

The X-ray diffraction patterns of the irradiated samples are similar to those reported in our previous work for heated samples, Fig. 1. Therefore, the crystalline structure of cesium-exchanged zeolites is not altered by the γ-irradiation at the present dose. However, X-ray diffraction only detects crystalline compounds whose crystallite size is larger than 30 Å and whose content is higher than 3%.

3.3. ^{27}Al MAS NMR spectroscopy

Fig. 2 shows that the combined action of temperature and γ-irradiation is able to propitiate octahedral aluminum formation (signal close to 0 ppm) in both zeolites, CsA and CsX. Indeed, in calcined zeolites the ratio of octahedral aluminum to tetrahedral aluminum is close to 0.12 but in the calcined and irradiated sample it is close to 0.21. Such ratios were determined by the relative intensities of the ^{27}Al NMR signals.

If the zeolite CsX is heated at 973 K and irradiated at 6 MGy, the crystalline structure is maintained but a fraction of aluminum (resonance at 54 ppm) turns out to correspond to octahedra and distorted tetrahedra, resonances at 0 and 42 ppm, respectively, Fig. 2. The partially destroyed zeolite, CsA heated at 1073 K, has a larger fraction of octahedral aluminum.

3.4. ^{133}Cs MAS NMR spectroscopy

Figs. 3 and 4 include ^{133}Cs MAS NMR spectra for gamma-irradiated samples, CsX and CsA, heated at 673 and 973 or 1073 K. The assignment of peaks was made as in Norby et al. [15] and Hunger et al. [16]. As described by Norby et al., the peak intensities may represent the population of cesium in the various sites of the

zeolite. In Table 2 we report the integrated intensities of ^{133}Cs MAS NMR. Cesium cations are redistributed in the various exchange sites as a consequence of the gamma irradiation. For instance, in sample CsX-1 heated at 673 K the site I′ is unoccupied but cesium cations reach this site with the irradiation.

3.5. Cs$^+$ leaching

The amount of cesium retained in leached samples, non-irradiated and γ-irradiated at 6 MGy, determined by neutron activation analyses is shown in the histograms of Fig. 5. With
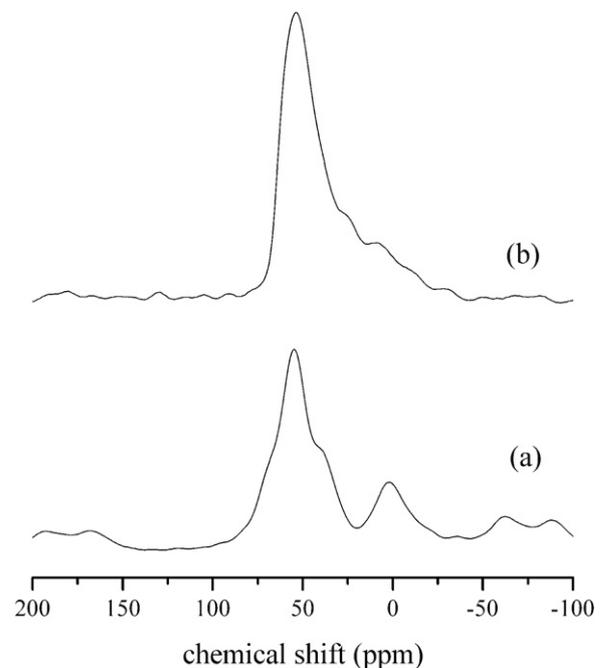
Fig. 2. ^{27}Al MAS NMR spectra of (a) CsA-2 heated at 1073 K and (b) CsX-2 heated at 973 K. Both zeolites were gamma irradiated at 6 MGy after thermal treatment.
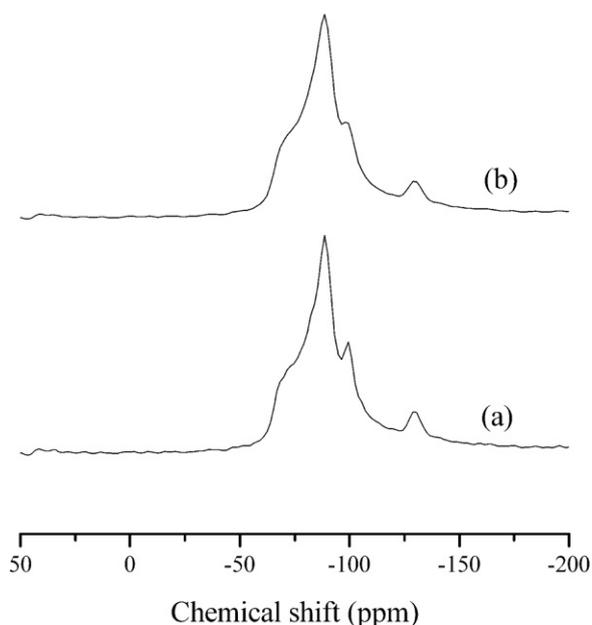
Fig. 3. ^{133}Cs MAS NMR spectra of CsX-2 gamma irradiated at 6 MGy. Samples treated thermally before irradiation (a) at 673 and (b) at 973 K.

