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Radiation and thermal effects on cobalt retention by Mexican aluminosilicates

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Abstract

Thermal and radiation effects on the leaching of cobalt from two cobalt exchanged zeolites and one clay were determined. The cobalt exchanged aluminosilicates were heated at different temperatures (500, 700, 900 and 1100 °C), and the materials were then treated with NaCl (1 and 5 M) and HNO_3 (0.001 and 1 M) solutions to determine the leaching behavior of cobalt from the materials. Cobalt showed greater stability when the materials were heated at the highest temperature. The unheated samples and those heated at 1100 °C were gamma irradiated, and it was found that cobalt leaching from gamma irradiated aluminosilicates was higher than that for non-irradiated materials.

1. Introduction

Nuclear reprocessing plants generate highly active waste. The many purification and washing cycles produce large volumes of waste solutions which contain ^{60}Co, ^{137}Cs, ^{90}Sr, ^{99}Tc. The quest for an efficient ion exchanger for the treatment of such solutions is challenging [1].

Ion exchange is one of the most effective methods for the treatment and minimisation of nuclear waste volumes to reduce the radioactivity of the final liquid waste. Materials like zeolites and clays are natural, inexpensive, efficient and selective inorganic cation exchangers. Reversible cation exchange is one of the most important properties of zeolites. The utility of zeolitic materials has been demonstrated for the treatment of nuclear waste contaminated with cations [2]. However, there are limited data on the effects of radiation and the release of the adsorbed radionuclides on these materials, due primarily to the difficulties in studying the chemical properties of the post-irradiated materials [3]. Because the ion exchange reaction is a reversible

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process, the radiation induces structural changes that may also effect the release of adsorbed radionuclides when the zeolite phases are in contact with aqueous solutions [3]. One of the main problems is that these cations can be exchanged again if water is in contact with the exchanged materials. Therefore, the exchanged materials should be stabilized. As zeolites are intended to retain radionuclides, they will receive considerable radiation doses over time, and the cumulative doses in zeolites utilized as exchange media, waste forms or near-field back-fill can be substantial.

Some studies have reported that zeolites are susceptible to various types of radiation and temperature damage. Wang et al. [3] have reported the evaluation of long term radiation and thermal effects on porous and layered materials that may function as getters for radionuclides.

Zeolite NaY is susceptible to both radiation and thermally-induced amorphization. A desorption study indicated that the amorphization of cesium-loaded zeolite-NaY enhances the retention capacity of Cs due to closure of structural channels [4].

Bosch et al. [5] showed that thermal treatment of natural zeolites (fillipsite and erionite) at 1000 °C forms new mineral phases that may retain caesium. It has been reported as well [6] that with temperature the zeolite structures of NaA and NAX collapse and cobalt is trapped in the amorphous lattice of the vitrified materials, and cobalt does not diffuse out from the vitrified solid when it is left in contact with a sodium chloride solution. Zeolite X is more sensitive to irradiation effects than zeolite A [7].

As shown above, some studies have been conducted on the effects of temperature and gamma radiation on synthetic zeolites, but little research has been done with natural materials. Therefore, the aim of this research is to compare the leaching behavior of Co^{2+} from heated (500, 700, 900 and 1100 °C) cobalt exchanged zeolitic tuffs and clay as well as to determine the effects of gamma radiation on those materials.

2. Experimental procedures

Two clinoptilolite rich tuffs (Zcrem and Zfran) were obtained from the Graben of Villa de Reyes in the central part of Mexico in San Luis Potosi and Guanajuato States, between the parallels 22°50′ to the N and 21°07′ to the S. The tuffs were in the shape of a collapsed block 200 km large by 15 km wide, filled by lacustrine and alluvial sediments and ash flow tuffs [8]. Their compositions have been reported elsewhere [9]. The kaolinite clay rock was collected from Sombrerete in the State of Zacatecas, Mexico.

2.1. Ion exchange and thermal treatment

The zeolitic rocks were milled and sieved with a grain size between 8 and 10 mesh. Kaolinite clay rock was crushed and sieved between 60 and 100 mesh. Seven grams of each zeolite and clay sample initially in the sodium form were put into contact with 700 mL of a 0.5 M cobalt nitrate solution (made from reagent grade Baker hexahydrated cobalt nitrate 99%) under agitation for 24 h at room temperature. The liquid was separated from the solid by centrifugation and the cobalt uptake from the liquids was determined by atomic absorption spectrometry [10]. The cobalt exchanged materials were then thermally treated at 500, 700, 900 and 1100 °C for 2 h.

