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Combustion treatment of Co^{2+} and Cs^+ exchanged zeolites

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Abstract

The capacity of A, X and clinoptilolite zeolites to remove Co^{2+} or Cs^+ is compared. The Co^{2+} and Cs^+ exchanged zeolites were thermally and combustion treated until vitrification. Desorption of cobalt and cesium from those treated solids was tested by lixiviation with 1 N NaCl solution. As the calcining temperature increased, the cristallinity of cobalt and cesium exchanged zeolites decreased. The retention of cobalt and cesium in thermally treated exchanged zeolites is slightly higher than in combustion treated zeolites ignited at 1000 °C. The difference is attributed to the compounds (amorphous and crystalline) formed during the treatments. The cobalt and cesium content were determined by neutron activation analyses and the solids were characterized by X-ray diffraction, IR-spectroscopy and scanning electron microscopy (SEM).

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1. Introduction

Nuclear waste waters from nuclear plants, hospitals, or industries may contain radioactive atoms in solution. As the disposal of such polluted liquids is hazardous, the radioactive ions have to be retained in non-leaching solids to be deposited in nuclear cemeteries [1].

Ionic exchangers may be used to retain radioactive atoms. On the one hand, anion exchangers as hydrotalcites, or, on the other, cation exchangers as resins, clays or zeolites have been tested. The two last materials are more resistant to radioactivity

and temperature than resins. Unfortunately, clays have a low exchange capacity and, due to their bidimensional structure, they may be delaminated in solution. Instead, zeolites retain cations in severe conditions. That is the reason why, in the nuclear accident of Chernobyl, 1 500 000 tons of zeolites were used [1].

If in contact with water, exchanged zeolites may leach. To avoid leaching, Dyer and Abou-Jamous have proposed to block the pores of the zeolites with large cations as barium [2]. Still, the most commonly proposed solution is thermal treatment. The exchanged minerals have to be treated thermally up to vitrification or to form other crystalline compounds. In this way, the radioactive materials are encapsulated [3]. However, with time and

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radioactivity, defects and cracks may appear in the initially safe compounds. Thus, new treatments have to be attempted in order to avoid leaching and reduce costs.

In this study, we have chosen two radioactive cations, Co^{2+} and Cs^+, as they are both representative of nuclear wastes. Radioactive cesium whose half-life is 30 years (^{137}Cs) is, indeed, a main product of the ^{235}U fission reaction. Cobalt is present in many radioactive wastes and has a half-life of 5.2 years [4]. Cesium has an ionic radius of 0.174 nm. Instead, cobalt is much smaller (0.075 nm) [5].

The chosen cationic exchangers are zeolites A, X and clinoptilolite which differ in their Si/Al ratios (1.0, 1.2 and 5.0, respectively) [6,7]. The first two are synthetic and the last one is natural. The window sizes are comprised between 0.28 nm and 0.75 nm [7]. The collapse temperature of zeolites A, X and clinoptilolite in air is 700 °C, 700 °C and 750 °C, respectively as reported by Breck [7]. Hence, the effect of window size and Si/Al ratio on the features of combustion or thermally treated materials may be discussed.

The purpose of our work is, indeed, to compare the immobilization of Co or Cs in exchanged zeolites by treating the samples thermally or by a combustion process with urea (CH_4N_2O) ignited at different temperatures. The last method is known to provide ceramics or vitreous compounds as urea combustion is highly exothermic [8–10]. This technique is inexpensive and has not been tested in nuclear waste disposal.

2. Experimental

2.1. Materials

The synthetic zeolites, NaA (Union Carbide Corp.) and NaX (Sigma Chemical Company), and the natural clinoptilolite from San Luis Potosí (Central Mexico) supplied by Dr. Krasoń were utilized to prepare cobalt or cesium exchanged zeolites. They are alluded in this text, as AZ, XZ and C, respectively. Urea (Merck) was utilized in the combustion process (particles sizes 150 μm). Synthetic powdered A and X zeolites were passed through 400 mesh sieve (10 μm) and the clinoptilolite through a 150 mesh (100 μm).

Before cobalt or cesium exchange, each zeolite sample (50 g) was left for 8 days in a 5 N NaCl solution. It was, then, washed several times with distilled water until the solution was free of chloride ions i.e.

when AgCl did not precipitate when in contact with $AgNO_3$ solution [11]. Analytical reagents were used for both analyses and ion-exchange processes. The resulting materials were labeled NaAZ, NaXZ and NaC.

2.2. Cobalt or cesium exchange

23.5 g of NaAZ, NaXZ or NaC were shaken for 1 day in 470 ml of $Co(NO_3)_2$ or $CsNO_3$ 0.06 N solutions in order to obtain the respective Co^{2+} and Cs^+ exchanged zeolites. The solids were then separated by centrifugation and the residual content of cobalt or cesium in the remnant solution, in each experiment, was determined by neutron activation analysis. The amount of Co^{2+} or Cs^+ exchanged in the zeolite was calculated in milliequivalent (meq) uptake per gram of hydrated zeolite.

The experimental conditions were selected in order to obtain low Co^{2+} and Cs^+ exchanged zeolites (about 1 meq/g of zeolite) thereby preventing Co^{2+} and Cs^+ desorption from the solid in absence of external agents. Of course, such conditions are far from those of practical applications which require high loadings. But, in our extreme situation the differences in leaching out samples are enhanced.

The samples exchanged with the $Co(NO_3)_2$ solution are referred to as Co,NaAZ; Co,NaXZ and Co,NaC and those exchanged with $CsNO_3$ are labeled as Cs,NaAZ; Cs,NaXZ and Cs,NaC.

2.3. Thermal treatment

Two hundred milligrams of Co and Cs exchanged zeolites were calcined in air from 600 to 1000 °C for 3 h and some from 500 to 800 °C for 5 min.