temperature, in all cases, cesium immobilization is increased with the exception of samples CsX-3 in which cesium retention was reduced from 76.5 to 71.8%, as temperature increased from 673 to 973 K. In the case of γ-irradiated samples at 6 MGy, two behaviors are observed. On the one hand, the irradiation favors cesium retention (CsX-1, CsA-1, CsX-2 and CsA-2 (673 K)). On the other, although not as clearly, the irradiation promotes cesium leaching (CsX-3, CsA-3 and CsA-2 (1073 K)).

The distribution of cesium cations after the leaching step, obtained from integrated ^{133}Cs MAS NMR peaks, is reported in Table 3. It is worth mentioning that, in contrast with heated samples, the heated and γ-irradiated samples have a similar cation distribution, before and after cesium leaching.

4. Discussion

4.1. Crystalline samples prepared with CsCl

If samples in series 1 are compared, the irradiation effect is clear: in CsCl-exchanged samples, irradiation favors cesium retention. Therefore, the long range order does not alter cesium leaching, only local configurations are determinant, as the non-crystalline or the zeolite X or A structure behave similarly. It seems, then, that irradiation creates small detrital clusters or bridges through the zeolite cavities which inhibit cesium (which has a large size) diffusion. Such proposition is supported by the ^{27}Al MAS NMR
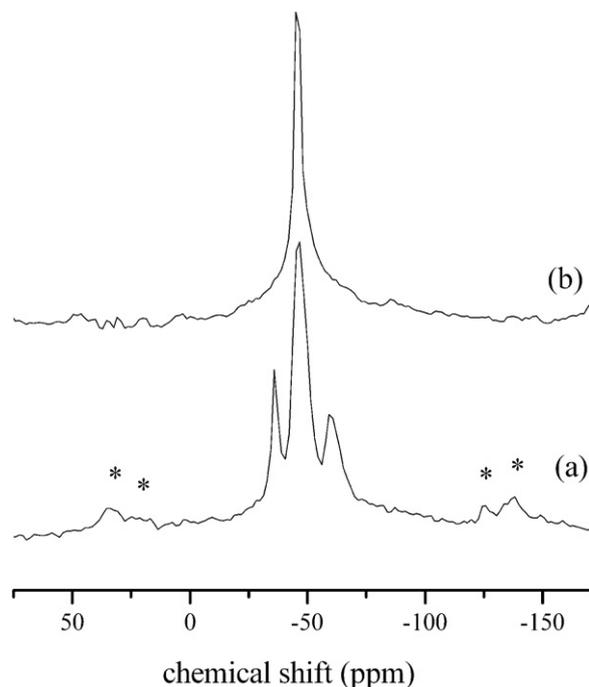
Fig. 4. ^{133}Cs MAS NMR spectra of CsA-2 gamma irradiated at 6 MGy. Samples treated thermally before irradiation (a) at 673 and (b) at 1073 K. Peaks labeled * indicate spinning sidebands.

