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Chao-Yeuh Yang[a]; Jonh-Shen Chen[a]; Yu-Chai Yeh[a]
[a] Institute of Nuclear Energy Research Lung-Tan, Taiwan

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Preparation and Sorption Properties of Spherical Polyacrylamide–Zirconium Phosphate Ion-Exchanger

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CHAO-YEUH YANG,* JONH-SHEN CHEN, and YU-CHAI YEH

INSTITUTE OF NUCLEAR ENERGY RESEARCH
LUNG-TAN, TAIWAN

Abstract

Spherical particles of polyacrylamide–zirconium phosphate (PZP) ion-exchanger have been prepared by the conversion of hydrous zirconia with the sol–gel technique using acrylamide and *N,N'*-methylenebisacrylamide copolymer as binders. Some chemical properties, stabilities, and sorptions of 1–3 valent cations have been studied. An elution curve of ^{137}Cs is reported, and the effective separation of Cs^+, Co^{2+}, and Ce^{3+} has been achieved with a small column of PZP.

INTRODUCTION

Zirconium phosphate is one of the best known inorganic ion exchangers due to its stability toward ionizing radiation, high temperatures, and most chemical reagents (especially in acidic solutions), and the extremely high decontamination factors which can be achieved in radioactive waste treatment (*1–7*). Since the zirconium phosphate precipitate is gelatinous and difficult to filter, and the dry grains with poor mechanical properties are not suitable for column operation, the sol–gel method for preparing spherical particles as Hardy and Pekarek (*8, 9*) reported was used. Instead of urea and hexamethylenetetraamine, acrylamide and *N,N'*-methylenebisacrylamide copolymer were used as binder in this study; thus a very quick and easy way for preparing the spherical polyacrylamide–zirconium phosphate (PZP) ion-exchanger has been developed. This product possesses advantages of both

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To whom correspondance should be addressed at Department of Chemistry, Texas A&M University, College Station, Texas 77843.

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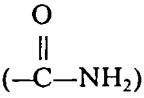
inorganic and organic ion-exchangers; that is, higher selectivity, easily reproducible preparations (PZP possessed physical characteristics and exhibited ion-exchange behavior which can be reproduced from sample to sample), and excellent mechanical and chemical stabilities. The polyacrylamide binder product has higher elasticity than the former polyurea binder product which is fragile and not suitable for repeated use.

Since sorption is a surface reaction (*7*), acrylamide–*N,N'*-methylenebisacrylamide, the highly porous copolymer (gaining a reputation in the gel electrophoresis field) is used as a binder (*10, 11*), and indeed it makes a good binder since the copolymer with a polaramide ($-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$) end is easily bonded to positively charged trimeric or tetrameric polymeric Zr(IV) ions. As previous reported, kinetic studies on ZrP have indicated that the rate of exchange is controlled by the rate of diffusion of ions through the exchanger particles (*12*), so the resultant spherical particle with small ZrP dispersed in the porous polyacrylamide is kinetically favorable for ion exchange. Moreover, the product, which has low flow resistance characteristics, is very suitable for column operation.

EXPERIMENTAL

Preparation of PZP Ion-Exchanger

Spherical particles of polyacrylamide–zirconium phosphate were prepared in the following way: 30 g zirconyl chloride in 30 mL 1 *N* hydrochloric acid was mixed under vigorous stirring with the addition of 15 g acrylamide and 1.5 g *N,N'*-methylenebisacrylamide [to obtain a suitable mean pore size (cross-linkage), a 1/10 of *N,N'*-methylenebisacrylamide to acrylamide ratio was chosen (*10, 11*)]. After adding 0.5 g ammonium persulfate, the amount of ammonium persulfate used for initiation is a compromise between the rate of polymerization and the degree of polymerization (*13*). The resulting viscous solution was fed through a needle to a solidification column through which a countercurrent of silicone oil heated to 95°C was circulated. The polyacrylamide–zirconium hydroxide spheres, which were 20 mesh in diameter, fell to the column bottom and were collected. The spheres were rinsed and thoroughly washed with acetone and trichloroethylene in order to remove organic substances. After immersion in 1 *N* H_3PO_4 for at least 2 h, the PZP ion-exchanger was washed with 3 *N* hydrochloric acid and rinsed with water until it reached pH 3. It was then ready for use.