2.4. Combustion treatment

Each exchanged zeolite (200 mg) was mixed with urea (400 mg) and 5 cm³ of distilled water. The resulting dispersion was heated until most water was evaporated. Then, the mixture was transferred into an oven preheated up to 500, 750 or 1000 °C, for 5 min.

2.5. Neutron activation analysis

Cobalt and cesium in solution were analyzed by neutron activation [12]. Samples were irradiated in the TRIGA MARK III reactor for 10 min with

an approximate neutron flux of 10^{13} n/cm^2 s.[1] The photopeaks of 1170 and 1330 keV from ^{60}Co produced by the nuclear reaction ^{59}Co(n, γ)^{60}Co and 605 and 796 keV from ^{134}Cs produced by the nuclear reaction ^{133}Cs(n, γ)^{134}Cs were measured with a Ge/hyperpure solid-state detector coupled to a computerized 4096 channel pulse height analyzer.

The amount of Co and Cs was estimated by comparing the activities of the corresponding liquid aliquots and blanks of standard Co(NO$_3$)$_2$ and CsNO$_3$ solutions. The assigned errors correspond to the standard deviation for the Poisson distribution obtained from three different analyses.

2.6. X-ray diffraction

All zeolite powders were studied by X-ray diffraction with a Bruker axs, D8 Advance powder diffractometer coupled to a copper anode X-ray tube. Each sample was studied by X-ray diffraction to identify the crystalline compounds. The amount of the identified compound ($\pm 3\%$) was estimated from the sum of the X-ray diffraction peak areas assuming that the X-ray absorption was the same in all materials. These values are relative and reveal the trend of the sample composition. The cell parameters of the zeolites were obtained, using a sodium chloride standard, from the (644) and the (751) peak positions for the A and X zeolites, respectively. For clinoptilolite the peak positions (40 −2, 002, 350, 061) were used to calculate the a,b and c parameters of the monoclinic cell. The peaks were all scanned at an angular speed of (1/4)°/min. The assigned uncertainties were derived with the program LSUCRI (least squares unit cell refinement with indexing) [13].

2.7. Infrared spectroscopy

The infrared spectra were recorded in the range 4000–400 cm^{-1} with a Nicolet 510P spectrometer. The Pellets were obtained mixing the samples with KBr.

2.8. Scanning electron microscopy

A Jeol JSM 5900LV scanning electron microscope (SEM) was used to determine the sample morphologies. All samples were mounted on the sample holder with conductive carbon glue and coated with a thin gold film by sputtering for 50 s.

2.9. Leaching out test

Immobilization in the zeolites was measured through lixiviation of Co^{2+} and Cs$^+$ with a 1 N NaCl solution. Samples (100 mg), thermally treated or treated by combustion, were shaken with 20 ml of a 1 N sodium chloride solution (pH = 5.5) for 3 h. The pH readings were obtained with a Hanna Instrument, model HI223 pH meter. Conventionally, the solid was separated from the liquid by centrifugation, the solid was, then, washed with distilled water and dried at 100 °C, as at this temperature zeolites are stable and only the sample humidity is lost [6]. The remnant solutions reached pH values between 6.1 and 7.0. In the lixiviated solution, the cobalt or cesium content was measured by neutron activation analysis.

3. Results

3.1. Neutron activation analysis

Zeolites NaAZ; NaXZ and NaC were exchanged with Co^{2+} and Cs$^+$. Zeolites A, X and clinoptilolite, whose exchange capacities are 5.5 meq/g, 4.7 meq/g and 2.2 meq/g respectively, were, under our working conditions, only partially exchanged. The Co^{2+} and Cs$^+$ content in the prepared samples were, indeed, comprised between 0.1 and 1.33 meq/g of zeolite, as shown in Table 1.

3.2. X-ray diffraction

Fig. 1 compares the diffraction patterns of the Na exchanged zeolites with those exchanged with Co^{2+} or Cs$^+$. All samples were found to be fully crystalline. In A and X based preparations no other compounds than the respective A, X zeolites were observed. Instead, in clinoptilolite based prepara-

Table 1
Co^{2+} and Cs$^+$ content in the exchanged zeolites

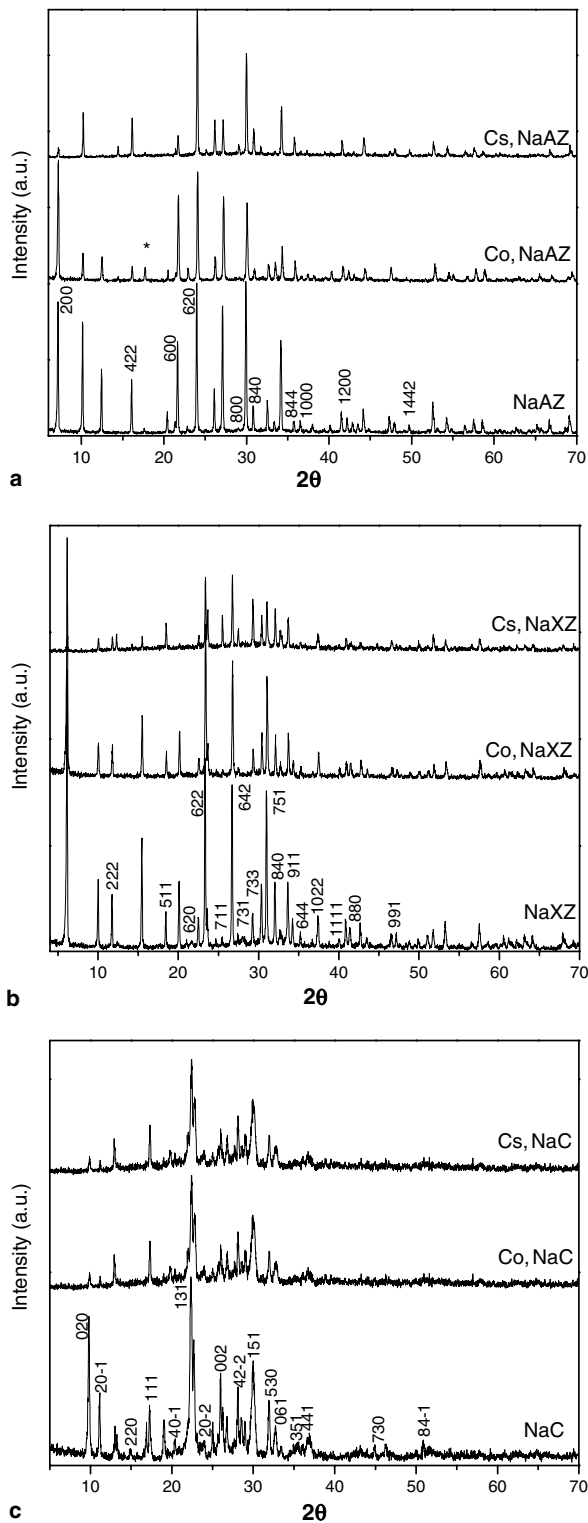| Sample	Co^{2+} (meq/g)	Cs$^+$ (meq/g)
Co,NaAZ	1.191	
Cs,NaAZ		1.082
Co,NaXZ	1.180	
Cs,NaXZ		1.337
Co,NaC	0.162	
Cs,NaC		1.072

