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UPTAKE OF VARIOUS RADIONUCLIDES BY HYDROTHERMALLY PREPARED MOLYBDENUM PHOSPHATES

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ABSTRACT

A series of molybdenum phosphates with three different structures were synthesized hydrothermally. The types include a one-dimensional polymer, $(\text{PPh}_4)_2[(\text{H}_3\text{O})_2\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7] \cdot 5\text{H}_2\text{O}$; a microporous material with a framework structure, $(\text{TMA})_2(\text{NH}_4)_2[\text{Fe}_2\text{Mo}_{12}\text{O}_{30}(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_2] \cdot n\text{H}_2\text{O}$; and three compounds with layered structures, $[\text{N}(\text{C}_3\text{H}_7)_4(\text{NH}_4)][(\text{MoO})_4\text{O}_4(\text{PO}_4)_2]$, $\text{KMo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$, and $\text{NH}_4\text{Mo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$. These compounds were tested for their ability to remove the radionuclides commonly found in nuclear waste solutions (^{85}Sr , ^{134}Cs , ^{57}Co , ^{65}Zn , ^{59}Fe , ^{54}Mn , ^{51}Cr , ^{110}Ag , ^{236}Pu , and ^{241}Am). Experiments were carried out to determine the distribution coefficients (K_{D}) of the radionuclides in several “model” solutions (0.1 M HNO_3 , 0.1 M NaNO_3 , 0.1 M $\text{NaNO}_3/0.1\text{ M}$ NaOH). A well-known ammonium 12-molybdochosphate (AMP), prepared by cold synthesis, was tested in parallel for reference in acidic media. Of the tested materials, ferric molybdenum phosphate took up several radionuclides rather well in neutral and alkaline conditions and was selective for ^{241}Am in 0.1 M HNO_3 ($K_{\text{D}}=2140\text{ mL/g}$). The hydrothermally prepared NH_4MoPO_4 was very selective for ^{134}Cs , having a K_{D} of 23,400

mL/g in 0.1 *M* HNO₃, about half of that of AMP (44,000 mL/g). Sodium molybdenum phosphate took up both ²³⁶Pu and ²⁴¹Am in 0.1 *M* HNO₃ well, the K_{DS} being 3350 and 8600 mL/g, respectively. Otherwise, the materials took up few of the tested radionuclides selectively as the K_{DS} were usually below 1000 mL/g.

INTRODUCTION

Selective separation of radionuclides from nuclear waste solutions is a highly effective and desirable method for the minimization of waste volumes for final disposal. Several selective inorganic ion exchangers (zeolites, sodium titanates, titanosilicates, hexacyanoferrates) are available commercially, and the number of their applications at nuclear sites is increasing. Almost all of these exchangers have been developed for the separation of ¹³⁷Cs and ⁹⁰Sr, and they often have limited selectivity for other radionuclides as well. Because separation of ¹³⁷Cs and ⁹⁰Sr has been historically the main emphasis in the developmental work, little information is available for the selectivity of inorganic exchangers for other radionuclides. There is an increasing demand for the selective removal of activated corrosion product nuclides (e.g., ⁶³Ni, ^{58,60}Co, ⁵¹Cr, ⁵⁴Mn, ⁵⁹Fe, and ⁶⁵Zn) at nuclear power plants.

A large number of traditional and novel inorganic exchangers were prepared and evaluated for their ability to remove a wide range of radionuclides commonly found in nuclear waste solutions (⁸⁵Sr, ¹³⁴Cs, ⁵⁷Co, ⁶⁵Zn, ⁵⁹Fe, ⁵⁴Mn, ⁵¹Cr, ¹¹⁰Ag, ²³⁶Pu, and ²⁴¹Am). This paper reports some preliminary results obtained for a group of hydrothermally synthesized molybdenum phosphates with framework and layered structures. The molybdenum phosphates were included in the hope of finding similar, or superior, properties in these compounds to the traditional cesium-selective sorbent, ammonium 12-molybdate (AMP), prepared by cold synthesis. Experiments were carried out by determining the distribution coefficients (K_{DS}) of the radionuclides in several "model" solutions (0.1 *M* HNO₃, 0.1 *M* NaNO₃, 0.1 *M* NaNO₃/0.1 *M* NaOH). In some cases more acidic solutions were used. AMP was tested in parallel for reference. In addition, natural clinoptilolite (obtained from BNFL, UK) and a sodium titanosilicate was used as reference materials in cesium uptake tests.

