This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Sorption of ^{239}Np and ^{235}U Fission Products by Zeolite Y, Mexican Natural Erionite, and Bentonite

M. T. Olguín[a][b]; M. Solache[a]; J. L. Iturbe[a]; P. Bosch[a][c]; S. Bulbulian[a]
[a] INSTITUTO NACIONAL DE INVESTIGACIONES NUCLEARES, MÉXICO, D.F. [b] UNIVERSIDAD AUTÓNOMA METROPOLITANA, IZTAPALAPA MICHOACÁN Y PURÍSIMA APDO., MÉXICO, D.F.
[c] UNIVERSIDAD AUTÓNOMA METROPOLITANA, IZTAPALAPA MICHOACÁN Y PURÍSIMA APDO, MÉXICO, D.F.

To cite this Article Olguín, M. T. , Solache, M. , Iturbe, J. L. , Bosch, P. and Bulbulian, S.(1996) 'Sorption of ^{239}Np and ^{235}U Fission Products by Zeolite Y, Mexican Natural Erionite, and Bentonite', Separation Science and Technology, 31: 15, 2021 — 2044

To link to this Article: DOI: 10.1080/01496399608001029

URL: http://dx.doi.org/10.1080/01496399608001029

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **31**(15), pp. 2021–2044, 1996

Sorption of ^{239}Np and ^{235}U Fission Products by Zeolite Y, Mexican Natural Erionite, and Bentonite

M. T. OLGUÍN
INSTITUTO NACIONAL DE INVESTIGACIONES NUCLEARES
A.P. 18-1027, COL. ESCANDÓN, DELEGACIÓN MIGUEL HIDALGO
C.P. 11801, MÉXICO, D.F.

UNIVERSIDAD AUTÓNOMA METROPOLITANA, IZTAPALAPA
MICHOACÁN Y PURÍSIMA APDO. POSTAL 55-532
IZTAPALAPA, C.P. 09340, MÉXICO, D.F.

M. SOLACHE and J. L. ITURBE
INSTITUTO NACIONAL DE INVESTIGACIONES NUCLEARES
A.P. 18-1027, COL. ESCANDÓN, DELEGACIÓN MIGUEL HIDALGO
C.P. 11801, MÉXICO, D.F.

P. BOSCH
INSTITUTO NACIONAL DE INVESTIGACIONES NUCLEARES
A.P. 18-1027, COL. ESCANDÓN, DELEGACIÓN MIGUEL HIDALGO
C.P. 11801, MÉXICO, D.F.

UNIVERSIDAD AUTÓNOMA METROPOLITANA, IZTAPALAPA
MICHOACÁN Y PURÍSIMA APDO. POSTAL 55-532
IZTAPALAPA, C.P. 09340, MÉXICO, D.F.

S. BULBULIAN
INSTITUTO NACIONAL DE INVESTIGACIONES NUCLEARES
A.P. 18-1027, COL. ESCANDÓN, DELEGACIÓN MIGUEL HIDALGO
C.P. 11801, MÉXICO, D.F.

ABSTRACT

Zeolite Y, erionite, and bentonite have been used in this work to remove ^{239}Np and ^{235}U fission products from aqueous solutions at various pH values. It was found that the sorption of fission products by aluminosilicates takes place by different mechanisms, mainly ion exchange, precipitation, and electrostatic surface interaction. The radionuclides content was determined by γ-spectrometry, and x-ray diffraction was used to learn whether the solids maintained their crystallinity at different pH values.

Key Words. Zeolite; Clay; Erionite; Bentonite; Sorption; Ion exchange; Neptunium; Fission products; Radioactive waste water

INTRODUCTION

The use of natural aluminosilicates to decontaminate aqueous low and intermediate level radioactive waste has received considerable attention in recent years (1–3).

Hallaba et al. (4) were able to remove mobile long-lived fission products successfully as ^{131}I, ^{90}Sr, and ^{137}Cs using modified clays from Saudi Arabia. ^{131}I, which is difficult to sorb, was completely retained by silver-exchanged phosphate clays as well as by organo-clays (5). Neptunium from natural waters has been retained successfully by soils (6). Legoux et al. (3) studied the sorption of heavy elements in water by clays as well as by concrete.

In previous work by our group, the sorption of isolated radioactive elements has been presented (7, 8). The use of zeolite Y and erionite to remove UO_2^{2+} ions from aqueous solutions was studied (9) and correlated to temperature and concentration. The diffusion coefficients and the ion-exchange isotherms were estimated. It was found that UO_2^{2+} ions exchange with the cations of the large cavity in zeolite Y, and in the case of natural erionite with the cations localized in highly charged sites.

All the previously mentioned studies used prepared solutions containing selected radionuclides. In the present work, neutron-irradiated uranyl nitrate solutions were utilized. The radionuclides obtained can be described by the following nuclear reactions:

$$^{238}U(n, \gamma)^{239}U \xrightarrow{\beta^-} {}^{239}Np \quad (1)$$

$$^{235}U(n, f) \rightarrow \text{fission products} \quad (2)$$

As a consequence of these reactions, the stock solution of radionuclides used in this work contained a mixture of neptunium and fission products which may be found as various chemical species. The concentration of these radionuclides was always less than 10^{-14} g/mL in the presence of macroscopic amounts of uranium. Therefore, the elements present in the solution may be detected by measuring their radioactivity. Then, to identify the various species, an adequate technique is high voltage electrophoresis. The aim of the present paper is to discuss the sorption of neptunium and ^{235}U fission products present in these aqueous solutions by the following synthetic and natural aluminosilicates: zeolite Y, erionite, and bentonite. Erionite and zeolite Y have different lattice structures, but some of their sites present the same charge distribution (10). Bentonite is a clay whose main component, montmorillonite, is layer structured.

EXPERIMENTAL METHODS

Materials

The sorbers used, treated as reported elsewhere (9), were the following.

Erionite, referred in this work as ER, was obtained from Agua Prieta, Sonora, Mexico. It was powdered to <250 mesh. As determined by chemical analyses, the natural material contained the following exchangeable cations: 1.96 wt% Na, 1.60 wt% Ca, 2.16 wt% K, 1.12 wt% Fe, 161 ppm Mn, and 50 ppm Cu and Ni. The Si/Al atomic ratio was 3.8 (11).

Synthetic zeolite Y, referred in this work as YZ, powdered to less than 250 mesh in the NH_4^+ form, was supplied by Valfor (CP301-68); Si/Al = 2.25 (12).

Natural bentonite, referred to as NB, was supplied by Minerales no Metálicos, S.A. It contained the following exchangeable cations as determined by chemical analyses: 1.32 wt% Na, 0.75 wt% Ca, 0.45 wt% K, 0.81 wt% Fe, 1.46 wt% Mg (8).

X-Ray Diffraction

Powder diffractograms were obtained with a Siemens D500 diffractometer coupled to a copper anode x-ray tube. The $K\bar{\alpha}$ radiation was selected with a diffracted beam monochromator. Compounds were identified by comparison with JCPDS cards in the conventional way. The crystallinity percentage was estimated from the peaks less sensitive to humidity by comparison with the initial materials. The (331), (333), (440), and (533) peaks were selected for YZ samples. For the ER samples the peaks were (201), (211), (104), and (302), and for the NB samples they were the (001), (002), (005), and (007).

pH Variation in the Solutions

The pH values of the fission product solutions were adjusted from 1 to 10 by adding dilute NH_4OH or HNO_3 solutions. The fission product solutions were mixed and stirred for 10 seconds with each aluminosilicate and left in contact with these materials for 72 hours. Then they were stirred again for 10 seconds and separated by centrifugation. The pH in the solution was determined at the end of the process.

Neutron Irradiation of Uranyl Nitrate Solutions

Aliquots of the uranyl nitrate (20% enriched in ^{235}U) solutions were irradiated for 5 hours with an approximate neutron flux of $10^{12}/cm^2 \cdot s$ in a Triga Mark III nuclear reactor. They were stored for 10 days before analysis to allow for the decay of the short half-life radioisotopes. The irradiated samples were then diluted with water to obtain a 6.4×10^{-6} M uranyl nitrate solution. The radioactivity of the nuclides, ^{239}Np and ^{235}U fission products (FP), was detected by γ-spectrometry with a Ge/hyperpure solid-state detector coupled to a 4096 channel pulse height analyzer.