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[1] Neutron flux density.

Fig. 1. X-ray diffraction patterns of (a) NaAZ; Co,NaAZ and Cs,NaAZ; (b) NaXZ; Co,NaXZ and Cs,NaXZ; (c) NaC; Co,NaC and Cs,NaC.

tions (NaC, Co,NaC and Cs,NaC) albite was present and, if Co or Cs were exchanged, a small fraction of the sample turned out to be amorphous. As the relative intensities of the zeolite diffraction peaks of the Co^{2+} and Cs^+ exchanged samples varied, the corresponding ion exchanges were performed [14,15]. Cell parameters were 2.467 ± 0.006, 2.454 ± 0.007 and 2.460 ± 0.004 nm for the zeolite present in NaAZ; Co,NaAZ; Cs,NaAZ and 2.504 ± 0.005, 2.502 ± 0.003 and 2.505 ± 0.002 nm, for NaXZ; Co,NaXZ; Cs,NaXZ. The cell parameters for clinoptilolite samples NaC; Co,NaC and Cs,NaC are presented in Table 2.

Tables 3–5 compare the composition of NaAZ, NaXZ and NaC to the corresponding exchanged materials, and thermally or combustion treated. In the NaAZ thermally treated at 800 °C, a fraction of zeolite A remained unaltered (23%) and a high percentage of amorphous compound (70%) and carnegieite (7%) appeared. Instead, in Co,NaAZ treated at 800 °C no zeolite remained, carnegieite was the main compound (67%), amorphous compound was also observed (33%). In Cs,NaAZ thermally treated at 800 °C the original zeolite (73%) and some amorphous material (27%) were identified.

In 1000 °C treated NaAZ, 63% of carnegieite and 37% of nepheline were formed. Instead, nepheline (62%) was the main component of the Co,NaAZ, together with amorphous material (28%) and carnegieite (10%). Carnegieite (62%), amorphous material (25%) and nepheline (13%) were the main compounds found in Cs,NaAZ treated at 1000 °C.

NaAZ sample treated by combustion at 750 °C did not show carnegieite, instead the original zeolite (42%), amorphous compound (38%) and a crystalline sodium aluminum silicate hydrated (20%) were found. However, in the same conditions, 28% of the cobalt containing sample, Co,NaAZ, remained unaltered while 55% of amorphous compound, 10% of carnegieite and 7% of crystalline sodium aluminum silicate hydrated were formed. The compounds obtained by combustion at 750 °C in Cs,NaAZ were crystalline sodium aluminum silicate hydrated (54%) and amorphous material (46%).

The NaAZ, combustion treated at 1000 °C, formed sodium aluminum silicate hydrated (80%) and carnegieite (20%), while Co,NaAZ produced only carnegieite, instead Cs,NaAZ formed, the sodium aluminum silicate hydrated (19%), amorphous material (50%), albite (25%) and carnegieite (6%), Table 3.

Table 2
Cell parameters of NaC; Co,NaC and Cs,NaC

Samples	a_0 (nm)	b_0 (nm)	c_0 (nm)	β (°)
NaC	1.775 ± 0.046	1.802 ± 0.029	0.723 ± 0.009	116.2 ± 0.2
Co,NaC	1.776 ± 0.023	1.804 ± 0.028	0.740 ± 0.010	116.1 ± 0.1
Cs,NaC	1.753 ± 0.063	1.802 ± 0.056	0.743 ± 0.015	116.3 ± 0.2

Table 3
Compounds formed by thermal treatment for 3 h (TT) and combustion treatment (CT) of samples NaAZ; Co,NaAZ and Cs,NaAZ

T (°C)		500		750		800		1000	
Samples			%		%		%		%
NaAZ	TT					am	70	car	63
						NaAZ	23	nep	37
						car	7		
	CT	NaAZ	100	NaAZ	42			sas	80
				am	38			car	20
				sas	20				
Co,NaAZ	TT	Co,NaAZ	100			car	67	nep	62
						am	33	am	28
								car	10
	CT	Co,NaAZ	100	am	55			car	100
				Co,NaAZ	28				
				car	10				
				sas	7				
Cs,NaAZ	TT					Cs,NaAZ	73	car	62
						am	27	am	25
								nep	13
	CT	Cs,NaAZ	100	sas	54			am	50
				am	46			alb	25
								sas	19
								car	6

alb = albite [(Na,Ca),Al$_4$Si$_4$O$_8$), JCPDS card 20-0548]; am = amorphous compound; car = carnegieite [(NaAlSiO$_4$), JCPDS card 11-0220]; nep = nepheline [(NaAlSiO$_4$), JCPDS card 35-0424]; sas = sodium aluminum silicate hydrated [(Na$_6$Al$_6$Si$_6$O$_{24}$ · H$_2$O), JCPDS card 42-0216].