Distribution Coefficients

The equilibrated distribution coefficients of various ions were determined by shaking 1 g PZP with a 50-mL solution containing 100 μg/mL metal chloride or metal nitrate at pH 2. The amounts of metal ion adsorbed were determined from the difference between the intial and final concentrations of the metal ions in the clear supernatant by using a Varian-Techtron AA6 atomic absorption spectrometer.

Column Experiments

A column, 8.2 × 1.5 cm (i.d.), containing 5 g PZP was used for column experiments which were carried out at a flow rate of 0.8 mL/min.

RESULTS AND DISCUSSION

Chemical and Adsorptive Properties of PZP

Chemical analysis of the polymarization product showed a phosphorous to zirconium ratio of 2.0. The typical composition is 69% H_2O, 10% acrylamide copolymer, and 21% zirconium bis(monohydrogen orthophosphate), $Zr(HPO_4)_2$. The capacity of PZP was determined by percolating 0.1 *N* sodium chloride solution through the PZP column and titrating the liberated acid with standard sodium hydroxide. This was found to be 0.75 meq/g PZP, which is close to that corresponding to the exchange of one hydrogen ion per stoichiometric formula. The titration curve of the PZP after crushing it exhibited the same inflection contour as Amphlett's earlier report (*2*), as shown in Fig. 1. The optimum immersing solution was found to be 1 *N* H_3PO_4, the concentration which results in the highest PZP capacity.

The product PZP is insoluble in most acidic reagents except flouride-containing reagents, sulfuric acid, and oxalic acid. In strongly alkaline solution the acrylamide copolymer swells and bursts into fragments when it contacts acid.

Table 1 shows the distribution coefficients of some cations of various valencies. It can be seen that the distribution coefficients for the alkali metal cations follow the order of the hydrated ionic radii, the same as with zirconium phosphate amorphous powders. This order indicates that exchange takes place primarily with the hydrated cations. The adsorptivity of ions can be attributed to two main factors. The first one is the pore size cavity