γ-Spectra of the Radionuclides

^{239}Np and the fission products ^{95}Zr, ^{99}Mo, ^{103}Ru, ^{131}I, ^{132}Te, ^{140}Ba, ^{140}La, and ^{141}Ce were chosen for this study. The selected photopeaks of these radionuclides did not overlap. Table 1 presents the identified nuclides, their nuclear features, and fission yields.

High Voltage Electrophoresis

Electrophoresis can identify cations, anions, and neutral species clearly. Furthermore, the mobility of the species along the paper strip can give additional information on the charge and mass of each complex. This information can be utilized to assign a chemical formula to each species according with data.

Neptunium and fission products chemical species formed at different pH values (1, 3, 5, 7, and 10) were determined by high-voltage electropho-

TABLE 1
Nuclear Features and Fission Yields of the Identified Radionuclides

Half-life (days)	Isotope	Energy (keV)	Fission yield (%)
64.0	Zr-95	726	6.4
2.7	Mo-99, Tc-99m	140	6.3
39.0	Ru-103	497	2.9
8.0	I-131	364	2.9
3.2	Te-132	230	4.2
13.0	Ba-140	537	6.4
1.7	La-140	487	6.4
32.4	Ce-141	145	5.6
2.3	Np-239	106	—

resis for 30 minutes. For this purpose, 1.0-cm-wide Whatman papers which were impregnated with a supporting electrolyte solution (HNO_3 or NH_4OH, according to the studied pH value) were used. The fission product solutions (10 μL) were deposited 10 minutes after the pH adjustment at the origin of the paper strip (0 cm). The voltage used was 2000 V. Once the electrophoresis was complete, the papers were air dried. After cutting the paper strips in 1 cm long fractions, the radioactivity of the fission products was measured. The radionuclides found in the paper fractions were identified by γ-spectrometry.

When possible, standard solutions were used to identify the species. All the proposed species have been reported by other authors (3, 13, 14). These standard solutions were $(NH_4)^{99}MoO_4$, $^{103}RuCl_3$, $^{139}Ba(NO_3)_2$, $^{140}La(NO_3)_3$, $^{141}Ce(NO_3)_3$, and $(NH_4)_2{}^{141}Ce(NO_3)_6$.

pH Effects on the Sorption of Radionuclides

YZ, ER, or NB samples (50 mg) were transferred into centrifuge tubes (25 mL capacity), and 5 mL samples of the previously pH adjusted fission product solution were added. They were stirred for 10 seconds and stored for 72 hours as described above, after which the liquid phase was separated by centrifugation. The solids were then washed with water (5 mL). The effects of 0.1 M $ZrOCl_2$ (ZrIV) and $(NH_4)_2Ce(NO_3)_6$ (CeIV) carriers were also studied.

Carriers

As the content of the fission products was always less than 10^{-14} g/mL in the presence of 1 mg/mL of uranium, we assumed that carriers for the fission products should increase the retention in the aluminosilicates by coprecipitation. Only two carriers were tested which could affect all elements in the solutions: 0.1 M $ZrOCl_2$ (ZrIV) and $(NH_4)_2Ce(NO_3)_6$ (CeIV).

As in the aqueous solution, all the fission products were present. The carriers were therefore added in the presence of all elements.

RESULTS AND DISCUSSION

Effect of pH on the Crystallinity of Sorbents

Figure 1 shows the effect of pH on the crystallinity of YZ, ER, and NB. At low pH values, both zeolites were noncrystalline solids; however, the degree of crystallinity increased as the pH was increased. The crystallinity of bentonite remained constant with pH variation.

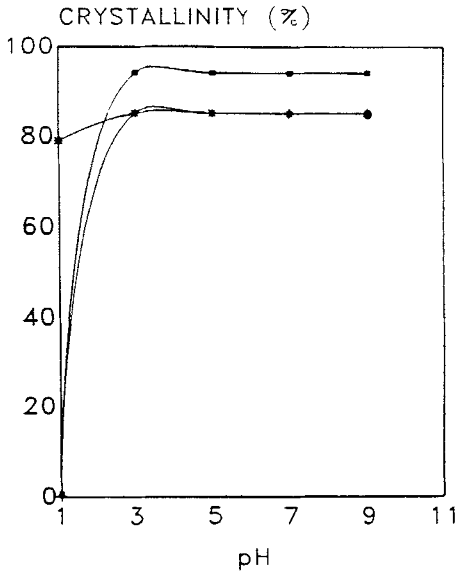

FIG. 1 Crystallinity of the (+) ER, (■) YZ, and (∗) NB samples, as a function of the pH.

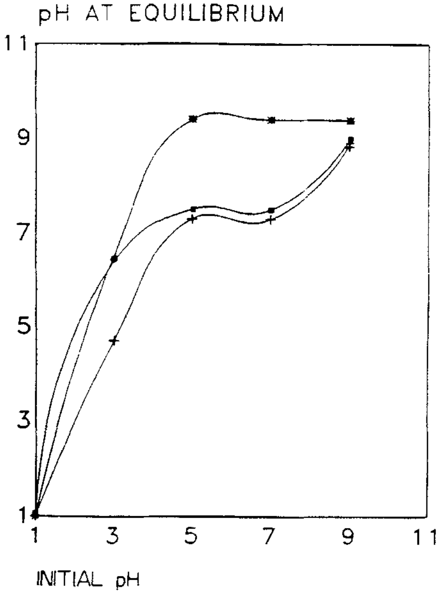

FIG. 2 Variation of the equilibrium pH versus the initial pH of the solutions. (+) ER, (■) YZ, and (∗) NB.

Buffering Effects of Sorbents on pH of Test Solutions

When the aluminosilicates were left in contact with the solutions at the various pH values for 72 hours, the initial pH varied as shown in Fig. 2. A high buffering power of the solid phases was clearly observed over a wide pH range. The solid phases consumed either H^+ or OH^- ions, depending on the initial pH value. This effect has also been reported for other materials (3).

pH Effect on Radionuclide Sorption

Figures 3 and 4 show the activity percentage of the radionuclides retained by YZ, ER, and NB at different pH values. As they were produced by a (n,f) reaction during relatively short time periods, the fission product concentrations were very small; therefore, their behavior may differ from the chemical behavior of macroscopic concentrations of the corresponding elements (15). Because the pH of the solutions was modified during the sorption of the radionuclides (Fig. 2), the chemical species of the carriers were expected to vary as well during this process (14). These chemical species may precipitate with other fission products on the surface of the materials.

High Voltage Electrophoresis

Figures 5 to 12 summarize our high voltage electrophoresis results. They show the chemical species formed by the various elements as a function of the pH values.

Barium and lanthanum in acid or neutral solutions were present as cationic species. Other elements, such as tellurium and neptunium, formed cations, anions, or neutral species. Zirconium and ruthenium nuclides were present as neutral or anionic species. Molybdenum was present only in the form of anions. Cerium was present as a cationic or neutral species.

Chemical Species and Sorption Behavior of Radionuclides

High voltage electrophoresis is the only suitable technique to analyze the very low concentration (traces) of the fission products present in the aqueous solution (less than 10^{-14} g/mL). This technique displaces the charged chemical species in the paper strip according to their charge and mass. It is therefore possible to determine the various species of each radionuclide according to the literature.

The sorption of fission products by the studied aluminosilicates (Figs. 3 and 4) was due to interaction mechanisms between the chemical species in solution and the sorbent materials (3):