EXPERIMENTAL METHODS

Reagents

All reagents were of analytical grade (Fluka, Riedel-de Haen, Merck) and used without further purification. The radioactive tracers used in ion-exchange experiments were obtained from Amersham International (UK).



Syntheses of the Materials

All the syntheses were carried out in Teflon-lined pressure vessels under hydrothermal conditions at temperatures 170-200°C. The products were filtered, washed with distilled water, and dried at 100°C. Removal of the template by calcining was attempted on some of the samples, but it tended to break the structure. Therefore, uncalcined samples were used in the ion-exchange experiments.

One-Dimensional Polymer: $(\text{PPh}_4)_2[(\text{H}_3\text{O})_2\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7] \cdot 5\text{H}_2\text{O}$

One-dimensional polymeric sodium molybdenum phosphate (1) (NaMoPO), was synthesized by diluting 85% H_3PO_4 with distilled water to which PPh_4Br was added while stirring. To this solution, molybdenum metal and Na_2MoO_4 were added. The hydrothermal reaction was carried out at 176°C for 29 h. The mol ratio of the reagents (Na_2MoO_4 , molybdenum metal, H_3PO_4 , PPh_4Br , and H_2O) was 2.6:2.6:8.2:1:141. Molybdenum metal was needed to reduce the Mo(VI) of the starting material to Mo(V) in order to avoid the formation of the Keggin-type heteropolytungstate. Consequently, the $\text{Mo}_6\text{P}_4\text{O}_{24}(\text{OH})_7$ unit has a charge of 5, which is compensated for by the two PPh_4^+ cations, the Na^+ cation, and two H_3O^+ cations. $[(\text{H}_3\text{O})_2\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7]^{2-}$ clusters are hydrogen-bonded into two-dimensional sheets. Between these sheets are the PPh_4^+ cations, which complete the three-dimensional structure (1). The orange material obtained was calcined at 240 and 420°C.

Framework Structure: $(\text{TMA})_2(\text{NH}_4)_2[\text{Fe}_2\text{Mo}_{12}\text{O}_{30}(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_2] \cdot n\text{H}_2\text{O}$

Microporous ferric molybdenum phosphate with a framework structure (2), FeMoPO , was synthesized by mixing Na_2MoO_4 , Mo, FeCl_3 , $(\text{NH}_4)_2\text{HPO}_4$, tetramethylammonium hydroxide (TMAOH), H_3PO_4 , and H_2O in a mol ratio of 5:1:1:2:7:16:150. The hydrothermal reaction was carried out at 200°C for 66 h. The building block $[\text{Mo}_6\text{P}_4\text{O}_{24}(\text{OH})_7]^{5-}$ in the product is the same as that in NaMoPO . The structure of FeMoPO is built up from $\text{Fe}[\text{Mo}_6\text{P}_4\text{O}_{24}(\text{OH})_7]_2$ units bridged together, forming a three-dimensional structure whose pores are filled with water and TMA^+ cations (2). Samples were calcined at 180 and 300°C.

Layered Structure, Type 1: $[\text{N}(\text{C}_3\text{H}_7)_4\text{NH}_4][(\text{MoO})_4\text{O}_4(\text{PO}_4)_2]$

A layered oxide with octahedral molybdenum(V) and phosphate tetrahedra (3), MoPO was synthesized by dissolving ammonium dimolybdate ("molybdic



acid") in H_3PO_4 (diluted with distilled H_2O). Tetrapropylammonium bromide (TPA Br) was added while stirring. The hydrothermal reaction was carried out at 195°C for two weeks. The layered compound is made up of sheets of Mo_4O_8 cubes that are linked to phosphate tetrahedra. The TPA $^+$ cations and the ammonium molecules are located between the layers. Mo(VI) is reduced to Mo(V) possibly by ammonium, thus avoiding the formation of the Keggin structure (3), $[PMo_{12}O_{40}]^{3-}$. The reddish-brown product was calcined at 240 and 420°C.