spectra where the relative amount of octahedral and tetrahedral aluminums may be determined. These species appear with gamma irradiation and they are due to the presence of small alumina particles or aluminum and oxygen dangling radicals [17]. It would be a local amorphization similar to the one proposed by Acosta [18] and Gu et al. [12,19,20] when zeolites are irradiated with an electron beam. Note that, although we found consistence with the results of Acosta and Gu, they used smaller ionizing doses and the nature of radiation was different. Gamma irradiation, used in our work, penetrates deeper than electrons or protons.

The anchoring effect of irradiation can also be attributed to cesium location. As temperature increases, cations are mainly positioned in the large cavity and are free to move. Instead, irradiation propitiates redistribution, the population turns to be more homogeneous and a larger fraction of cesium cations is found in the sodalite cavities. Most probably both effects, obstruction by alumina particles and/or redistribution of Cs cations due to γ-irradiation, are complementary in these samples.

4.2. Crystalline samples prepared with CsOOCCH$_3$

In samples prepared with cesium acetate, series 3, the γ-irradiation promotes leaching independently of the previous

Table 2
Cesium population in the heated (columns named C) and heated and irradiated (columns named C-γ) Cs/zeolites as determined by their relative signal intensities in the ^{133}Cs MAS NMR spectra

T (K)	Site	CsX-1		CsX-2		CsX-3		CsA-1		CsA-2		CsA-3	
		C	C-γ	C	C-γ	C	C-γ	C	C-γ	C	C-γ	C	C-γ
673	SIII	0.57	0.40	0.59	0.42	0.41	0.44	0.43	0.50	0.43	0.33	0.4	0.34
	SII	0.33	0.30	0.29	0.30	0.27	0.31	0.31	0.27	0.30	0.33	0.29	0.36
	SII′	0.11	0.23	0.12	0.20	0.22	0.16	0.27	0.23	0.27	0.34	0.31	0.30
	SI′	0.0	0.07	0.0	0.08	0.09	0.09	0.0	0.0	0.0	0.0	0.0	0.0
973/1073	SIII	0.49	0.37	0.53	0.39	0.33	0.40	0.0	0.0	0.0	0.0	0.0	0.0
	SII	0.29	0.36	0.17	0.32	0.26	0.32	1.0	1.0	1.0	1.0	1.0	1.0
	SII′	0.11	0.17	0.12	0.19	0.32	0.19	0.0	0.0	0.0	0.0	0.0	0.0
	SI′	0.11	0.10	0.18	0.10	0.09	0.09	0.0	0.0	0.0	0.0	0.0	0.0
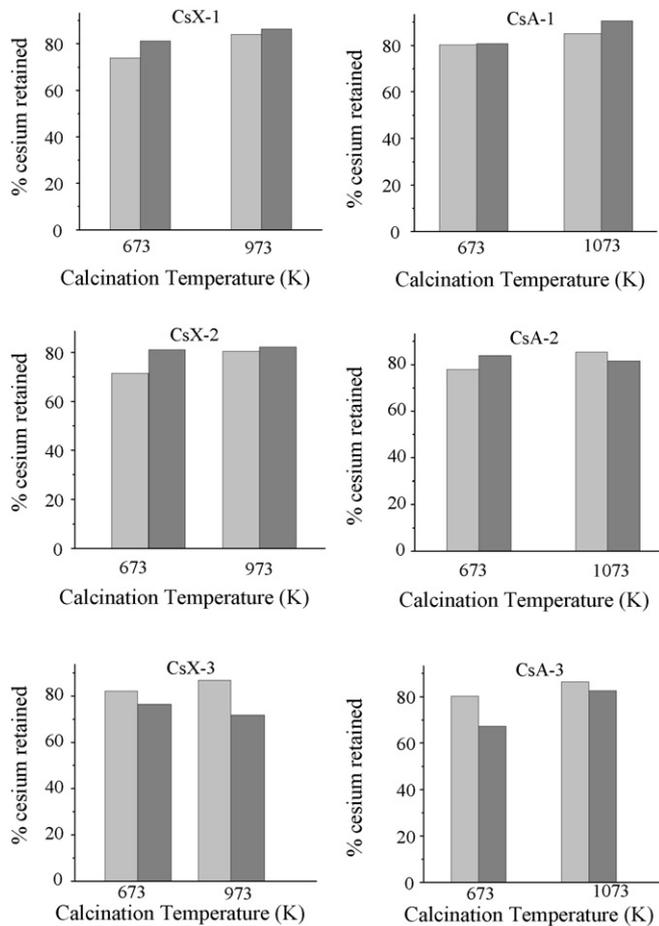
Fig. 5. Cesium retained in zeolites after leaching step. Histograms (▢) correspond to samples calcined at temperature indicated and histograms (■) correspond to samples calcined at temperature indicated and gamma irradiated at 6 MGy.