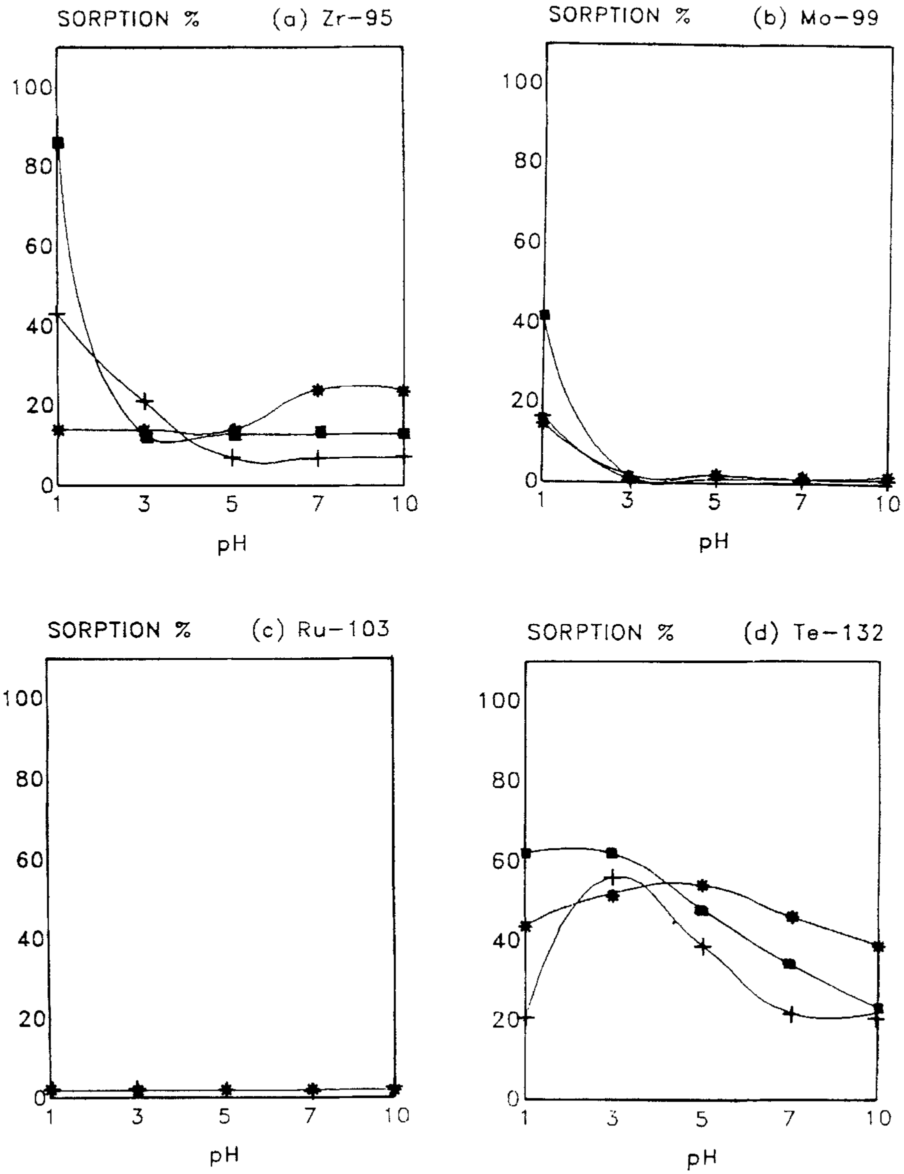

FIG. 3 Sorption of (a) Zr-95, (b) Mo-99, (c) Ru-103, and (d) Te-132, in (+) ER, (■) YZ, and (*) NB versus pH.

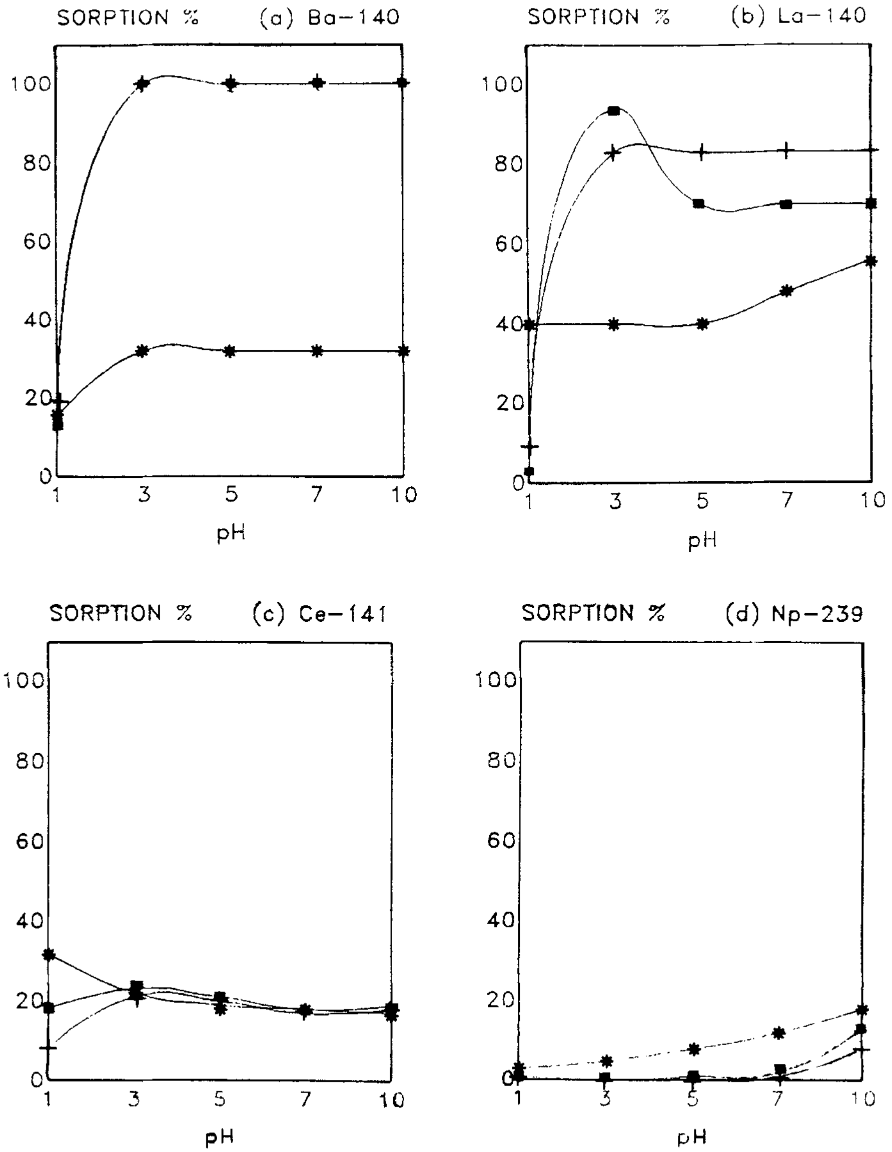

FIG. 4 Sorption of (a) Ba-140, (b) La-140, (c) Ce-141 and (d) Np-239, in (+) ER, (■) YZ, and (*) NB versus pH.

1. Electrostatic adsorption–desorption
2. Ion exchange
3. Coprecipitation

The retention behavior of each radionuclide studied in the aluminosilicate is discussed separately.

^{95}*Zr*

High voltage electrophoresis showed two ^{95}Zr species (Fig. 5), one of which is probably ZrO_2. Its abundance increased from pH 3 to pH 10, and it was the only species found at pH 10. On the other hand, an anionic species, probably $Zr(OH)_5^-$, was the only species found at pH 1 but its abundance decreased as the pH increased, and at pH 10 it was not observed by high voltage electrophoresis.

When studying the sorption of ^{95}Zr in the aluminosilicates at various pH values, we observed that at pH 1 it was sorbed in a considerably high proportion in the zeolites (but not in the bentonite) (Fig. 3a). At pH 3 the sorption decreased strongly, and at higher pH values it remained almost constant at a low sorption value.

One peculiarity in the sorption behavior of zirconium at pH 1 is that ^{95}Zr was retained strongly by YZ and to a lesser degree by ER and NB. This was probably due to the surface charge of each aluminosilicate according to the following reactions (3):

$$\geqslant\mathrm{SiOH_2^+} \rightleftharpoons \geqslant\mathrm{SiOH} \rightleftharpoons \geqslant\mathrm{SiO^-}$$

$$=\mathrm{AlOH_2^+} \rightleftharpoons =\mathrm{AlOH} \rightleftharpoons =\mathrm{AlO^-}$$

The reactions show that at a low pH value the solid phase becomes positively charged and, hence, the $^{95}Zr(OH)_5^-$ anionic species may be retained on the surface by electrostatic interaction. At higher pH values the solids become negatively charged and, as expected, the sorption of $Zr(OH)_5^-$ decreased. However, the zero point charge of the alumina-rich aluminosilicates are higher than those of alumina-poor aluminosilicates. Therefore, as expected, the sorption behavior of negatively charged $Zr(OH)_5^-$ followed the sequence:

$$\mathrm{YZ} > \mathrm{ER} > \mathrm{NB}$$

The effect of carriers at pH 3 showed that $(NH_4)_2Ce(NO_3)_6$ and $ZrOCl_2$ carriers increased the ^{95}Zr sorption by coprecipitation and by ion exchange.