Table 4 summarizes the behavior of NaXZ, Co,NaXZ and Cs,NaXZ samples thermally or combustion treated. As with zeolite A, the Co,NaXZ and Cs,NaXZ did not reproduce the behavior of the original NaXZ and the compounds obtained with thermal treatment differ from those combustion treated.

The clinoptilolite based samples, Table 5, reproduce these trends. Note, however, that only the cesium (or cobalt) samples prepared using zeolite X produce pollucite (or cobalt aluminate) when treated.

3.3. Infrared spectroscopy

To be sure that no remnants of urea were present in the 1000 °C combustion treated samples, the infrared spectra of the non-treated and 1000 °C combustion treated materials are compared in Fig. 2. No urea was found in the heated samples.

Zeolite infrared spectra can be understood if two types of vibration are considered [7,16], (1) those due to the internal vibrations of the TO$_4$ tetrahedron which are not sensitive to other structural variations and (2) vibrations which may be related to the linkages between tetrahedra. This second group, sensitive to the topology and mode of arrangement of the secondary unit of structure in the zeolite, occurs in the regions 500–650 and 300–420 cm^{-1}. The band in the 500–650 region is related to the presence of the double ring (D4R and D6R) and it is observed in all zeolite structures containing the double 4- and double 6-rings (clearly zeolites A and X). The absence of that vibration in the IR spectra shows

Table 4
Compounds formed by thermal treatment for 3 h (TT) and combustion treatment (CT) of samples NaXZ; Co,NaXZ and Cs,NaXZ

T (°C)		500		750		800		1000	
Samples			%		%		%		%
NaXZ	TT					am	62	nep	100
						NaXZ	38		
	CT	NaXZ	100	am	65			am	61
				NaXZ	20			sas	18
				alb	10			alb	13
				nep	5			nep	8
Co,NaXZ	TT					am	100	nep	69
								am	31
	CT	Co,NaXZ	100	am	51			am	57
				Co,NaXZ	23			alb	23
				nep	11			nep	9
				alb	10			o–a–c	6
				qua	5			qua	5
Cs,NaXZ	TT					Cs,NaXZ	62	nep	55
						am	38	pol	24
								am	21
	CT	am	67	am	45			am	51
		Cs,NaXZ	33	Cs,NaXZ	37			nep	26
				nep	8			pol	15
				pol	6			qua	8
				qua	4				

alb = albite [(Na, Ca), Al$_4$Si$_4$O$_8$), JCPDS card 20-0548]; am = amorphous compound; nep = nepheline [(NaAlSiO$_4$), JCPDS card 35-0424]; o–a–c = cobalt aluminate [(CoAl$_2$O$_4$), JCPDS card 44-0160]; pol = pollucite [(CsAlSi$_2$O$_6$), JCPDS card 29-0407]; qua = quartz [(SiO$_2$), JCPDS card 46-1045]; sas = sodium aluminum silicate hydrated [(Na$_6$Al$_6$Si$_6$O$_{24}$ · H$_2$O), JCPDS card 42-0216].

the disgregation of the corresponding zeolite. Such was the case in all combustion treated samples ignited at 1000 °C. This remark is in agreement with the X-ray diffraction results previously presented.

3.4. Electron microscopy

The morphological differences between thermal and combustion treatments were determined by scanning electron microscopy. Fig. 3 compares the micrographs of Co,NaXZ thermally (800 °C) or combustion (750 °C) treated. The thermally treated material as determined by X-ray diffraction is fully constituted by amorphous material. Most particles are large (25 μm) although particles of 1 μm are also found. In the combustion treated sample, the particles are spheroidal and their size is close to 2.5 μm, the morphology of the sample is very homogeneous. Although the sample contains 23% of crystalline Co,NaXZ, no zeolite faceted crystals are apparent. Thus, the zeolite must be occluded into the amorphous compound.

When this material, Co,NaXZ, was treated at 1000 °C, the thermally treated Co,NaXZ became a thick amalgam of amorphous (vitreous) material

and nepheline (small faceted particles). The bubbles (3–5 μm) in the vitreous compound are due to the high temperature, the material has evidently melted. In the combustion treated sample, the same bubbles in the vitreous compound are observed but the material is less dense. The smaller crystalline particles must be albite as determined by X-ray diffraction, Fig. 4.

This general behaviour is reproduced by the clinoptilolite samples, Fig. 5. In the Cs,NaC sample, treated thermally at 800 °C, which was composed by 56% of Cs,NaC and 44% of albite, a large number of coffin like crystals may be observed, they are characteristic of clinoptilolite. They are located on top of larger particles probably albite. Although the combustion treated clinoptilolite at 750 °C contains 80% of clinoptilolite and 20% of albite, no clinoptilolite crystals are visible. Only a thick layered material is found, then, again, the zeolite crystallites must be occluded into such material.

If the temperature was increased to 1000 °C, both materials turned out to be a heterogeneous mixture where no zeolite crystals were observed. The combustion treated sample was more dispersed than the thermally treated.

Table 5
Compounds formed by thermal treatment for 3 h (TT) and combustion treatment (CT) of samples NaC; Co,NaC and Cs,NaC

T (°C)		500		600		750		800		1000	
Samples			%		%		%		%		%
NaC	TT			NaC	69			NaC	44	am	61
				alb	31			am	37	tr	17
								alb	13	alb	15
								qua	6	qua	7
	CT	NaC	78			NaC	40			am	58
		alb	11			am	30			alb	33
		qua	11			alb	20			qua	5
						qua	10			cr	4
Co,NaC	TT			Co,NaC	55			am	61	am	50
				qua	41			qua	20	alb	47
				alb	4			Co,NaC	16	qua	3
								alb	3		
	CT	Co,NaC	80			Co,NaC	54			am	53
		alb	20			am	34			alb	29
						alb	8			qua	9
						qua	4			cr	9
Cs,NaC	TT			Cs,NaC	58			Cs,NaC	56	am	65
				alb	42			alb	44	an	32
										qua	3
	CT	Cs,NaC	82			Cs,NaC	80			am	50
		alb	18			alb	20			Cs,NaC	20
										alb	20
										qua	10

alb = albite [(Na, Ca), Al$_4$Si$_4$O$_8$), JCPDS card 20-0548]; am = amorphous compound; an = anorthite [(Na, Ca) Al$_2$Si$_4$O$_8$, JCPDS card 20-0528]; cr = cristobalite [(SiO$_2$), JCPDS card 39-1425]; qua = quartz [(SiO$_2$), JCPDS card 46-1045]; tr = tridymite [(SiO$_2$), JCPDS card 18-1170].