thermal treatment. As with chloride-exchanged samples, this effect is independent of the zeolite type, of the thermal treatment or the compounds observed by X-ray diffraction. However, the ^{27}Al MAS NMR results reveal the presence of extra framework aluminum in irradiated samples. Therefore, in this series the obstruction of channels, or cavities, with aluminum is also present.

In the thermally treated acetate samples, cesium was found to be located in positions different than those corresponding to cesium in non-irradiated CsX-1. If the promoting salt is cesium acetate, more cesium reaches the sodalite cavities. With irradiation, cesium was found to be distributed in large (close to 70%) and sodalite (close to 30%) cavities. To understand the opposite behavior of the acetate samples, if compared with the chloride samples, two models may be proposed. On the one hand, the very homogeneous occupation

Table 3
Cesium population in the heated and irradiated Cs/zeolites after leaching cesium as determined by their relative signal intensities in the ^{133}Cs MAS NMR spectra

T (K)	Site	CsX-1	CsX-2	CsX-3	CsA-1	CsA-2	CsA-3
673	SIII	0.39	0.40	0.45	0.43	0.39	0.42
	SII	0.29	0.31	0.26	0.31	0.34	0.29
	SII′	0.21	0.18	0.19	0.26	0.27	0.29
	SI′	0.11	0.11	0.10	0.0	0.0	0.0
973/1073	SIII	0.37	0.33	0.41	0.0	0.0	0.0
	SII	0.34	0.34	0.27	1.0	1.0	1.0
	SII′	0.20	0.22	0.23	0.0	0.0	0.0
	SI′	0.09	0.11	0.09	0.0	0.0	0.0

of the exchange sites may provide a high fragility of the zeolite grain to irradiation. Cracks or fractures may appear and facilitate cesium diffusion. Cesium has, indeed, a destabilizing effect on the structure of natural zeolites (chabazite and offretite). This effect is of course enhanced with irradiation. However, the expected broadening of the X-ray diffraction peaks is not observed, then, this hypothesis has to be discarded. On the other hand, even if cesium cations occupy exchange positions, the distribution in the zeolite grain may differ from series 1 and series 3 samples. In series 1, cesium reaches the core of the grain, whereas, in series 3, the external fraction is cesium enriched. Then, with irradiation, even if detrital alumina obstructs the channels, cesium in the external surface is free to leach.

4.3. Crystalline samples prepared from CsNO$_3$

As CsCl and CsNO$_3$ salts fully dissociate, we expected sample CsA-2 to reproduce the CsA-1 measurements. Furthermore, for all characterization techniques used in this work, these two materials were similar. The difference thus has to be attributed to the anions of the salts, as Cs$^+$ amount is similar.