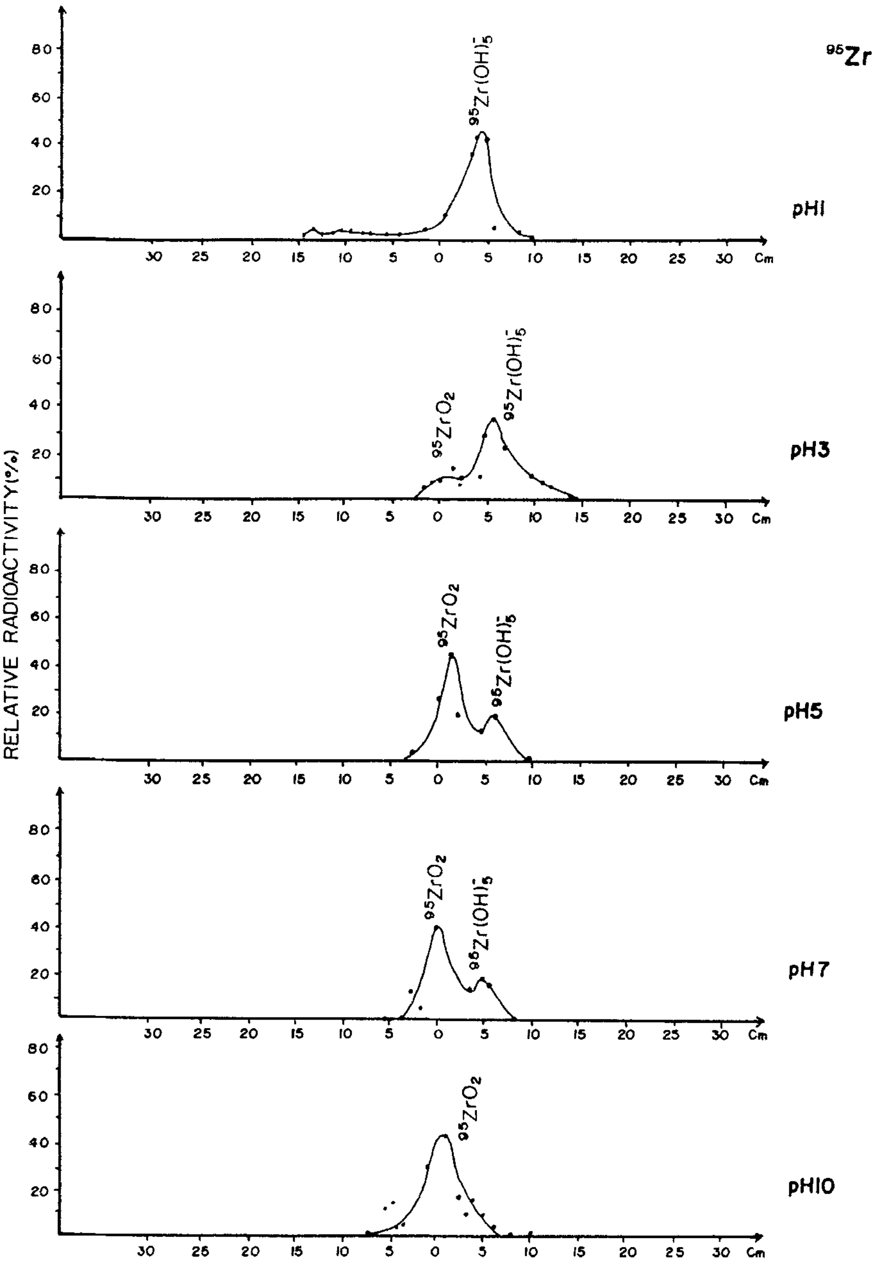

FIG. 5 Electrophoregrams of ^{95}Zr at different pH values.

These results showed that the sorption of ^{95}Zr has to be correlated to two factors; the chemical behavior of the element and the surface charge of the aluminosilicate.

^{99}Mo

Figure 6 shows the electrophoregram of the ^{99}Mo fission product and its decay product ^{99m}Tc at various pH values. ^{99}Mo and ^{99m}Tc were identified by theirs half lives as detailed elsewhere (16).

At pH 1 and pH 3 the ^{99m}Tc species found at 17 cm from the origin was attributed to $^{99m}TcO_4^-$ according to Iturbe et al. (13). At higher pH values, close to the origin, we found both ^{99}Mo and ^{99m}Tc, probably as oxides. The position of the species near the origin cannot be ascertained as they slowly decompose, probably into $^{99}MoO_4^{2-}$ and $^{99m}TcO_4^{2-}$. At pH 5 and 7, all ^{99}Mo was found as $^{99}MoO_4^{2-}$, but ^{99m}Tc as ^{99m}Tc and $^{99m}TcO_4^{2-}$ as identified in previous works (13).

Finally, at pH 10 we did not observe any definition of ^{99}Mo and ^{99m}Tc species by high voltage electrophoresis, probably because of the formation of heavy hydrolyzed chemical species.

^{99}Mo was partially sorbed on the aluminosilicates at pH 1 (Fig. 3b). At higher pH values the sorption decreased to very low values. This behavior has to be correlated to the chemical behavior of molybdenum. In aqueous media (pH 5–7) molybdenum forms anionic species that cannot occupy cationic sites in the aluminosilicates. At lower pH values, it forms $^{99}Mo_2O_3$, which may adhere to the surface of the aluminosilicates. The carrier effect at pH 3 showed that $(NH_4)_2Ce(NO_3)_6$ and $ZrOCl_2$ carriers increased ^{99}Mo sorption.

^{103}Ru

Figure 7 shows electrophoregrams of ^{103}Ru at various pH values. ^{103}Ru was found to be present mainly in the form of a noncharged species (probably RuO_4) and two anionic species which might be RuO_4OH^- and RuO_4^- (14). The lighter species is RuO_4^-. At pH 10, these species disappear.

Neither of these species was retained by the aluminosilicates in the pH range studied (Fig. 3c) because ruthenium forms many nitrosil complexes. There are no simple ruthenium species in solution; they are all complex ions.

$(NH_4)_2Ce(NO_3)_6$ or $ZrOCl_2$ carriers did not help to retain the ruthenium species which were always found in the solution. This behavior has also been observed in other materials (14).

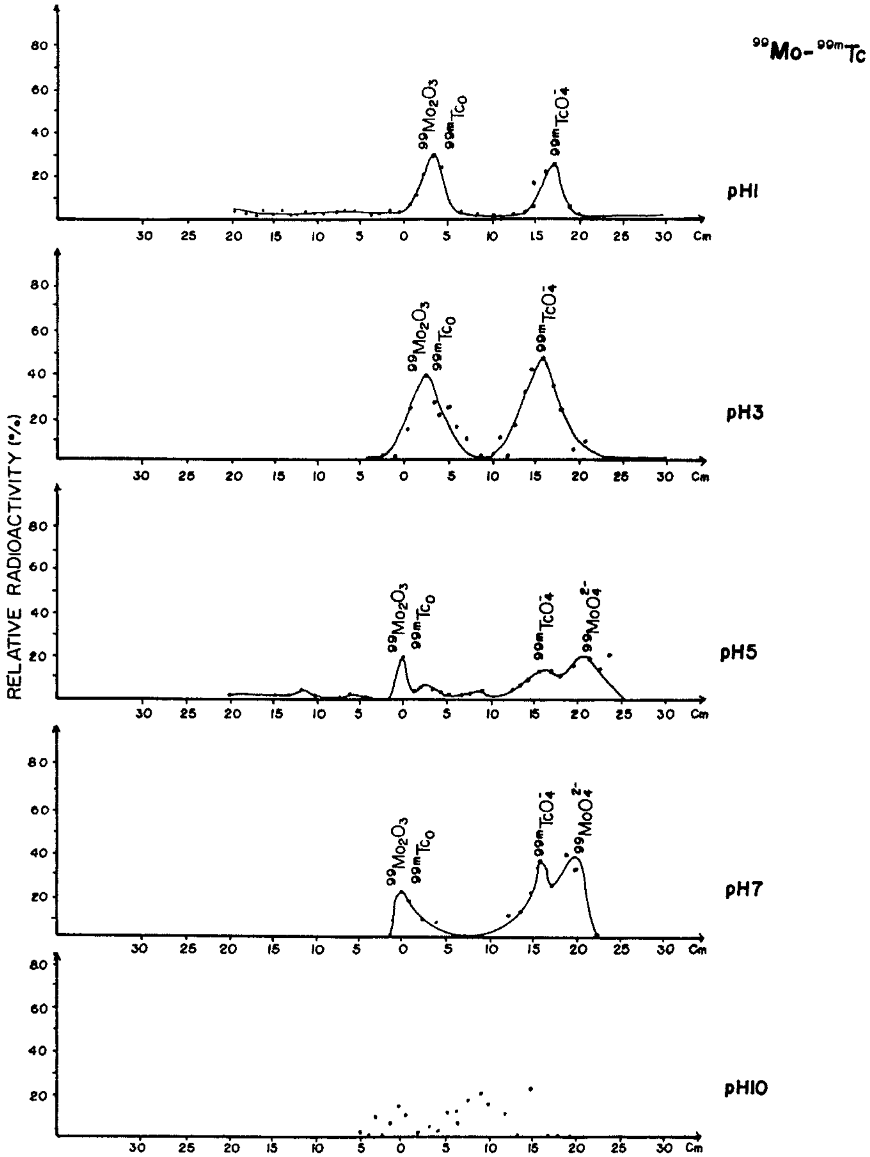

FIG. 6 Electrophoregrams of ^{99}Mo-^{99m}Tc at different pH values.