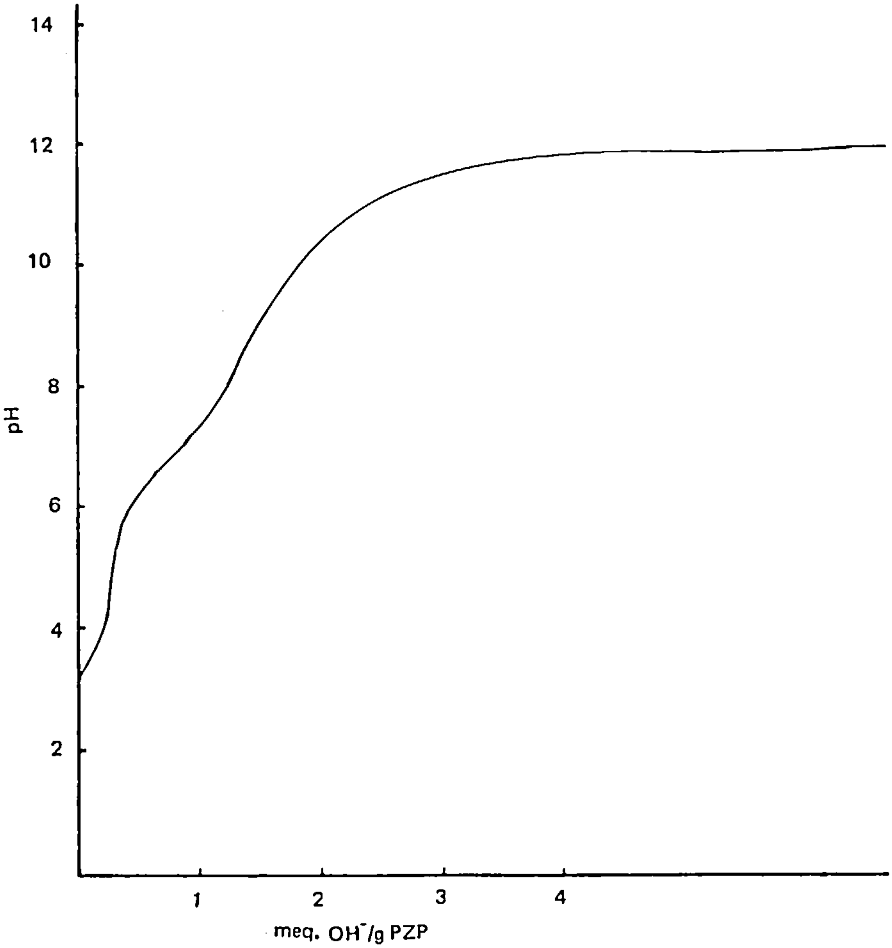


FIG. 1. Titration curve of crushed PZP.

of the polyacryamide–ZrP adsorber which provides an entrance pathway for ions diffusing into it. The second factor depends on the binding force between dihydrogen orthophosphate and metallic ions. The reaction that causes a larger decrease in Gibbs free energy of the system results in a higher K_d value. The influence of the effect of the hydrated ionic radii size on the distribution coefficient seems to be greater than the effect of the charge of the cations' valencies. In particular, the distribution coefficient of Ce decreases more steeply than does that of Cs as the acidity changes from pH 2 (10^{-2} N)

TABLE 1

Distribution Coefficients (K_d) of 1–3 Valent Cations on PZP Spherical Particles[a]

Cation	K_d (mL/g PZP)
Li^+	1.55
Na^+	3.01
K^+	7.47
Cs^+	24.5, 10[b]
Ag^+	3.94
Co^{2+}	8.71
Cu^{2+}	34.1
Zn^{2+}	11.3
Cd^{2+}	27.5
Pb^{2+}	91.8
Fe^{3+}	31.0
Ce^{3+}	30.4, 2.1[b]

[a] Experimental conditions: 50 mL of 100 μg/mL M^{n+}, mechanically shaking with 1.0 g of PZP for 30 min in separation funnel. Initial solution pH 2.

[b] Initial solution at 1 *N* acidity.

to 1 *N* acidity. It seems to tie in with the hydrated radii effect, and the resultant different K_d values makes the column separation of Ce^{3+} and Cs^+ an easy task.

Rate of Exchange of Cesium Ion

A solution of 100 μg/mL Cs^+ at pH 2 was shaken with 1.0 g PZP at different time intervals to perform a kinetic study. As acrylamide and *N,N'*-methylenebisacrylamide formed a highly porous copolymer, the dispersed PZP resulted in a rather rapid exchange rate. As shown in Fig. 2, the exchange equilibrium was reached within 10 min.

Qualitative Test of the Adsorptive Properties of PZP on Some Long Half-Life Fission Products Such as ^{137}Cs and ^{90}Sr by Coprecipitation X-Ray Fluorescence Spectrum

The adsorptive properties of PZP on some long half-life fission products was confirmed by eluting 10 mL of a pH 2 solution containing Cs, Ba, Nb, U, Eu, Ce, Dy, Sb, Sr, Ru, and Zr (each 100 μg/mL) through a PZP column. The elements not adsorbed by PZP, and which therefore remained