Layered Structure, Type 2: $KMo(H_2O)O_2PO_4$ and $NH_4Mo(H_2O)O_2PO_4$

Two isostructural molybdenum(VI) phosphates, potassium (KM₂PO) and ammonium (NH₄M₂PO) (4), with layered structures, were synthesized hydrothermally at 170°C for 6 days. The reaction mixture for KM₂PO contained MoO₃, H₃PO₄, KNO₃, and H₂O in a mole ratio of 6:21:10:170. The reaction conditions for NH₄M₂PO were the same except that NH₄NO₃ replaced KNO₃. Both compounds are composed of layers of [MoO₆] octahedra and [PO₄] tetrahedra with K $^+$ and NH₄ $^+$ cations between the layers (4). Both products had bright yellow color.

AMP

Ammonium 12-molybdocephosphate (AMP) was synthesized according to the cold synthesis procedure of van R. Smit (5). AMP, a well-known material, was used as a reference in the ion-exchange experiments for cesium because of its excellent selectivity.

Sodium Titanosilicate

A sodium titanosilicate $Na_2Ti_2O_5SiO_4 \cdot 2H_2O$, with a framework structure was synthesized in alkaline media (6). Its framework consists of tunnels into which the Cs $^+$ ions fit easily, thus making the material a highly cesium-selective ion exchanger.

Characterization

Diffraction data for the materials were collected with a Philips PW1710 powder X-ray diffractometer (XRD) with Cu K α radiation (1.54 Å), using a step counting method (step size, [2 θ] $^{\circ}$ 0.050, and time/step, 1.25-2.00 s) in the range of



20°, 5-60°. The X-ray source was a rotating anode operating at 40 kV and 50 mA. A Phillips PW1877 diffraction software program PC-APD version 3.5B was used to analyze the X-ray patterns.

Thermogravimetric analyses (TGA) were carried out on a Mettler-Toledo TA800 unit at a heating rate of 10°C/min from 25 to 600°C under a nitrogen atmosphere. Elemental-analysis studies of NaMoPO and the layered MoPO were performed by heating a mixture of the sample and LiBO₂ at 1000°C in a nickel crucible and dissolving the melt in HCl. The diluted samples were analyzed by inductively coupled plasma – atomic emission spectroscopy (ICP-AES). FeMoPO did not completely dissolve in concentrated HCl, HNO₃, HF, or NaOH. However, KMoPO, NH₄MoPO, and AMP dissolved in 1 M NaOH, but the samples were not analyzed.

Batch Exchange Studies

Distribution coefficients (K_D) were determined in batch experiments. A 0.06-g portion of each sample was equilibrated with 6 mL of acid or salt solution (4 M HNO₃, 0.1 M HNO₃, 0.1 M NaNO₃, or 0.1 M NaNO₃/0.1 M NaOH) that was traced with a radioactive isotope in an 8 mL polypropylene centrifuge tube (DuPont Sorvall). The batch factor (solution volume/exchanger mass) used was 100 mL/g, and the equilibration time was 1 or 4 days at room temperature with constant rotary mixing. The samples were centrifuged using a Beckman L8-M Ultracentrifuge (velocity, 30,000 rpm; time, 30 min) and filtered with 0.22-μm Minispire PVDF Bulk Acrodisk 13 filters. Five milliliter aliquots of the filtered samples were measured for their activities (cpm) with a gammacounter Wallac 1480 Wizard™ 3 in the cases of ¹³⁴Cs, ⁸⁵Sr, ⁵⁷Co, ⁶⁵Zn, ¹¹⁰Ag, ⁵⁴Mn, ⁵⁹Fe, ⁵¹Cr, and ²⁴¹Am and with a liquid scintillator Wallac LKB 1217 Rackbeta in the case of ²³⁶Pu. The distribution coefficient (K_D) values were calculated according to

$$K_D = \frac{\text{concentration in exchanger}}{\text{concentration in solution}} = \frac{(A_0 - A_{eq})}{A_{eq}} \frac{V}{m} \quad (1)$$

where A₀ and A_{eq} are the activities of the tracer initially and at equilibrium, respectively, and V/m is the solution volume to exchanger mass ratio (batch factor, mL/g).