2.2. Cobalt leaching

The ion exchanged heated materials were left in contact for 24 h with 1 M and 5 M sodium chloride and 0.001 M and 1 M nitric acid solutions and deionized water. The mixtures were centrifuged and the liquid phases decanted. Cobalt was analysed in the remaining solutions by atomic absorption spectrometry.

2.3. Irradiation of samples

The irradiation effects on the cobalt exchanged materials without any treatment and on the samples previously heated at 1100 °C were studied. Samples were γ-irradiated with a ^{60}Co gamma source at 767 Mrad. The solids were characterized and left in 5 M NaCl or 1 M HNO_3 solutions for 24 h. Solids and liquids were separated by centrifugation and the Co^{2+} present in the NaCl or HNO_3 solutions was determined by atomic absorption spectrometry.

2.4. Characterization

Power diffractograms of the aluminosilicate samples were obtained with a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms were used to identify the compounds and to verify crystalline structure.

IR spectra of the samples in KBr pellets were recorded in the 4000–400 cm^{-1} range using a Nicolet Magna-IR spectrometer.

3. Results and discussion

Figs. 1(a)–3(a) show the X-ray diffraction patterns of the cobalt exchanged materials. The Zcrem tuff is mainly composed of clinoptilolite–heulandite, the Zfram tuff is primarily clinoptilolite with minor anorthite content, and the clay is mainly composed of kaolinite, wallastonite and quartz. The ion exchange capacities and chemical composition of the zeolitic rich tuffs have been reported elsewhere [9]. Figs. 1–3 show the X-ray diffraction patterns of cobalt exchanged and heated at 500 and 1100 °C for Zcrem tuff, Zfran tuff and kaolinite clay, respectively. It is clear in these figures that at 500 °C the structures of the materials did not collapse in these conditions but they collapsed at 1100 °C. When the samples were heated at 1100 °C, albite was found for the Zcrem tuff, albite and tridymine were found for the Zfran tuff and quartz was found for kaolinite clay.

The infrared spectra of the cobalt exchanged, unheated and 1100 °C heated, gamma irradiated Zcrem tuff, Zfran tuff and kaolinite clay samples are shown in Figs. 4–6, respectively. The interest of this study is to determine the stability of the framework structure of these aluminosilicates after thermal treatment and gamma irradiation. Fig. 4(a) shows the IR spectrum of the unheated cobalt exchanged Zcrem tuff. The vibration frequencies present at 1195 and 1066 cm^{-1} were assigned to

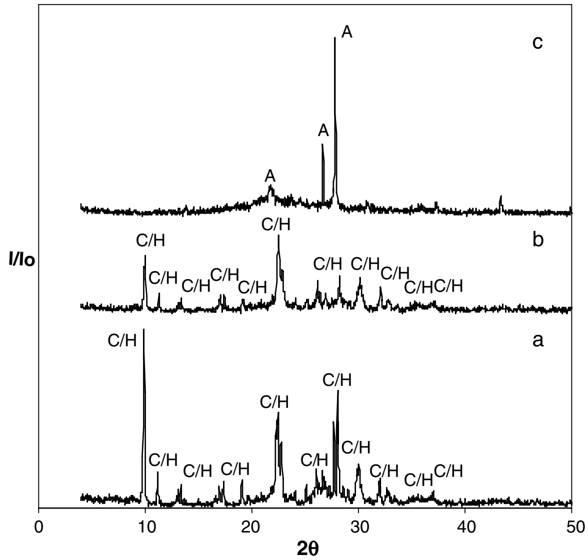

Fig. 1. X-ray diffraction patterns of Zcrem tuff: (a) Co-exchanged sample, (b) Co-exchanged sample heated at 500 °C, (c) Co-exchanged sample heated at 1100 °C. C/H: Clinoptilolite–Heulandite; A: Albite.