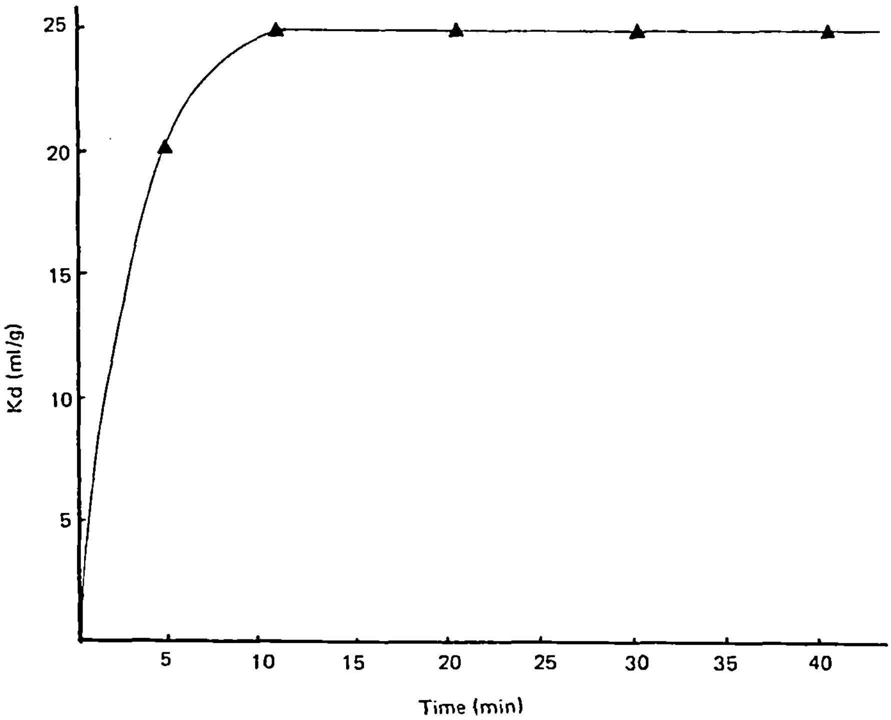


FIG. 2. Rate of uptake of Cs on PZP.

in the eluate, were detected by the coprecipitation-x-ray fluorescence method (*14, 15*) using a Tracor North, Model NS-880, instrument equipped with a lithium-drifted silicon energy-dispersive detector. Only Ru was detected; thus all of the above elements except Ru were retained.

Separation of Cesium from Cobalt and Cerium

A 5-mL radioactive waste water sample from the Taiwan Research Reactor containing 1 μCi/mL of ^{137}Cs and small amounts of ^{60}Co and ^{144}Ce was loaded on a PZP column. ^{60}Co, ^{144}Ce, and ^{137}Cs were selectively eluted with the elutriants 0.1 *N* HCl, 1 *N* HCl, and 5 *N* HN_4Cl, respectively. The elution curve is shown in Fig. 3.

The radiochemical purity of the separated cesium was confirmed by gamma spectrometry using a 35-cm^3 Ge(Li) detector coupled to a Hewlett-