In catalysis, to avoid the trapping effects of Cl$^-$, nitrated salts are often used. Chlorides associate with amorphous alumina or aluminosilicates, altering their sorption properties. Instead, nitrate anions are easily washed.

In our crystalline samples, the small particles of detrital alumina, whose presence is inferred from the NMR results (octahedral aluminum), retain Cl$^-$ and not NO$_3^-$. The chlorinated surface of these alumina agglomerates is highly charged and it is prone to retain cesium and hydronium ions, although Cl$^-$, being a residue of the salt solution used for the exchange, may not be completely removed from the zeolite surface.

To verify such hypotheses a complementary measurement by XPS spectroscopy [21] was made. In Fig. 6, the XPS peaks corresponding to cesium ($3d_{3/2}$ and $3d_{5/2}$) and to chlorine ($2p$) are shown.

The CsX-1 and CsX-2 samples are compared. Two spectra were obtained for each preparation, on the one hand, the sample was just eroded to eliminate residual carbon and, on the other, to elimi-
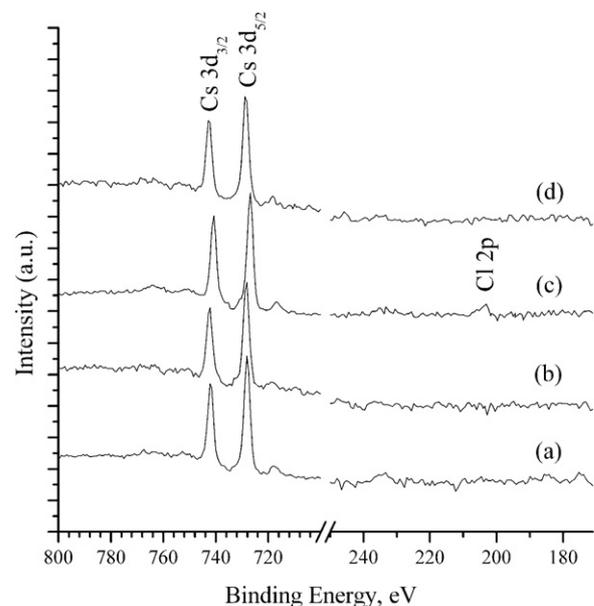
Fig. 6. Comparison of XPS spectra of zeolites containing cesium: (a) CsX-2; (b) CsX-2 after ion sputtering; (c) CsX-1 and (d) CsX-1 after ion sputtering. XPS analyses shown that Cl (0.5 wt%) was present in spectrum (c).

Table 4
Cesium retained per T atom on the surface of cesium zeolites

Sample	$Cs^+/(Al^{3+} + Si^{4+})$[a]
CsX-1 non-eroded	0.140
CsX-1 eroded[b]	0.065
CsX-2 non-eroded	0.075
CsX-2 eroded	0.043

[a] Values determined by XPS analyses.
[b] Ion sputtering for 5 min, the vacuum was 1×10^{-8} mb.

nate the first layers of the zeolite, i.e., the sample was eroded. Only the non-eroded CsX-1 sample presents a chlorine peak showing that chlorine (0.5%) is only present on the surface of CsX-1 zeolite particles.

Then, chlorine, as previously proposed, is associated to surface cesium enrichment. Indeed, if the ratio $Cs^+/(Al^{3+} + Si^{4+})$ is calculated, Table 4, the amount of cesium on the CsX-1 surface is 0.14 while after erosion it turns out to be 0.065, i.e., 2.1 times higher. Instead, in the CsX-2 sample, on the surface of non-eroded sample, the ratio $Cs^+/(Al^{3+} + Si^{4+})$ is 0.075 while in the inner section it is 0.043, the ratio is in this case 1.7. Note that the absolute values may be compared: the absolute amount of cesium per T atom on the surface of the zeolite particles is much higher in the chlorine containing sample.