3.5. Leaching out test

Lixiviation results in non-treated, thermally treated (TT) and combustion treated (CT) samples are displayed in Tables 6–11. Cobalt lixiviated through Co,NaAZ sample was $10.7 \pm 1.05\%$ but in thermally and combustion treated zeolites, the values were much lower, Table 6. Percentages of Co lost in both treatments were similar for similar temperatures within experimental error range.

Results obtained by TT for 3 h and CT samples for 5 min in Table 6 are similar within the experimental error range. As there was the possibility that the effect of heating periods of 5 min and 3 h could be the same, an additional set of 2 experiments was performed, Table 6-A. At 500 °C, 5 min heating did not produce any apparent damage in the solid as the Co^{2+} lixiviated from Co,NaAZ zeolite ($13.9 \pm 2.60\%$) is similar to Co^{2+} lixiviated from non-treated Co,NaAZ ($10.7 \pm 1.05\%$). However at 800 °C, thermal treatment of 5 min (Table 6-A) produced a reduction of lixiviated Co^{2+} to $5.9 \pm 2.24\%$, being considerably higher than the amount lixivi-

ated from the samples thermally treated for 3 h at 800 °C ($1.9 \pm 0.43\%$). Therefore, the combustion process favours cobalt retention and it is worthwhile to compare it to conventional thermal treatments. Combustion treatment produces crystal damage, not only because of the heating period in the muffle furnace but because of the combustion process itself which provides additional heat.

Cesium lixiviated through the non-treated Cs,NaAZ sample was $62.0 \pm 2.50\%$, but in the treated zeolites it decreased considerably, Table 7. Note that Cs percentage lost in the 1000 °C combustion treated sample is rather close to the amount lost in the corresponding thermally treated sample, Table 7.

The amount of cobalt lixiviated through Co, NaXZ sample in the thermally treated zeolite at 800 and 1000 °C, after being in contact with the NaCl solution, turned out to be 1.4 ± 0.52 and $0.3 \pm 0.26\%$, respectively, whereas the non-treated zeolite lixiviated $32.7 \pm 2.35\%$ of Co^{2+}. The zeolite treated at 1000 °C retained efficiently the cobalt, Table 8, as only $0.3 \pm 0.26\%$, less than 1% of Co,
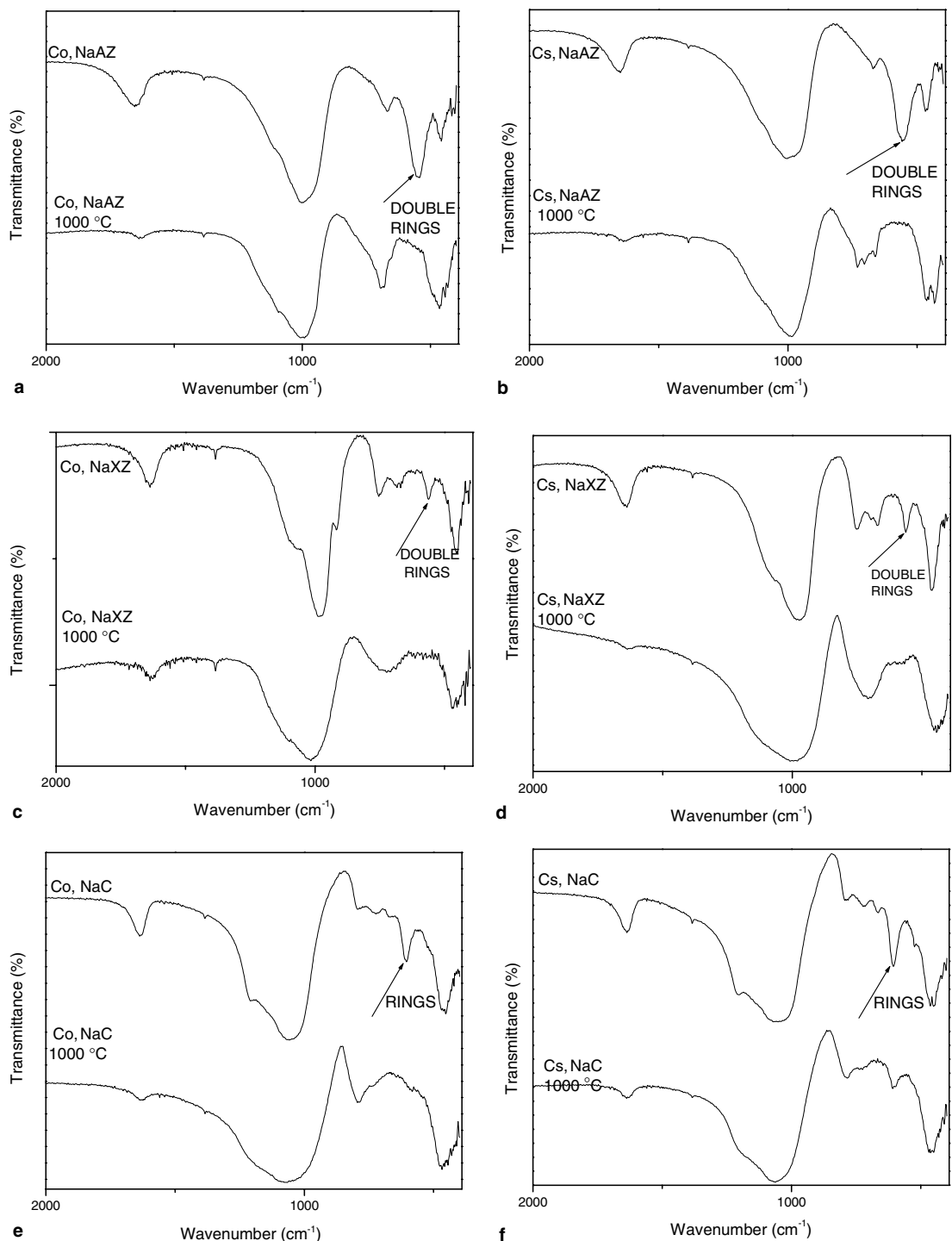
Fig. 2. IR spectra of Co^{2+} or Cs^+ exchanged zeolites, non-treated and combustion treated at 1000 °C (a) Co,NaAZ; (b) Cs,NaAZ; (c) Co,NaXZ; (d) Cs,NaXZ; (e) Co,NaC; (f) Cs,NaC.