Determination of Ion-Exchange Capacity by Titration

Ion-exchange capacities of the materials were determined in 0.1 M NaNO₃ + NaOH solutions. The materials were converted to the H⁺ form by equilibrating 0.5 g of exchanger with 100 mL of 0.1 M HNO₃. Fresh HNO₃ was changed sev-



eral times until a pH of about 1.0 was reached. Titrations were carried out in successive batch equilibrations by adding varying amounts of NaOH into 0.1 *M* NaNO₃. A 0.02-g portion of the exchanger was equilibrated with 10 mL of 0.1 *M* NaNO₃ + NaOH solution (BF = 500).

RESULTS AND DISCUSSION

Materials Prepared Hydrothermally

One-Dimensional Polymer: (PPh₄)₂[(H₃O)₂NaMo₆P₄O₂₄(OH)₇]·5H₂O

Calcination of the material at 420°C causes the compound structure to collapse. This can be seen from both the powder XRD traces and the TGA, which showed that the organic template is removed soon after a temperature of 420°C is reached (16% of 9.75-g sample). Calcination at 240°C does not destroy the structure or remove the PPh₄⁺ cations. Therefore, the material is relatively stable but its charge practically neutral.

Framework Structure: (TMA)₂(NH₄)₂[Fe₂Mo₁₂O₃₀(H₂PO₄)₆(HPO₄)₂]·nH₂O

The powder XRD trace of the product indicated that the correct structure was obtained. This was confirmed by a prediction of the powder diagram calculated from the interatomic distances (Å) for FeMoPO given in ref. 2 (since no powder XRD data were provided in the reference). Calcination of the product at 300°C caused the structure to collapse; partial breakage of the compound occurred by 180°C. According to the TGA run there is a slight weight loss after 60°C, when evaporation of surface water becomes significant. A loss of NH₃ occurs in the 120-340°C range, and a large weight loss at 340-440°C indicates that decomposition of the template cations (TMA⁺) has occurred, leading to the structure breakdown.

Layered Structure, Type 1: [N(C₃H₇)₄(NH₄)][(MoO)₄O₄(PO₄)₂]

According to the TGA run, the TPA⁺ template is removed at 400-480°C. Calcination at 240°C does not affect the highly crystalline structure, but at 420°C the sample is destroyed as the template is removed from between the layers. The elemental analysis by ICP-AES showed that the Mo:P ratio in the material was 2:1, which corresponds to that in the molecular formula. The amount



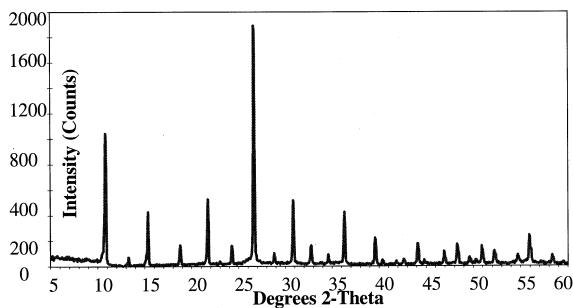


Figure 1. Powder XRD trace of the ammonium molybdenum phosphate AMP.

of molybdenum in the product was 290 mmol/g, while that of phosphorous was 140 mmol/g.

Layered Structure, Type 2: $\text{KMo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$ (KM₂PO₄) and $\text{NH}_4\text{Mo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$ (NH₄M₂PO₄)

The powder XRD trace of KM₂PO₄ corresponds to that of $\text{K}_2\text{PO}_4 \cdot (\text{MoO}_2)_{12} \cdot 4\text{H}_2\text{O}$ [reference data from the Joint Committee on Powder Diffraction Standards (JCPDS)], and the structure is stable up to 300°C. According to the TGA run, the compound loses water between 300 and 450°C. For NH₄M₂PO₄, a weight loss of 8.3% was observed between 380 and 600°C. The powder XRD of NH₄M₂PO₄ is similar to that of $(\text{NH}_4)_2\text{PO}_4 \cdot (\text{MoO}_2)_{12} \cdot 4\text{H}_2\text{O}$ (from JCPDS). It is also practically identical to the XRD pattern of AMP (Figs. 1 and 2). The structure of the compound is unaffected when calcination is done at 400°C.