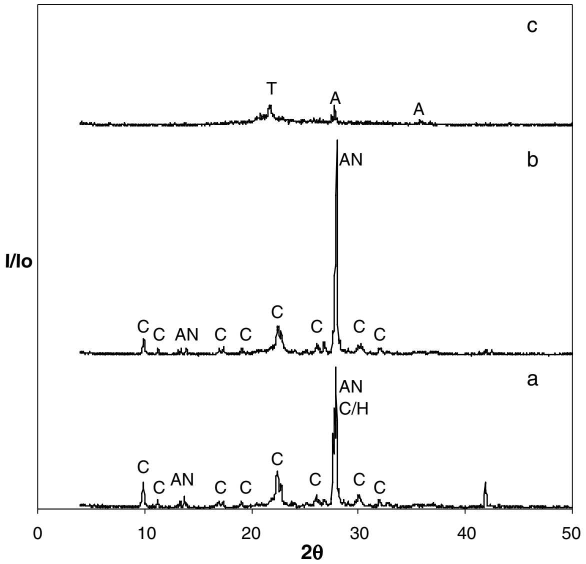

Fig. 2. X-ray diffraction patterns of Zfran tuff: (a) Co-exchanged sample, (b) Co-exchanged sample heated at 500 °C, (c) Co-exchanged sample heated at 1100 °C. C: Clinoptilolite; AN: Anorthite; A: Albite; T: Tridymite.

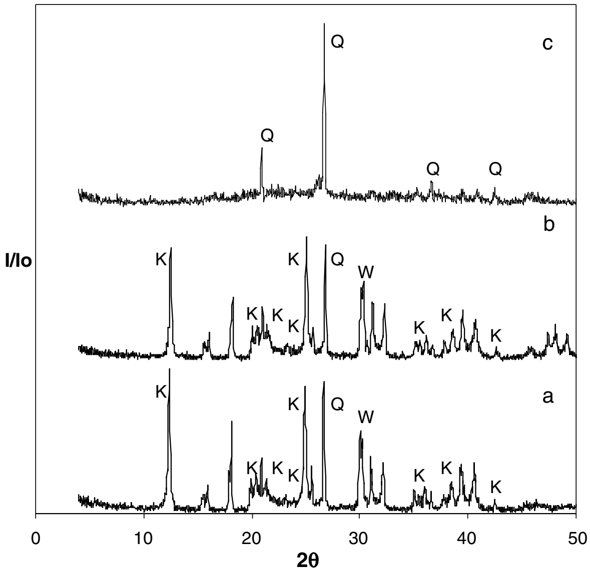

Fig. 3. X-ray diffraction patterns of kaolinite clay: (a) Co-exchanged sample, (b) Co-exchanged sample heated at 500 °C, (c) Co-exchanged sample heated at 1100 °C. K: Kaolinite; W: Wallastonite; Q: Quartz.

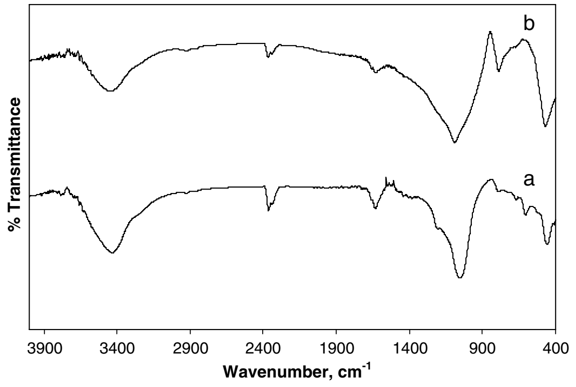

Fig. 4. IR spectra of Zcrem tuff samples: (a) unheated, (b) heated at 1100 °C.

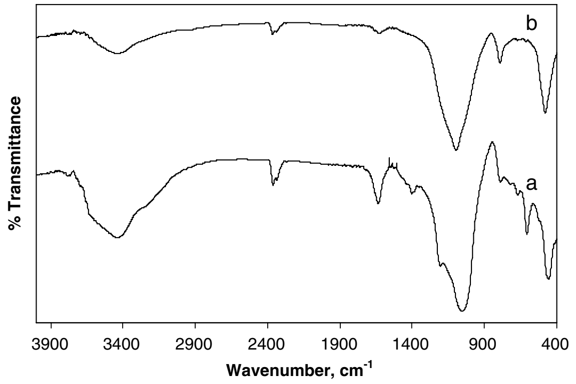

Fig. 5. IR spectra of Zfran tuff samples: (a) unheated, (b) heated at 1100 °C.