4.4. Glassy materials

With high temperature treatment, i.e., with zeolite amorphization and recrystallization, two compounds are formed in the same proportion. This material, independently of the cesium salt, leaches

the same amount. Irradiation is equivalent to a further thermal treatment which differentiates these samples where Cs is bonded to the surface grain with different strength. It is, indeed, less labile if attached to chlorinated surface. Then, the difference in the irradiated samples has to be attributed to the amount of residual chlorine. Retention is, therefore, favored by a combined action of chlorine and irradiation in the amorphous compounds.

The sample CsA-3 prepared from acetates does not contain any chlorine or other similar anions. Then, it reproduces the behavior of the CsA-2 sample. The three collapsed samples are most interesting, as they seem to follow a "random" behavior. Although they are all constituted by an amorphous compound and carnegeite, the sample CsA-1, heated at 1073 K, retains more cesium with irradiation whereas the samples CsA-2 and CsA-3, heated at 1073 K, follow an opposite trend. The amount of cesium retained by non-irradiated zeolite A, treated at 1073 K, is in all cases 85–86%, showing that the thermally treated samples are similar as far as the leaching behavior is concerned. The high reproducibility of the results is clear.

The starting materials as already discussed are different. Chlorinated and nitrated samples are homogeneous. In the series 1, cesium reaches the core of the grain which contains a high amount of chloride. Instead, the sample prepared from acetates provides zeolite grains that are cesium enriched in the outer region. With temperature, in the two first series, the obtained aluminosilicate has a homogeneous distribution of cesium into its lattice. In samples of series 3, cesium is mainly found in the external layers of the grains. As these amorphous materials present, most probably, a high amount of cracks and defects which favor the diffusion; the leaching is the same in the same conditions.

Irradiation effect may be understood as a second thermal treatment which alters the composition of the amorphous compound
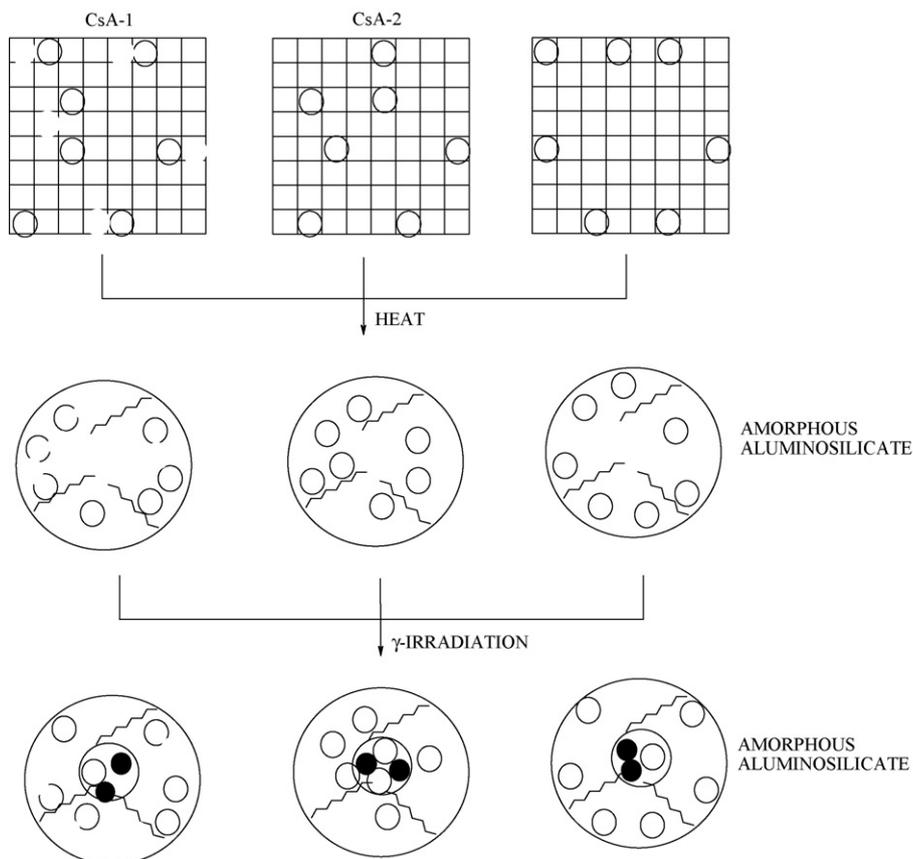
Fig. 7. Representation of the temperature and gamma irradiation action on the cesium-exchanged zeolites; (○), Cs^+; (⬤ grey), Cl^- and (●), Al^{3+}.