leached from the solid. Instead, when NaXZ was treated by combustion, ignited at 500, 750 and 1000 °C, the cobalt lixiviated from the sample was

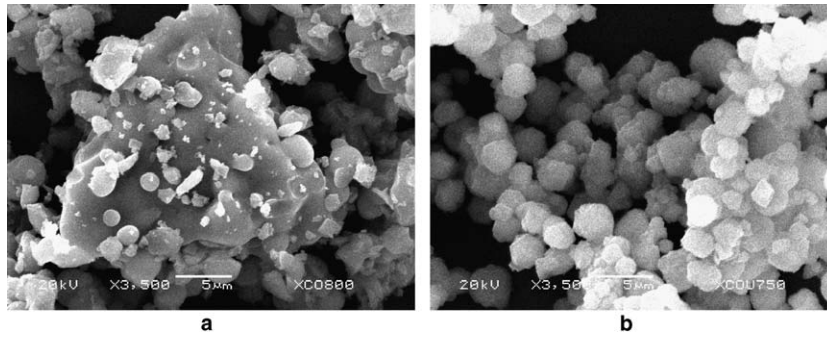$18.6 \pm 3.08\%$; $3.5 \pm 1.17\%$ and $2.2 \pm 0.71\%$, respectively, Table 8. Note that the percentage of Co lost in the 1000 °C combustion treated sample was 2.2%,

Fig. 3. SEM images of Co,NaXZ thermally treated at 800 °C (a) and combustion treated at 750 °C (b).
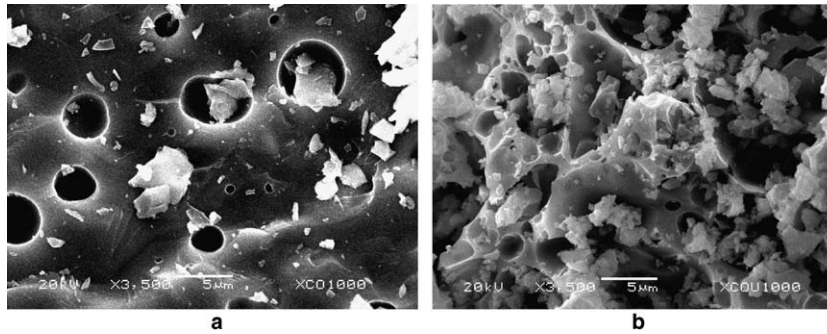

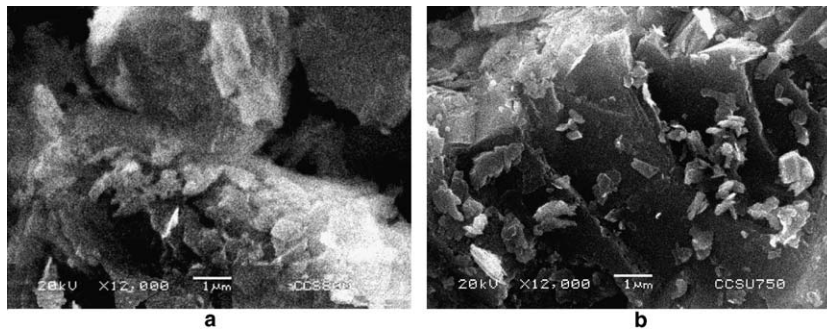Fig. 4. SEM images of Co,NaXZ thermally treated at 1000 °C (a) and combustion treated at 1000 °C (b).

Fig. 5. SEM images of Cs,NaC thermally treated at 800 °C (a) and combustion treated at 750 °C (b).

considerably higher to the amount lost in the corresponding thermally treated sample at 1000 °C (0.3%).

Cesium lixiviated through the non-treated Cs,NaXZ sample was $75.3 \pm 3.32\%$, but in thermally treated zeolites at 800 and 1000 °C the lixiviation decreased to $27.7 \pm 1.62\%$ and $0.4 \pm 0.22\%$, respectively, Table 9. When the same Cs,NaXZ was treated by combustion, ignited at 500, 750 and 1000 °C, cesium lixiviated through the sample was $66.4 \pm 2.86\%$; $22.2 \pm 1.32\%$, and $1.6 \pm 0.19\%$,

respectively. The percentage of Cs lost in the 1000 °C combustion treated sample was 1.6%, considerably higher than the amount lost in the thermally treated sample (0.4%), Table 9.