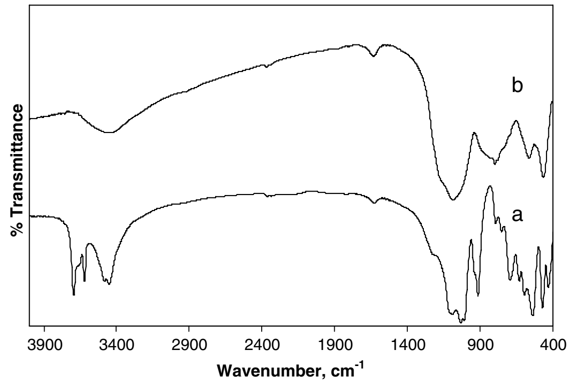

Fig. 6. IR spectra of kaolinite clay samples: (a) unheated, (b) heated at 1100 °C.

asymmetric stretching. The weak vibration frequencies at 798, 727, 676 and 611 cm^{-1} can be related to symmetric stretching, and the frequency at 462 cm^{-1} can be assigned to T–O bending [16]. Unlike various synthetic zeolites (X, Y, A, ZK-5, Ω, L, and the chabazite group), mineral zeolites like clinoptilolite do not show frequency sensitivity to the linkages between tetrahedral groups and the topology and mode of arrangement of the secondary units since they do not contain double 4 or double 6 rings [16]. The characteristic infrared absorption which might be attributed to the pore opening aspect of the structure was not observed since these frequencies generally occur below 400 cm^{-1}, beyond the region studied [16]. The frequencies assigned to the symmetric stretching are not observed in the sample heated at 1100 °C (Fig. 4(b)). The unheated Zfran tuff shows vibration frequencies in the same regions as the Zcrem tuff (Fig. 5(a)). Also, the frequencies of the symmetric stretching were not observed in the Zfran tuff heated at 1100 °C (Fig. 5(b)).

Fig. 6(a) shows the IR spectrum of unheated cobalt exchanged kaolinite clay, and the frequencies at 1230, 1112 and 1039 were assigned to Si–O stretching. The band at 916 cm^{-1} belongs to OH deformation and those placed at 796–432 cm^{-1} were identified as mixed Si–O deformations and octahedral sheet vibration [17]. Some frequencies in the regions 1200–900 and 796–432 cm^{-1} were not observed in the kaolinite clay sample heated to 1100 °C (Fig. 6(b)). These results show effective damage of the materials after thermal treatment and gamma irradiation.

As shown in Table 1, cobalt leaching into deionized water was not observed in the samples heated at 700 °C or higher. According to Figs. 1–3, at 500 °C the aluminosilicates are not destroyed and therefore cobalt may be exchanged by cations in solution even despite the small H^+ cations concentration in pH 6 deionized water [11]. Table 1 shows the Co^{2+} leaching with 1 and 5 M NaCl and 0.001 and 1 M HNO_3 from the cobalt exchanged aluminosilicates heated at 500, 700, 900 and 1100 °C for 2 h. High cobalt retention in samples heated at 700, 900 and 1100 °C may be attributed to the collapse of the material structures (Figs. 1–3). Cobalt leaching behavior is similar in all cases and the highest cobalt leaching was observed for the samples heated at 500 °C because the aluminosilicates are not destroyed at this temperature as shown above.

Although the cobalt leaching was low in the samples heated at 700, 900 and 1100 °C, the highest leaching was observed when the 5 M NaCl solution was put into contact with the aluminosilicates, making it clear that the high concentration of Na^+ may

Table 1
Cobalt leached with deionized water, 1 and 5 M NaCl and 0.001 and 1 M HNO_3 after thermal treatment of the cobalt exchanged aluminosilicates

Temperature (°C)	Co^{2+} leached (%)		
	Kaolinite	Zfran	Zcrem
Deionized water			
500	6.8	1.4	1.5
700	0.1	0.1	0.1
900	0.1	0.3	0.1
1100	0.1	0.3	0.3
1 M NaCl			
500	7.9	30.2	33.0
700	1.7	3.2	3.8
900	1.1	4.3	4.1
1100	1.6	3.6	2.8
5 M NaCl			
500	10.0	30.5	40.3
700	3.0	4.9	4.8
900	7.5	7.5	8.3
1100	6.3	6.8	6.6
0.001 M HNO_3			
500	11.5	4.9	4.9
700	0.9	0.5	0.5
900	0.2	4.2	3.9
1100	0.1	1.4	1.4
1 M HNO_3			
500	17.4	35.4	8.7
700	3.70	7.5	1.1
900	1.74	7.7	7.8
1100	0.94	1.8	1.5