as described by Fripiat et al. [22]. The principal radiation-induced changes in the microstructures of interest for nuclear waste glasses are phase changes, phase separation, micro-fracturing and bubble formation. The radiation-induced micro-cracking can significantly increase the surface area for radionuclide release [23,24]. Each particle of solid is constituted by a core constituted by a tetrahedra network whose cavities are occupied by a high number of Al^{3+} cations. Hence in chlorinated and nitrated samples the external layer contains, now, a low amount of cesium but CsX-1 and CsA-1, prepared with CsCl, contain chlorides occluded into the crystals. In series 3, the external layers of the amorphous compound are, now, enriched with aluminum and cesium. Al^{3+} does not retain cesium, although, if it is enriched with Cl^-, the opposite behavior is expected. Fig. 7 represents a simple model corresponding to these considerations.

5. Conclusion

In a previous paper, the thermal treatment on cesium-exchanged zeolites A and X showed that cesium leaching is lower for glassy compounds. In this work, we show that γ-irradiation favors cesium retention depending on the cesium precursor salt. If the salt is cesium chloride or cesium nitrate, gamma irradiation favors the retention in crystalline samples treated at 673 K (X and A zeolite) or 973 K (X zeolite). The pH of the cesium solution in the cationic exchange step determines the cation distribution into the zeolite grain. This parameter explains the opposite behavior of the zeolite exchanged with a solution prepared with cesium acetate.

When the cesium solution was CsCl, γ-irradiation only enhanced cesium retention in the glassy materials obtained by thermal treatment. Chloride, indeed, anchors cesium. Instead, in the zeolites prepared with nitrate or the acetate solutions, irradiation promotes cesium leaching as cesium is preferentially retained on the grain surface.

Acknowledgment

References

[1] W. Hensel, E. Hoinkis, The diffusion of cesium in the graphitic matrix A3-3 in the presence of helium at pressures up to 10^7 Pa, J. Nucl. Mater. 224 (1995) 1–11.

[2] W. Hensel, E. Hoinkis, The diffusion of cesium in the graphitic matrix A3-3 under irradiation by a fast neutron flux of 2×10^{17} m^{-2} s^{-1}, J. Nucl. Mater. 224 (1995) 230–235.

[3] K. Hayashi, K. Fukuda, Diffusion coefficients of cesium in un-irradiated graphite and comparison with those obtained from in-pile experiments, J. Nucl. Mater. 168 (1989) 328–336.

[4] B. De Gennaro, A. Colella, P. Aprea, C. Colella, Evaluation of an intermediate-silica sedimentary chabazite as exchanger for potentially radioactive cations, Micropor. Mesopor. Mater. 61 (2003) 159–165.

[5] N.F. Chelishchev, in: D.W. Ming, F.A. Mumpton (Eds.), Use of Natural Zeolites at Chernobyl: Natural Zeolites '93. Occurrence, Properties, use, International Committee on Natural Zeolites, New York, USA, 1993, p. 525.

[6] D.H. Siemens, D.E. Knowlton, M.W. Shupe, Three Mile Island zeolite vitrification demonstration program, AIChE Symp. Ser. 78 (1982) 41.