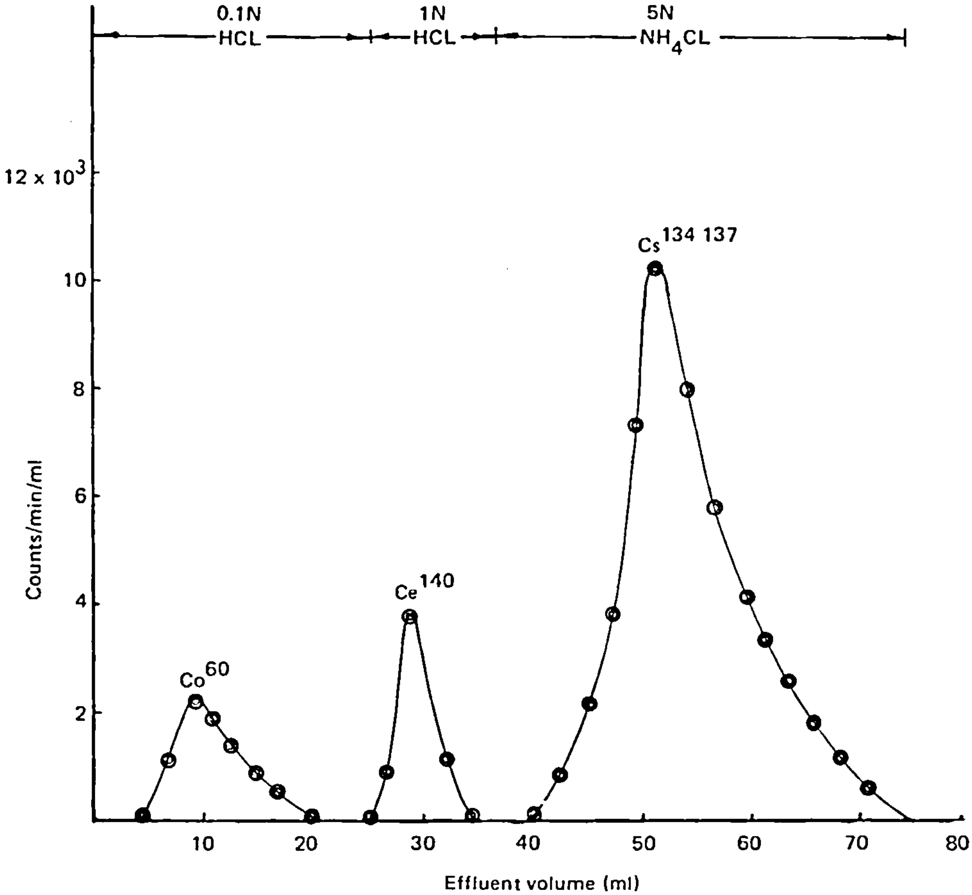


FIG. 3. Separation of Co, Ce, and Cs at tracer concentrations on PZP.

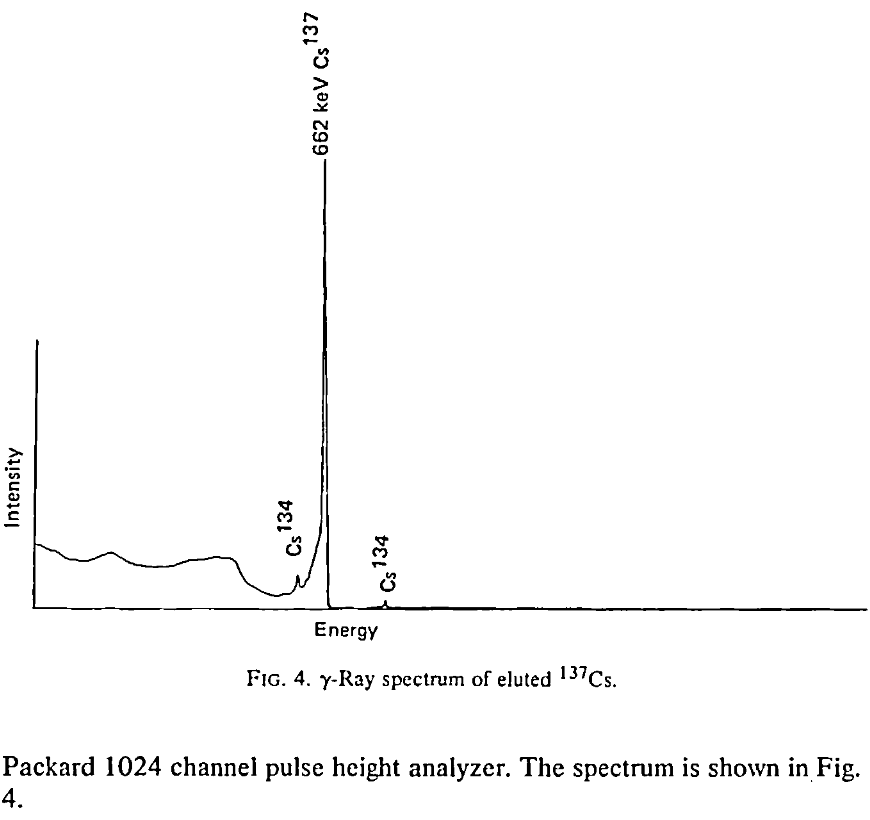


FIG. 4. γ-Ray spectrum of eluted ^{137}Cs.

Packard 1024 channel pulse height analyzer. The spectrum is shown in Fig. 4.

The PZP ion-exchanger can be repeatedly used without deterioration (the K_d value of the ions in Table 1 after a number of runs does not change). Since the separated ^{137}Cs could be a resource (*16*), an economic value can be anticipated.

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