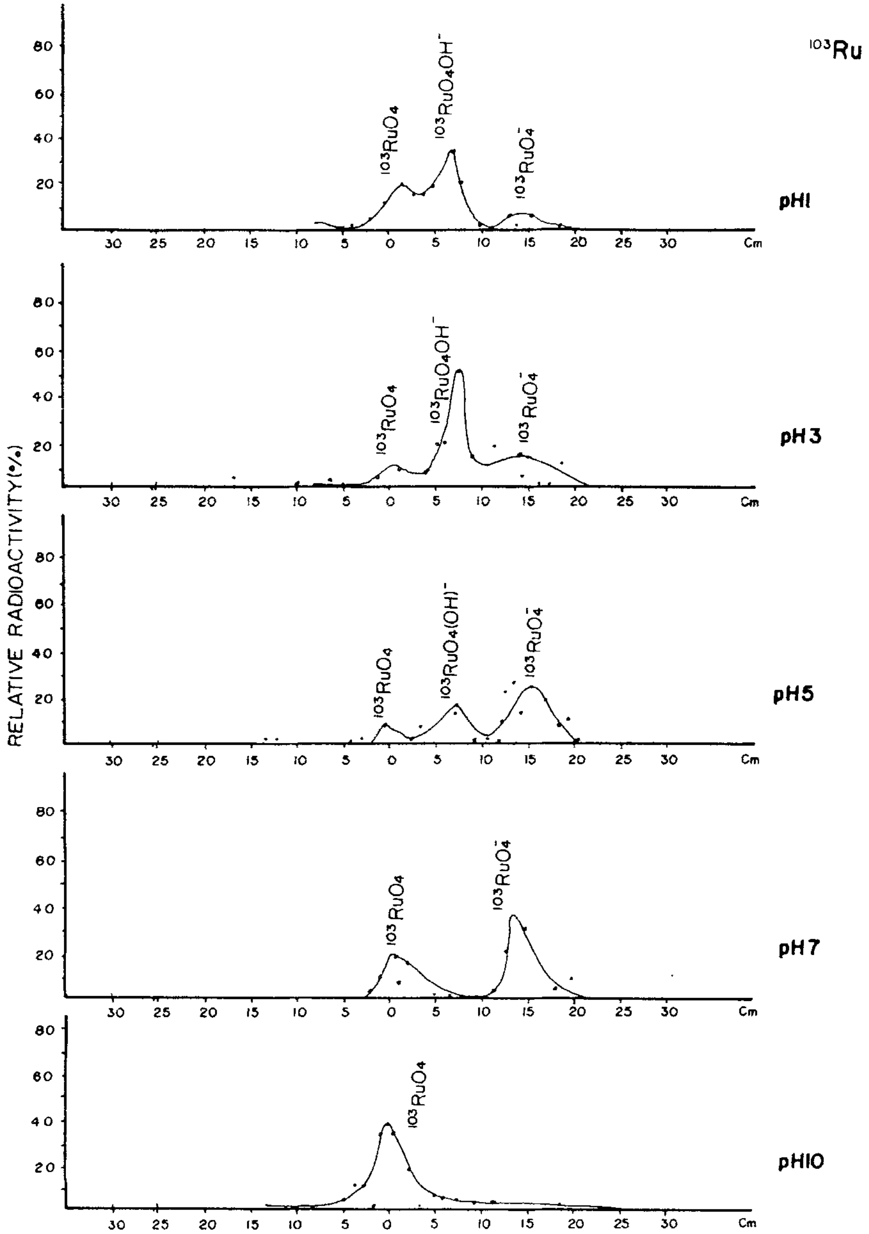

FIG. 7 Electrophoregrams of ^{103}Ru at different pH values.

^{131}I

Electrophoresis of fission product solutions did not show the presence of ^{131}I in any definite chemical species; instead, it showed a diffuse presence along the paper strip without clear separation into any species. We concluded that speciation of the transformation of physicochemical forms of iodine as a result of oxidation–reduction reactions was impossible because of the very small iodine concentration used. Small amounts of elemental iodine present were not retained by any of the aluminosilicates, and the addition of carriers did not affect this sorption behavior. We attributed this to the formation of elemental iodine through oxidation by dissolved oxygen in the water (17):

$$4I^- + 4Na^+ + O_2 + 2H_2O \rightleftharpoons 2I_2 + 4Na^+ + 2OH^-$$

^{132}Te

The electrophoregram of the ^{132}Te fission products shows the presence of three chemical species (Fig. 8): A main neutral species, probably TeO_2 (14), one cationic species present only at pH 1, probably $Te(OH)_3^+$ (14), and finally an anionic species present only at pH higher than 7, which can be any of the hydrolysis products of Te(IV) or Te(VI): $TeO(OH)_3^-$, $TeO_2(OH)_2^{2-}$, $TeO(OH)_3^-$, or $TeO(OH)_5^-$, $TeO_2(OH)_4^{2-}$, $TeO_3(OH)_3^{3-}$ (14). At pH 3 and 5, only the neutral species was present in the fission product solutions. Thereafter, the retention of ^{132}Te increased, and at pH 7 and 10 an anionic species was formed, probably $TeO_3(OH)_3^{3-}$, and the retention again decreased. Added carriers at pH 3 did not significantly affect the retention of ^{132}Te.

^{140}Ba

Figure 9 shows high voltage electrophoresis analysis for ^{140}Ba species. From pH 1 to 7 only one barium species (Ba^{2+}) was found; it was identified by comparison with a standard solution of $^{139}Ba(NO_3)_2$. At pH 10 only a cationic species was found which, according to Ref. 15, may be $Ba(OH)^+$.

While studying the sorption of ^{140}Ba (Fig. 4a) at various pH values, we observed that ^{140}Ba retention was very low at pH 1. However, at pH 3 the sorption increased strongly in the zeolites and slightly in the bentonite. Therefore, this retention of ^{140}Ba species in zeolites may be due to an ion-exchange mechanism. Furthermore, at pH 1 the zeolites were destroyed and the trapped original cations could not be exchanged, but at higher pH values, when the zeolite structure was not destroyed, Ba^{2+} ions were exchanged easily in the zeolite sites. For bentonite we observed