[7] S. Bulbulian, P. Bosch, Vitrification of gamma irradiated ^{60}Co^{2+} zeolites, J. Nucl. Mater. 295 (2001) 64–72.

[8] L. Thamzil, Waste Treatment Immobilization Technologies Involving Inorganic Sorbents, International Atomic energy Agency, Vienna, 1997.

[9] E. Lima, P. Bosch, S. Bulbulian, Immobilization of cobalt in collapsed non-irradiated and γ-irradiated X zeolites, Appl. Radiat. Isot. 65 (2007) 259–265.

[10] P. Bosch, D. Caputo, B. Liguori, C. Colella, Safe trapping of Cs in heat-treated zeolite matrices, J. Nucl. Mater. 324 (2004) 183–188.

[11] B.X. Gu, L.M. Wang, R.C. Ewing, The effect of amorphization on the Cs ion exchange and retention capacity of zeolite-NaY, J. Nucl. Mater. 268 (2000) 64–72.

[12] B.X. Gu, L.M. Wang, S.X. Wang, D.G. Zhao, V.H. Rotberg, R.C. Ewing, The effect of H$^+$ irradiation on the Cs-ion exchange capacity of zeolite-NaY, J. Mater. Chem. 10 (2000) 2610–2616.

[13] E.J. Lima, I.A. Ibarra, M.A. Vera, V.H. Lara, P. Bosch, S. Bulbulian, I. Cs leaching in CsX and CsA zeolites, J. Phys. Chem. B 108 (2004) 12103–12110.

[14] E.J. Lima, V.H. Lara, S. Bulbulian, P. Bosch, Fractal dimension and cobalt leaching in CoX and CoA zeolites, Chem. Mater. 16 (2004) 2255–2258.

[15] P. Norby, F.I. Poshni, A.F. Gualtieri, J.C. Hanson, C.P. Grey, Cation migration in zeolites: an in situ powder diffraction and MAS NMR study of the structure of zeolite Cs(Na)-Y during dehydration, J. Phys. Chem. B 102 (1998) 839–856.

[16] M. Hunger, U. Schenk, B. Burger, J. Weitkamp, Synergism between the guest compound and the host framework in zeolite CsNaY after impregnation with cesium hydroxide, Angew. Chem. Int. Ed. Engl. 36 (1997) 2504–2506.

[17] L. Alvarez, A. Ramírez-Solís, P. Bosch, Mechanisms of formation of extra-framework Al_2O_3 in zeolites, Zeolites 18 (1997) 54–62.

[18] D.R. Acosta, G. Vazzquez-Polo, R. Garcia, V. Castano, Electron-beam degradation of Ca-A zeolite, Radiat. Eff. Defects Solids 127 (1993) 37–43.

[19] B.X. Gu, L.M. Wang, L.D. Minc, R.C. Ewing, Temperature effects on the radiation stability and ion exchange capacity of smectites, J. Nucl. Mater. (2001) 345–354.

[20] B.X. Gu, L.M. Wang, R.C. Ewing, The effects of radiation on the retention of strontium in zeolite-NaSrY, J. Mater. Chem. 12 (2002) 233–238.

[21] C. Colella, F. Mumpton, Natural Zeolites for the Third Millenium, de Frede Editore Napoli, Italy, 2000.

[22] J.J. Fripiat, J. Chaussidon, A. Jelli, Chimie-Physique des phenomenes de Surface, Mason et Cie Paris, France, 1971.

[23] N. Bordes, K.E. Sickafus, E.A. Cooper, R.C. Ewing, Structural damage in spinel after ion irradiation, J. Nucl. Mater. 225 (1995) 318–323.

[24] R.C. Ewing, W.J. Weber, F.W. Clinard, Radiation effects in nuclear waste forms for high-level radioactive waste, Prog. Nucl. Energy 29 (1995) 63–127.