The cobalt content of the prepared Co,NaC was 0.162 Co meq/g of clinoptilolite which is much lower than the exchange capacity of clinoptilolite 2.2 meq/g. This difference is most probably due to the size of the aqueous complex $[Co(H_2O)_6]^{2+}$ which cannot enter the small windows of clinoptilolite. Cobalt lixiviated through the non-treated Co,NaC

Table 6
Retained and leached Co^{2+} in non-treated sample (NT), thermally treated (TT) for 3 h and combustion treated (CT) Co,NaAZ samples

Sample	Temperature (°C)	Retained Co (meq/g of zeolite)	Leached Co (meq/g of zeolite)	Leached Co (%)
NT		1.064	0.127	10.7 ± 1.05
TT	500	1.123	0.068	5.7 ± 1.62
TT	800	1.168	0.023	1.9 ± 0.43
TT	1000	1.183	0.008	0.7 ± 0.29
CT	500	1.140	0.051	4.3 ± 1.46
CT	750	1.168	0.023	1.9 ± 0.97
CT	1000	1.177	0.014	1.2 ± 0.78

Table 6-A
Retained and leached Co^{2+} in thermally treated zeolite A for 5 min

Sample	Temperature (°C)	Retained Co (meq/g of zeolite)	Leached (meq/g of zeolite)	Leached Co (%)
TT	500	1.026	0.165	13.9 ± 2.60
TT	800	1.121	0.070	5.9 ± 2.24

Table 7
Retained and leached Cs^+ in non-treated (NT), thermally treated (TT) for 3 h and combustion treated (CT) Cs,NaAZ samples

Sample	Temperature (°C)	Retained Cs (meq/g of zeolite)	Leached Cs (meq/g of zeolite)	Leached Cs (%)
NT		0.411	0.671	62.0 ± 2.50
TT	800	1.042	0.040	3.7 ± 0.30
TT	1000	1.057	0.025	2.3 ± 0.38
CT	500	0.211	0.871	80.5 ± 3.00
CT	750	0.975	0.107	9.9 ± 0.50
CT	1000	1.067	0.015	1.4 ± 0.18

Table 8
Retained and leached Co^{2+} in non-treated (NT), thermally treated (TT) and combustion treated (CT) Co,NaXZ samples

Sample	Temperature (°C)	Retained Co (meq/g of zeolite)	Leached Co (meq/g of zeolite)	Leached Co (%)
NT		0.794	0.386	32.7 ± 2.35
TT	800	1.163	0.017	1.4 ± 0.52
TT	1000	1.177	0.003	0.3 ± 0.26
CT	500	0.961	0.219	18.6 ± 3.08
CT	750	1.139	0.041	3.5 ± 1.17
CT	1000	1.154	0.026	2.2 ± 0.71

Table 9
Retained and leached Cs^+ in non-treated (NT), thermally treated (TT) and combustion treated (CT) Cs,NaXZ sample

Sample	Temperature (°C)	Retained Cs (meq/g of zeolite)	Leached Cs (meq/g of zeolite)	Leached Cs (%)
NT		0.330	1.007	75.3 ± 3.32
TT	800	0.967	0.370	27.7 ± 1.62
TT	1000	1.331	0.006	0.4 ± 0.22
CT	500	0.449	0.888	66.4 ± 2.86
CT	750	1.040	0.297	22.2 ± 1.32
CT	1000	1.315	0.022	1.6 ± 0.19

Table 10
Retained and leached Co^{2+} in non-treated (NT), thermally treated (TT) and combustion treated (CT) Co,NaC samples

Sample	Temperature (°C)	Retained Co (meq/g of zeolite)	Leached Co (meq/g of zeolite)	Leached Co (%)
NT		0.126	0.036	22.2 ± 2.83
TT	500	0.140	0.022	13.6 ± 4.64
TT	600	0.148	0.014	8.6 ± 2.57
TT	800	0.154	0.008	4.9 ± 2.48
TT	1000	0.156	0.006	3.7 ± 1.35
CT	500	0.128	0.034	21.0 ± 2.92
CT	750	0.143	0.019	11.7 ± 3.12
CT	1000	0.157	0.005	3.1 ± 1.54

Table 11
Retained and leached Cs^+ in non-treated (NT), thermally treated (TT) and combustion treated (CT) Cs,NaC samples

Sample	Temperature (°C)	Retained Cs (meq/g of zeolite)	Leached Cs (meq/g of zeolite)	Leached Cs (%)
NT		1.060	0.012	1.1 ± 0.16
TT	600	0.458	0.614	57.3 ± 2.14
TT	800	0.485	0.587	54.8 ± 2.45
TT	1000	1.056	0.016	1.5 ± 0.31
CT	500	0.457	0.615	57.4 ± 2.27
CT	750	0.857	0.215	20.1 ± 1.25
CT	1000	0.962	0.110	10.3 ± 0.81

sample was $22.2 \pm 2.83\%$. The sample Co,NaC was, then, thermally and combustion treated at several temperatures. The percentages of Co lost at 1000 °C in both treatments were similar within experimental error range, Table 10.

Cesium lixiviated through the non-treated Cs,NaC sample was $1.1 \pm 0.16\%$, but in thermally treated zeolites at 600, 800 °C the lixiviation increased up to $57.3 \pm 2.14\%$; $54.8 \pm 2.45\%$ and finally decreased at 1000 °C down to $1.5 \pm 0.31\%$, respectively, Table 11. When the same Cs,NaC was treated by combustion ignited at 500, 750 and 1000 °C, cesium lixiviated through the sample increased also to $57.4 \pm 2.27\%$; $20.1 \pm 1.25\%$, and $10.3 \pm 0.18\%$, respectively. Cs percentage lost in

the 1000 °C combustion treated sample was seven times the amount lost in the corresponding thermally treated sample, Table 11. It seems that Cs atoms migrate to surface sites in clinoptilolite and albite at temperatures between 500 and 800 °C and consequently they are easily leached with NaCl solution.