replace some Co^{2+} cations from the amorphous samples. In these materials, the effect of temperature is clear, as the initial order and the material structure is lost. It is important to note that the color of the cobalt exchanged zeolitic materials changed when they were heated and the darkest sample was that treated at 1100 °C. Godelitsas and Armbruster [12] and Godelitsas et al. [13] have proven that on cobalt-loaded heulandite type zeolite, there is an accumulation of cobalt around the rims of the cobalt-loaded zeolite grains and a lower concentration in the interior. These studies pointed out that the metal sorption was mainly attributed to surface precipitation of insoluble solid phases, while the incorporation of cobalt ions into the structure through the channels also took place by ion-exchange. Ouki and Kavannagh [14] have pointed out that unlike synthetic ion exchange resins, which tend to have an internal pH slightly lower than that measured in solution because of the influence of the Donnan potential, natural zeolites tend to have a higher internal pH which could cause precipitation of metals on the material.

It was found as well [12,13] that the pale-rose to brown layer of Co-containing phases covering the surface of faintly-white zeolite grains is not crystalline, corresponding most probably to a type of amorphous Co(III)-hydroxide and or -oxyhydroxide. This study found that Co(II)-hydroxide precipitated in an aqueous solution is crystalline, and is further rearranged to a black crystalline Co(III)-oxide at ~150 °C. The authors proposed that elevated temperature influences the Co(II) oxidation and causes a transformation of the primary $Co(OH)_2$ precipitate to CoOOH or even to $Co(OH)_3$. On the other hand, in the case of metal coordination with framework oxygen atoms, the zeolite framework may function as a ligand enhancing the possibility of an electron transfer reaction from Co(III) to O_2. Thermal treatment of CoHEU up to 800 °C indicated that the initial pale-rose to brown amorphous Co(III)-hydroxides and/or -oxyhydroxides are transformed to black amorphous Co-phases (possible oxides) still supported on an amorphous aluminosilicate substrate. This phenomenon is not characteristic for pure HEU-type zeolite crystals or for metal-loaded HEU-type zeolites containing non-hydrated metal hydroxides on the surface.

Molecular structure and binding sites of cobalt(II) surface complexes on kaolinite have been reported elsewhere [15], and the color of cobalt exchanged kaolinite samples did not change after heating, though this may be due to the small quantity of cobalt absorbed by this material. No evidence was found regarding the oxidation of cobalt absorbed in this kind of material.

It is well known that sodium ions may replace metals in exchanged zeolites, so we would expect that all cobalt ions should be replaced by sodium ions in the samples heated at 500 °C where the structure of the aluminosilicates did not collapse (Figs. 1–3). Table 1 shows the cobalt leaching behavior of the thermally treated exchanged materials at different temperatures and Figs. 1–3 show that the cobalt exchanged thermally treated and untreated materials at 500 °C are similar. Therefore, the zeolite structures have not collapsed at this temperature, and it would be expected that all cobalt would be released from the aluminosilicates. Therefore, two mechanisms should be considered for the cobalt retention by the zeolitic materials, the collapse of the structures and the oxidation of cobalt in the network with temperature.

3.1. Cobalt leaching in the gamma irradiated samples

Table 2 shows cobalt leaching from the gamma irradiated unheated and 1100 °C heated cobalt exchanged aluminosilicates after treatment with 5 M NaCl or 1 M HNO_3 solutions. Cobalt leaching from the gamma irradiated aluminosilicates is higher than that from the non-irradiated samples, which may be due to the formation of new phases in the samples due to the damage produced by gamma irradiation.

As observed in Table 2, cobalt leaching was higher for the samples treated with the 1 M HNO_3 solution than for those treated with 5 M NaCl solution, and cobalt leaching was the highest for the unheated cobalt exchanged aluminosilicates as expected. Cobalt leaching was lower for the unheated cobalt exchanged kaolinite than for the zeolitic samples, and it was similar for the different heated materials at 1100 °C.

Fig. 7 shows the X-ray diffraction patterns of gamma irradiated unheated and heated cobalt exchanged kaolinite clay. There is a clear presence of potassium calcium silicate which was not observed in the non-irradiated samples, and this new phase may be responsible for the low cobalt leaching, since one would expect that Co^{2+} should be exchanged by Na^+ or H^+ in the unheated samples when they are treated with the 5 M NaCl or 1 M HNO_3 solutions, respectively.

Fig. 8 shows that for the case of the cobalt exchanged Zcrem tuff, gamma irradiation leads to formation of the potassium calcium silicate phase in both unheated and heated samples, which was not observed for the non-irradiated samples (Fig. 1).