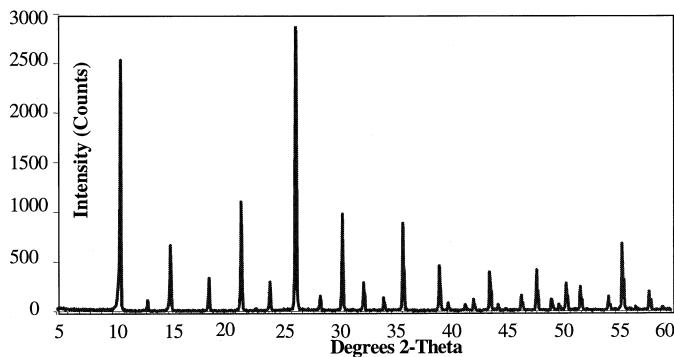


Figure 2. Powder XRD trace of the ammonium molybdenum phosphate $\text{NH}_4\text{Mo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$.



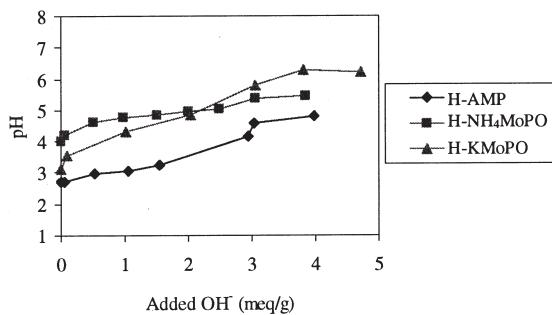


Figure 3. Equilibration pH as a function of added OH⁻ (meq/g) for AMP, NH₄MoPO, and KMoPO.

H⁺-Ion Exchange Capacities

In the titration from acidic to basic medium, AMP was dissolved by the time pH 4.5 was reached, NH₄MoPO by pH 5, and KMoPO at pH 6. The titration curves for AMP, NH₄MoPO, and KMoPO are shown in Fig. 3; those for NaMoPO and MoPO are presented in Fig. 4. The two isostructural molybdenum phosphates, KMoPO and NH₄MoPO, have H⁺-ion capacities of about 2.5 meq/g at pH 5. AMP behaves as the hydrothermally synthesized NH₄MoPO but starts to take up cesium at pH 2.8, whereas NH₄MoPO needs a higher pH. AMP has a capacity of about 2.8 meq/g at pH 4, while NH₄MoPO has a capacity of only 0.2 meq/g. The absence of a sharp inflection point in the titration curves indicates that all three exchangers are weakly acidic in nature.

MoPO displays a diprotic nature and has an ion-exchange capacity of about 2 meq/g at the second inflection point (pH 8.5). NaMoPO seems to be a weakly acidic exchanger as well and has a capacity of about 2.8 meq/g at pH 10.

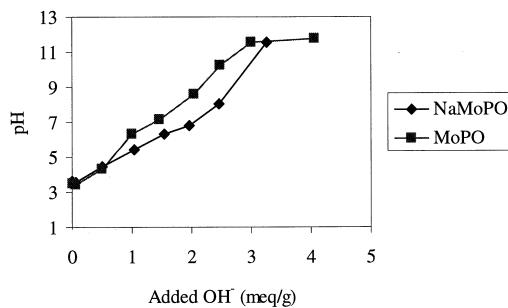


Figure 4. Equilibration pH as a function of added OH⁻ (meq/g) for NaMoPO and MoPO.