4. Discussion

The results on thermally treated Co^{2+} and Cs^+ exchanged zeolites reproduce those reported in previous studies [3,17–19]. In thermal treatment, as temperature increases, cobalt migrates from large cavities to sodalite cages which provide high coordination sites [20–22]. Cesium may reach as well sodalite cages. Cesium and cobalt act as modifiers in the zeolite structure and, therefore, the compounds obtained by heating an exchanged zeolite with Co^{2+} or Cs^+ are different than those obtained with the monocationic sodium zeolite. For instance Kosanović et al. [20] report that zeolite A–Na transforms at 900 °C into a mixture of carnegieite and nepheline. At increased temperature (>1000 °C) carnegieite completely transforms into nepheline. This result is reproduced in this work as Na–A zeolite (NaAZ sample) treated at 1000 °C turned out to be constituted by 63% of carnegieite and 37% of nepheline. When cobalt is present cobalt containing carnegieite is formed but if cesium is the cation, pollucite is found. These crystalline oxides guarantee an efficient retention of the waste cation as well as vitreous compounds whose most important property is chemical durability, particularly the ability to resist aqueous attack in our conditions.

Studying the cobalt environment in irradiated exchanged zeolites A and X, we found that leaching depended on the fractal dimension regardless of the nature of the zeolite [17]. In this sense, it is interesting to note that ion-exchange, followed by calcination, creates a porous surface on the zeolite crystals which initially restricts cation loss [23]. From such remark, it is easy to infer that a sudden thermal treatment could create a vitreous coating on zeolite crystals so that the channels end short of the surface. The leaching phenomenon would be then avoided.

Inspired by the combustion synthesis technique, i.e. the use of the exothermicity of an ignited fuel, we mixed the exchanged zeolites with urea and ignited the mixture during a short period, 5 min, at 500, 750 and 1000 ° C. We expected either to destroy the zeolite network and obtain similar compositions as those provided by the thermal treatments or to create vitreous coating on the crystalline zeolites. In both cases leaching should be as low as with thermal treatment.

Fuels used in combustion synthesis are specific for a particular class of oxides. Urea is the most adequate for alumina and related oxides [8]. It serves two purposes as, on the one hand, it is the source of C and H which on combustion form CO_2 and H_2O and liberate heat and, on the other, it forms complexes with the metal ions facilitating homogeneous mixing to form new compounds.

Our results show that this procedure leads to mixtures of compounds different than those obtained by thermal treatment, even when no remnant zeolite was observed, Tables 3–5. Hence, the reaction occurs through different mechanisms. In thermal treatment, temperature increases slowly propitiating ion migration. Instead, in combustion treated sample, temperature is suddenly increased and when the zeolite lattice collapses cations located in the large cavity have not had the chance to migrate.

If the samples treated at 800 °C or ignited with urea at 750 °C are compared, the amount of cobalt leached out in the combustion treated material has a tendency to be higher than in the thermally treated. In the combustion treated materials, more than 23% of crystalline zeolite is found, instead only in the thermally treated clinoptilolite, some zeolite remains (16%), otherwise all the zeolite collapses. Hence, as in Co,NaAZ the leaching out is the same within the experimental error range, 1.9% for the thermally treated sample and for the combustion treated sample, the vitreous coating has been formed. In zeolite X and natural clinoptilolite zeolite the percentage of cobalt leached out is higher in combustion treated than in thermally treated sample. Thus, the porous surface, although formed as amorphous compound, is present, but as it allows the exit of cobalt, it must be a non-continuous layer. The electron scanning micrographs of cobalt exchanged X zeolite show the morphological differences in thermally and combustion treated samples. They confirm the coating of zeolite particles at 750 °C in the combustion treated materials.

If cesium samples are compared, in zeolite A, the thermal treatment (3.7%) is more efficient than the combustion treatment (9.9%). But, in zeolite X and clinoptilolite, the combustion treatment is more effective (22.2% and 20.1%, respectively against 27.7% and 54.8%).

When the samples were thermally treated at 1000 °C, cobalt was very efficiently retained in zeolite A and X (0.7% and 0.3% leached out). If the same cobalt exchanged zeolites are treated by combustion more cobalt leaches out, 1.2% and 2.2% respectively. The difference between the thermally treated and combustion treated samples cannot be attributed to the leaching out from remnant zeolite through a non-continuous coating as all zeolite is destroyed. It has to be correlated with the composition and morphology of the final samples.

In a previous work we showed that nepheline does not contain cobalt [3]. Although, in cobalt exchanged zeolite X, 57% of amorphous compound is formed, the leaching out (2.2%) is higher than in the corresponding thermally treated sample which contains 31% of amorphous compound but leaches 0.3%. Thus, the composition of the amorphous compound or vitreous coating may vary and determine the amount of lixiviated cobalt. The attack of hydroxide ions on the Si–O bonds of the silicate structure depends on the surface composition of the glass, the easier the attack the higher the leaching. Comparing the leaching out from the three zeolites and the two exchanged cations, it seems that the formation of a homogeneous layer of vitreous or amorphous compound on the zeolite exchanged crystals through combustion treatment depends on the composition of the zeolites and the exchanged cation.

The combustion reaction provides a high amount of heat in the contact zone between urea and the zeolite crystal, but as well as the temperature increases abruptly partially melting the zeolite which reacts and forms a glass, the temperature decreases suddenly when the combustion is finished. Thermal gradients are produced, large enough to cause stresses that can modify the properties of the glass and increase its tendency to fracture on cooling [24].

5. Conclusion

The leaching of cobalt or cesium ions from thermally and combustion treated exchanged zeolites decreases as temperature increases. The retention of cobalt and cesium in thermally treated exchanged zeolites is slightly higher than in combustion treated zeolites ignited at 1000 °C. The difference is attributed to the different compounds (amorphous and crystalline) formed during the treatments. The comparison between thermal and combustion treatment

shows that combustion treatment is a valid option to sequestrate radioactive ions. A protective vitreous coating is formed in less than 5 min. However, the method has to be improved as the efficiency depends on ignition temperature, the type of zeolite and the nuclear waste. In our case, for instance, a combustion treatment ignited at 750 °C was more efficient than a thermal treatment at 800 °C if the cation was cesium and the zeolite was X or clinoptilolite.

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