Table 2
Cobalt leached with 5 M NaCl and 1 M HNO_3 after thermal and irradiation treatments of cobalt exchanged aluminosilicates

Temperature (°C)	Co^{2+} leached (%)		
	Kaolinite	Zfran	Zcrem
5 M NaCl			
Unheated (25)	20.0	23.8	20.0
Heated (1100)	4.3	2.6	3.6
1 M HNO_3			
Unheated (25)	20.0	56.1	57.7
Heated (1100)	15.0	12.7	18.8

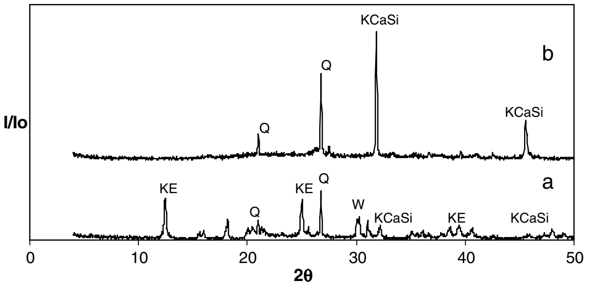

Fig. 7. X-ray diffraction patterns of kaolinite clay: (a) unheated Co-exchanged sample, (b) Co-exchanged sample heated at 1100 °C. KE: Kaolinite; W: Wallastonite; Q: Quartz; KCaSi: Potassium calcium silicate.

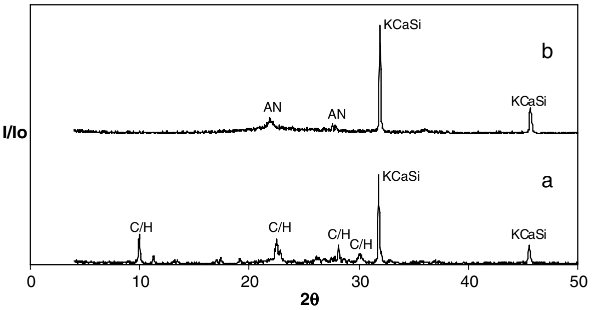

Fig. 8. X-ray diffraction patterns of gamma irradiated Zcrem tuff: (a) unheated Co-exchanged sample, (b) Co-exchanged sample heated at 1100 °C. C/H: Clinoptilolite–Heulandite; AN: Anorthite; KCaSi: Potassium calcium silicate.

For the case of the cobalt exchanged Zfran tuff the X-ray diffraction patterns (Fig. 9) were similar although the intensity of the anorthite peak at 28° with respect to the other diffraction peaks was clearly increased.

It has been reported [7] that some structures submitted to high doses of irradiation may develop

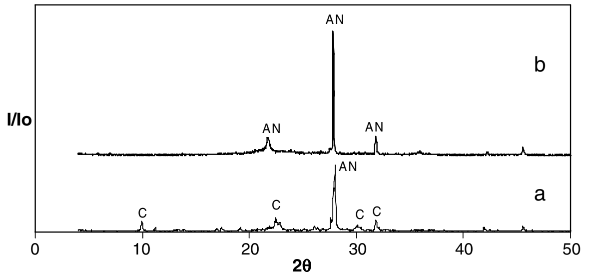

Fig. 9. X-ray diffraction patterns of gamma irradiated Zfran tuff: (a) unheated Co-exchanged sample, (b) Co-exchanged sample heated at 1100 °C. C: Clinoptilolite; AN: Anorthite.

defects or recrystallize as a new phase and the formation of composite materials is different from those obtained with thermal treatment.

Zeolitic tuffs were more sensitive to irradiation effects than kaolinite clay.

4. Conclusions

It was found that the structures of the aluminosilicates collapse when heated at 1100 °C but not at 500 °C. Low cobalt leaching was observed in the samples heated at 700, 900, and 1100 °C. The dark color of the zeolitic samples indicates that two mechanisms may be involved in the retention of cobalt by the aluminosilicates, the collapse of the structures and the oxidation of Co(II) in the samples, though this last effect was not observed in the kaolinite clay sample. The cobalt leaching from gamma irradiated aluminosilicates is higher than for non-irradiated samples, and the formation of potassium calcium silicate in the samples was observed due to the damage produced by gamma irradiation. Zeolitic tuffs were more sensitive to irradiation effects than kaolinite clay.

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