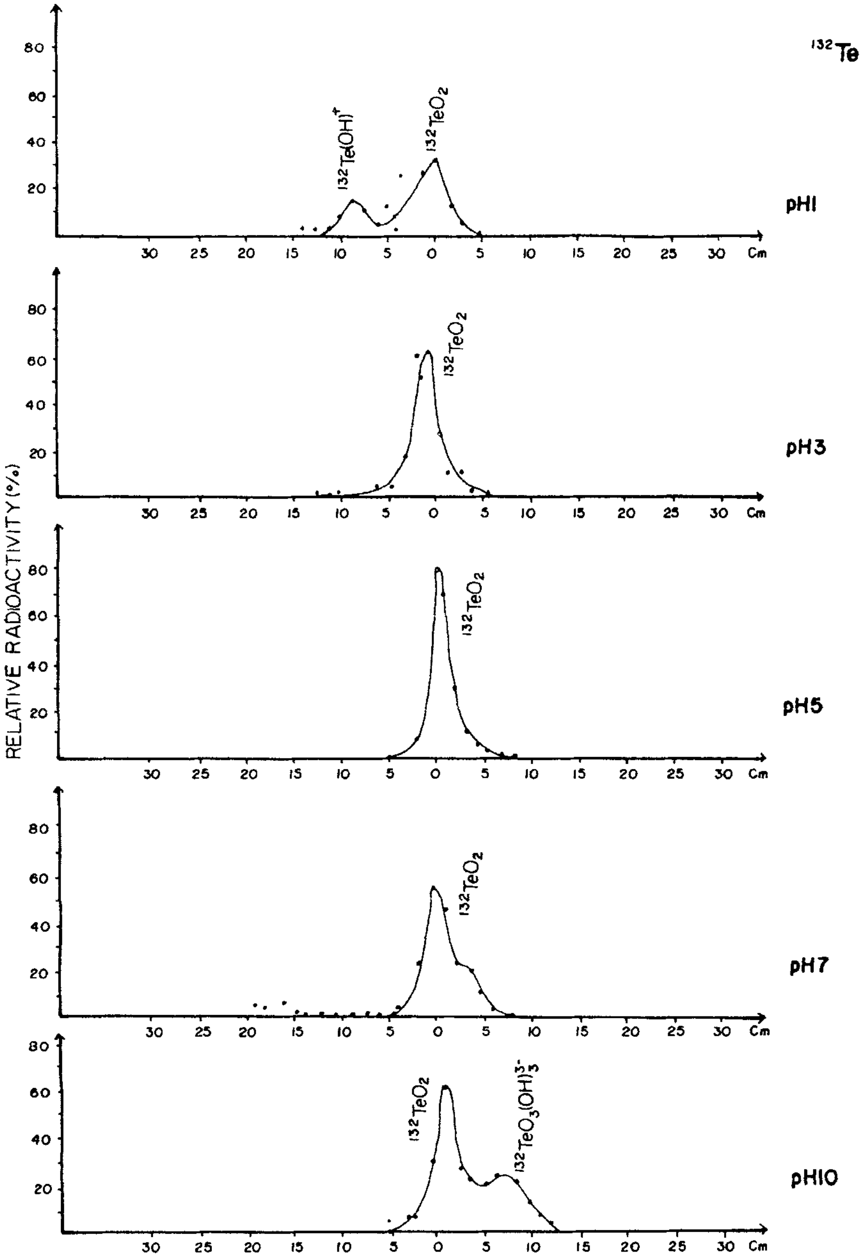

FIG. 8 Electrophoregrams of ^{132}Te at different pH values.

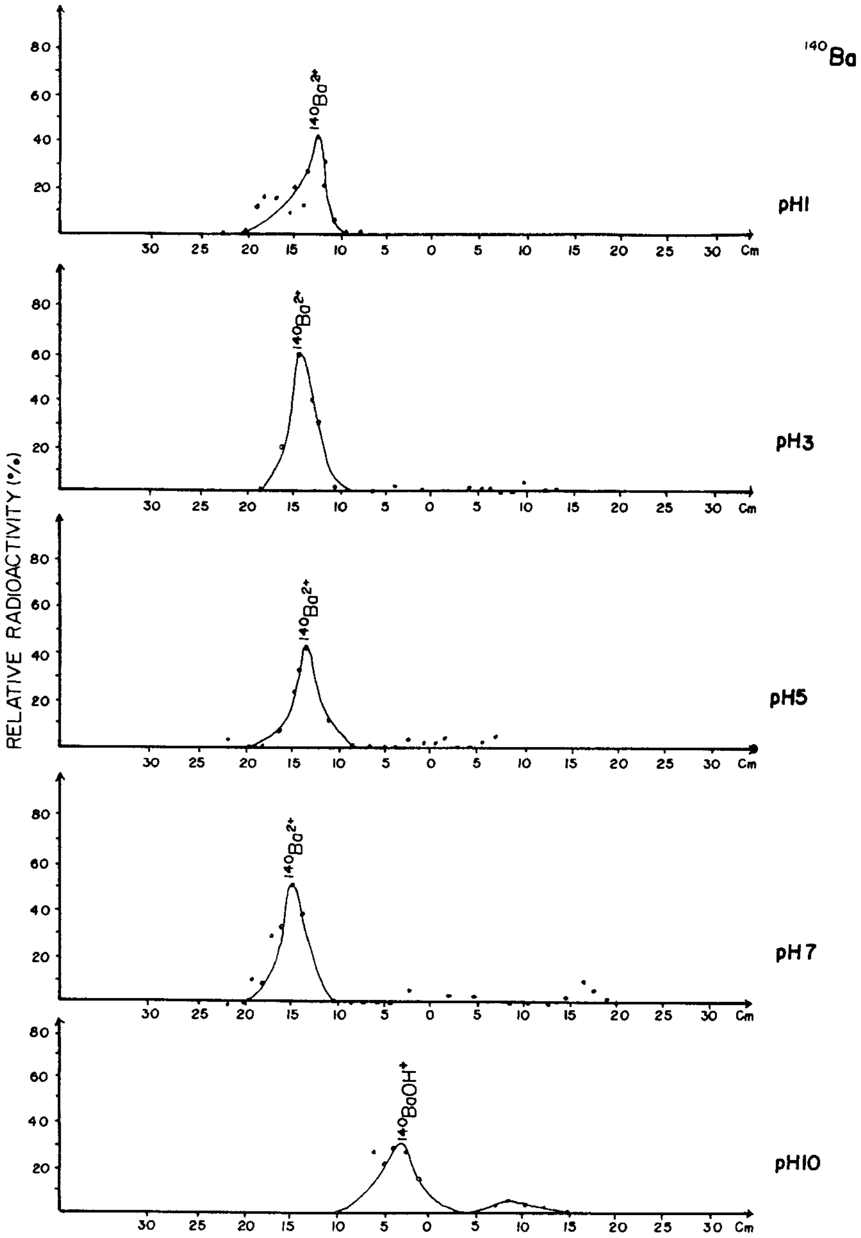

FIG. 9 Electrophoregrams of ^{140}Ba at different pH values.

that barium cationic species retention was much lower than in the zeolites, which could be due to the structural differences. At pH 3 barium sorption was already 100%, and the addition of $(NH_4)_2Ce(NO_3)_6$ and $ZrOCl_2$ carriers did not affect the retention.

^{140}La

High voltage electrophoresis (Fig. 10) on the ^{140}La fission product showed three main species: two cationic species, probably La^{3+}, which was observed from pH 1 to 7 and was identified by comparison with a standard solution of $^{140}La(NO_3)_3$. At pH 3, La^{3+} decreased and two hydrolyzed species appeared: one cationic and the second neutral, probably $La(OH)_2^+$ and $La(OH)_3$, respectively (14).

At higher pH values (5 to 7) the cationic species disappeared and La^{3+} as well as the neutral hydrolyzed species were present. At pH 10 only the neutral hydrolyzed species was found.

The sorption curves of ^{140}La (Fig. 4b) in the aluminosilicates showed that ^{140}La was not sorbed at pH 1, in the zeolites because the framework was destroyed. Erionite and zeolite Y, from pH 3 up to pH 10, retained a considerable amount of ^{140}La as $La(OH)_3$, which is insoluble. Therefore, we concluded that ^{140}La retention from pH 3 to 10 was higher because it precipitated as $La(OH)_3$.

In the case of bentonite it was observed that ^{140}La species retention was much lower than in the zeolites and almost independent of the pH. Carriers had no effect on ^{140}La sorption.

^{141}Ce

High voltage electrophoresis (Fig. 11) shows three ^{141}Ce species: a neutral and two cationic species. In order to identify them, two series of cerium standards were analyzed: $^{141}Ce(NO_3)_3$ and $(NH_4)_2{}^{141}Ce(NO_3)_6$ at pH 1 and pH 3. At pH 1 both samples were found in the same cationic position as Ce^{3+} (from 20 to 25 cm). Therefore, we assumed that Ce^{4+} was reduced to Ce^{3+} and oxidized the $(NO_3)^-$ ion according to the following reaction:

$$Ce^{4+} + (NO_3)^- \rightleftharpoons Ce^{3+} + NO_2 + {}^1\!/_2O_2$$

which is similar to the reaction reported elsewhere for $CeCl_4$ (14).

The behavior of both standards was different at pH 3. Although Ce^{3+} was found in the same position, Ce^{4+} was found immobile in the application point of the sample, probably as CeO_2, a hydrolysis product of Ce^{4+} (14).

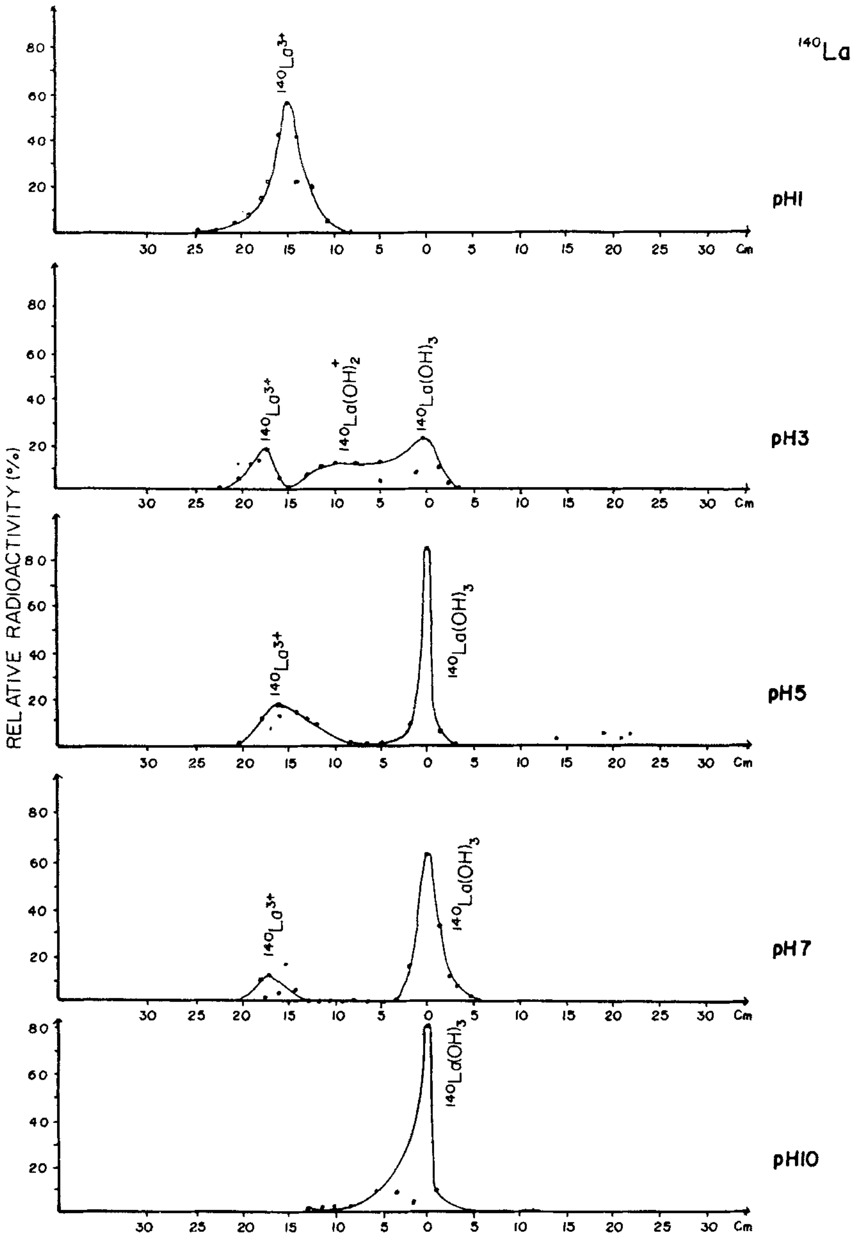

FIG. 10 Electrophoregrams of ^{140}La at different pH values.

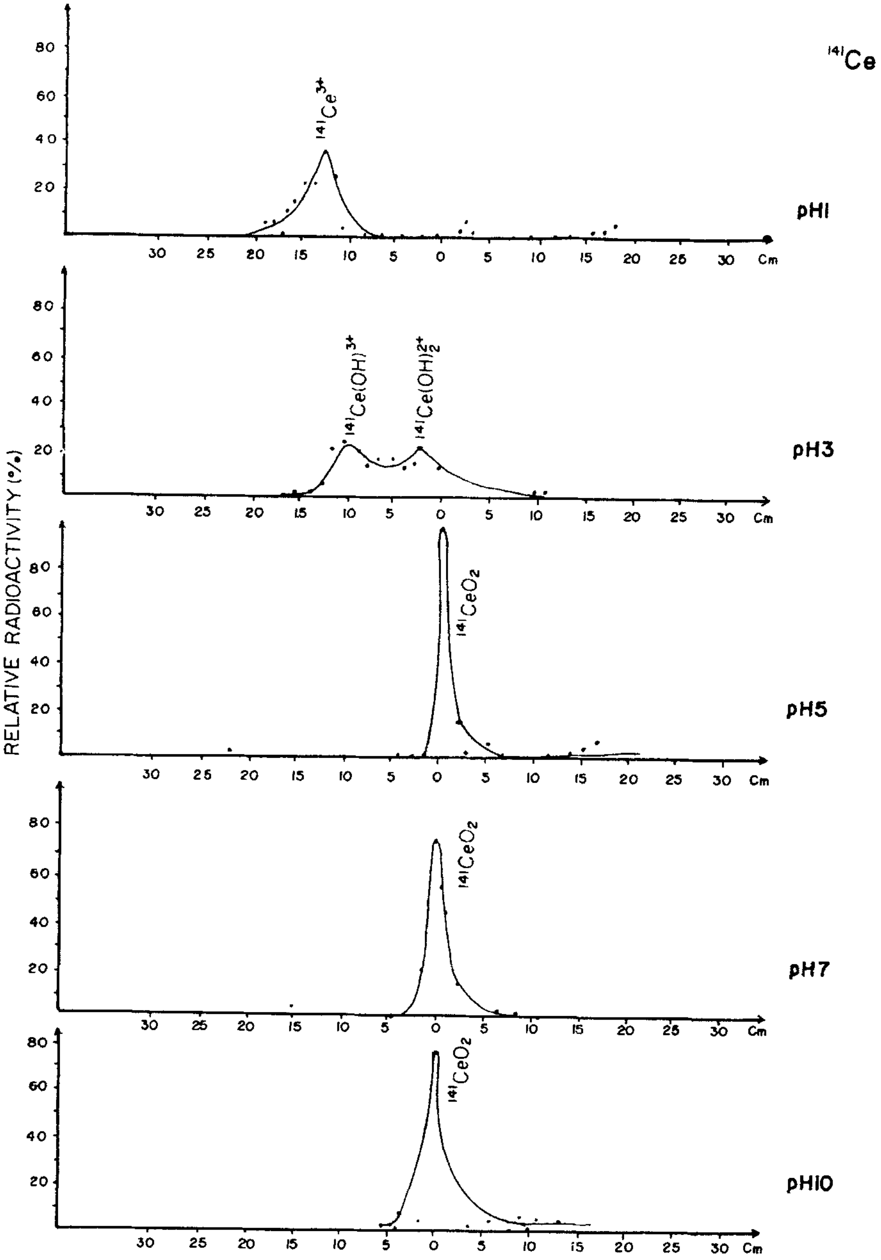

FIG. 11 Electrophoregrams of ^{141}Ce at different pH values.

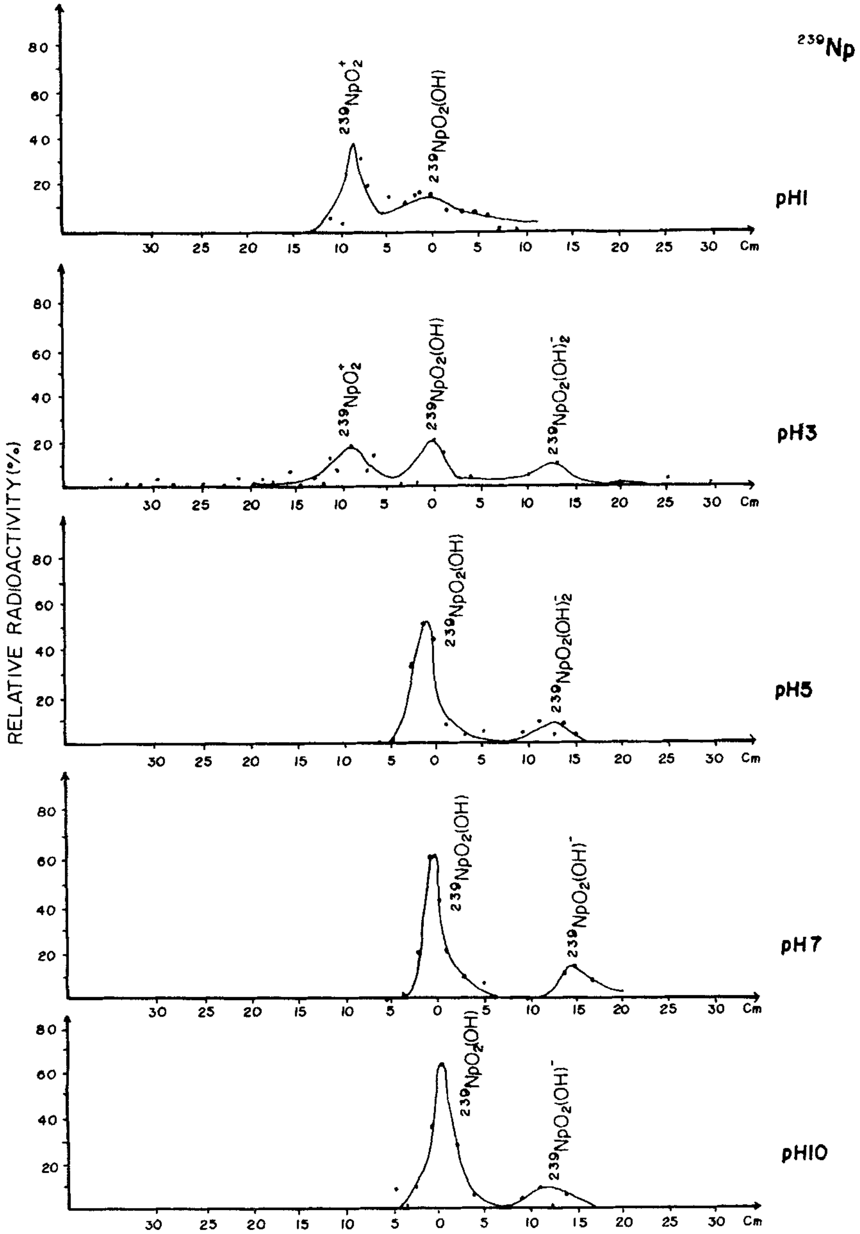

FIG. 12 Electrophoregrams of ^{239}Np at different pH values.

The hydrolysis products of Ce^{3+} in aqueous solution are reported to be $Ce(OH)_2^+$ and $Ce(OH)_3(aq)$ (14) above pH 6. On the other hand, the hydrolysis products of Ce^{4+}, which are formed even in 1 M $HClO_4$, are reported to be $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ (14).

In the ^{141}Ce fission product solution at pH 3 we found two other cationic species which might be the hydrolysis products [$Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$] of Ce^{4+} which can readily be hydrolyzed even in strongly acid solutions. We therefore conclude that in the original fission products solution, Ce is in the form of Ce^{4+} species and possibly also as Ce^{3+} species.

At higher pH values (from 5 to 10), only $^{141}CeO_2$ was formed (14).

The sorption curves of ^{141}Ce (Fig. 4c) show that cerium retention is very low. In the zeolites at pH 1, the cationic species $^{141}Ce^{4+}$ could not be retained by the destroyed zeolites, but it was slightly retained, probably by ion exchange, in the bentonite which maintained its crystalline structure. At pH 3 the sorption of the cationic species $^{141}Ce(OH)^{3+}$ and $^{141}Ce(OH)_2^{2+}$ was probably due to a cationic exchange mechanism. However, at higher pH values only the neutral $^{141}CeO_2$ species was present, and its retention on the aluminosilicates can be explained by its partial precipitation on the solids. Carriers had no effect on ^{141}Ce sorption by the YZ sample but they enhanced sorption in the other materials.

^{239}Np

High voltage electrophoresis on ^{239}Np (Fig. 12) showed mainly three species: a neutral, a cationic, and an anionic. The cationic and the neutral species were present at pH 1 and 3; at pH 3 an additional peak of an anionic species appeared. The neutral species can be either $NpO_2(OH)(aq)$ or NpO_2 (14). However, the cationic species can be one of the following: $NpOH^{3+}$, $NpO_2(OH)^+$, or $NpOH^{2+}$, and the anionic species can be $NpO_2(OH)_2^-$.

^{239}Np was slightly retained (Fig. 4d) by the aluminosilicates. A weak increase of ^{239}Np was observed at pH 10, probably because of the hydrolysis of the ^{239}Np species. The carriers did not affect the sorption behavior of this radionuclide in the aluminosilicates.

CONCLUSIONS

^{239}Np and ^{295}U fission products uptake from solutions, whose content was less than 10^{-14} g/mL by zeolite Y, erionite, and bentonite, showed that some of these radionuclides may be efficiently sorbed in the aluminosilicates. It was found that sorption takes place by different mechanisms, mainly ion exchange, precipitation, and electrostatic surface interaction. The chemical species in solution and the charge distribution of the surface of these materials at different pH values determine, in most cases, the sorption behavior of the radionuclides. However, in other cases ion exchange is the most important mechanism.

We found that nuclides as ^{140}La and ^{140}Ba were sorbed mainly in the zeolites by an ion-exchange mechanism and in smaller proportions in bentonite. In the zeolites, precipitation and electrostatic surface interaction did not play an important role for ^{140}La and ^{140}Ba retention. The low retention obtained in bentonite showed that sorption of ^{140}La and ^{140}Ba definitely depended on the structure of the aluminosilicates.

Other fission products, ^{95}Zr, ^{99}Mo, and ^{132}Te, present in the solution were only weakly sorbed by the solids. ^{95}Zr and ^{99}Mo were mainly sorbed by the aluminosilicates at pH 1. In the case of ^{95}Zr, it was sorbed by electrostatic interactions between its chemical species, $^{95}Zr(OH)_5^-$, and the surface of the materials. In the case of ^{99}Mo, Mo_2O_3 precipitated on the surface of these aluminosilicates. The highest sorption of ^{132}Te on these materials, found at pH 3, was probably due to the precipitation of the chemical species $^{132}TeO_2$.

It was also shown that ^{103}Ru was not sorbed in the aluminosilicates because it forms complexes which always remained in solution. This behavior has also been observed in other materials (18). ^{131}I was not sorbed because elemental iodine is formed during the sorption process and so is volatilized (17).

The retention mechanisms of ^{141}Ce on the aluminosilicates at the studied pH values were ion exchange and precipitation.

Finally, ^{239}Np was very slightly sorbed only at high pH values by precipitation of the chemical species $^{239}NpO_2(OH)$.

ACKNOWLEDGMENTS

We acknowledge V. H. Lara (UAM) and the technicians of the Chemistry Department (ININ) for technical help.

REFERENCES

1. A. Dyer, A. S. Abdel Gawad, M. Mikhail, H. Enamy, and M. Afshang, *J. Radioanal. Nucl. Chem. Lett.*, *154*(4), 265 (1991).
2. V. V. Milutin, V. M. Gelis, and R. A. Penzin, *Proceedings of the International Conference on Nuclear Waste Management and Environmental Remediation*, Vol. 2, 1993, p. 379.
3. Y. Legoux, G. Blain, R. Guillaumont, G. Ouzounian, L. Brillard, and M. Hussonnois, *Radiochim. Acta*, *58/59*, 211 (1992).

4. E. Hallaba, A. Al-Suhybani, and A. El-Sadik, *J. Radioanal. Nucl. Chem. Art.*, *83/2*, 215 (1984).
5. J. Bors, *Radiochim. Acta*, *58/59*, 235 (1992).
6. E. P. Kaiman and L. I. Konstantinova, *Radiokhimiya*, *33*(4), 210 (1991).
7. I. García, M. Solache-Ríos, P. Bosch, and S. Bulbulian, *J. Phys. Chem.*, *97*(6), 1249 (1993).
8. L. M. Carrera, S. Gómez, P. Bosch, and S. Bulbulian, *Zeolites*, *13*, 622 (1993).
9. M. T. Olguín, M. Solache-Ríos, M. Asomoza, D. Acosta, P. Bosch, and S. Bulbulian, *Sep. Sci. Technol.*, *29*(16), 2161 (1994).
10. W. Breck, *Zeolite Molecular Sieves*, Wiley-Interscience, New York, NY, 1974.
11. F. Aguilar, J. Aguilar, G. Díaz, A. de Ita, and A. Maubert. *Informe Semestral CYTED*, 1991 (in Spanish).
12. I. García and M. Solache-Ríos, Personal Communication.
13. J. L. Iturbe, *Appl. Radiat. Isot.*, *41*(7), 693 (1990).
14. F. Ch. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, NY, 1976.
15. D. C. Hoffman, *Chem. Eng. News*, *72*, 24 (1994).
16. S. Bulbulian, F. Ureña, and A. G. Maddock, *Radiochim. Acta*, *35*, 199 (1984).
17. D. Rancon, *Ibid.*, *44/45*, 187 (1988).
18. C. Loos-Neskovic, These de Doctorat d'Etat, Faculte des Sciences de Paris VI, 1986.

Received by editor February 13, 1995
Revision received December 11, 1995