Table 1. Distribution Coefficients (K_{Ds} , (mL/g) for the Molybdenum Phosphates

Material	Nuclide	4 M HNO ₃	0.1 M HNO ₃	0.1 M NaNO ₃	0.1 M NaNO ₃ / 0.1 M NaOH	Distilled H ₂ O
$\text{NH}_4\text{Mo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$	Sr-85	0	7	0	4	810
	Cs-134	1,400	23,400	22,300	190	16,600
	Co-57	5	8	3	60	220
	Zn-65	3	0	70	65	110
	Ag-110m	45	55	1,850	520	29,600
	Mn-54	1	0	3	1,800	310
	Fe-59	0	10	490	360	5,400
	Pu-236	—	490	240	180	360
	Am-241	1	22	22,000	—	16,800
	Cr-51	4	0	190	—	1,600
$\text{KMo}(\text{H}_2\text{O})\text{O}_2\text{PO}_4$	Sr-85	2	9	3	3	10
	Cs-134	160	870	780	45	1,570
	Co-57	2	3	3	35	5
	Zn-65	0	2	4	30	9
	Pu-236	0	105	270	—	35
$[\text{N}(\text{C}_3\text{H}_7)_4\text{NH}_4]$	Sr-85	1	15	335	9	58
$[(\text{MoO}_4)_4\text{O}_4(\text{PO}_4)_2]$	Cs-134	25	65	4,220	100	1,970
	Co-57	4	210	8	50	
	Zn-65	0	3	30	15	30
	Pu-236	—	9	380	75	260
$(\text{PPh}_4)_2[(\text{H}_3\text{O})_2$	Ag-110m	—	11,650	4,460	30,900	—
$\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7 \cdot 5\text{H}_2\text{O}$	Mn-54	—	0	395	55	—
	Am-241	—	6	—	1,270	2,120
	Cr-51	—	0	—	7	20
$(\text{PPh}_4)_2[(\text{H}_3\text{O})_2$	Sr-85	4	93	270	6,250	24,640
$\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7 \cdot 5\text{H}_2\text{O}$	Cs-134	2	1,170	870	1,440	3,750
	Co-57	0	5	10	160	—
	Zn-65	0	7	8	9,750	20
	Pu-236	90	3,350	14,250	290	—
	Ag-110m	2	20,900	92,600	118,000	91,700
	Mn-54	0	8	35	149,000	60
	Fe-59	0	11	6	18,700	0
	Am-241	2	8,600	6	90,900	0
	Cr-51	0	120	140	320	110
$(\text{TMA})_2(\text{NH}_4)_2$	Sr-85	2	10	1,670	48,800	85,800
$[\text{Fe}_2\text{Mo}_{12}\text{O}_{30}(\text{H}_2\text{PO}_4)_6 \cdot n\text{H}_2\text{O}$	Cs-134	1	500	210	15	2,710
	Zn-65	2	25	17,500	25,900	32,200
	Co-57	1	11	1,390	140	11,900
	Ag-110m	—	1,210	47,500	2,680	—
	Fe-59	—	15	8,920	327,000	—
	Am-241	—	2,140	17,200	29,040	1,680
	Cr-51	—	—	320	1,830	750



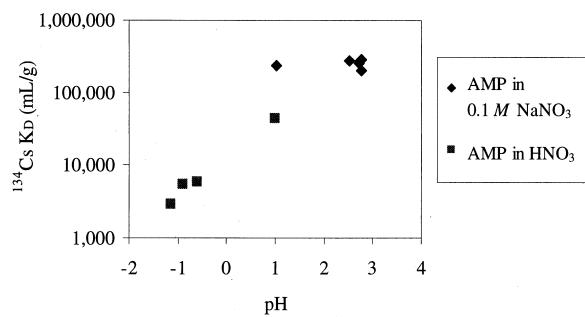
Table 2. ^{134}Cs Distribution Coefficients for NH_4MoPO and AMP

HNO_3 concentration (M)	$^{134}\text{Cs } K_D$ [mL/g]	
	AMP	NH_4MoPO
0.1	44000	23400
4	5900	—
8	5300	760
14	2900	40

Distribution Coefficients (K_D s) for Several Nuclides in 0.1 M HNO_3 , 0.1 M NaNO_3 and 0.1 M $\text{NaNO}_3/0.1$ M NaOH

The K_D values determined for the molybdenum phosphates in "model" solutions for several radionuclides are shown in Table 1. Of the materials tested, FeMoPO took up several radionuclides rather well in neutral and alkaline conditions. It was also selective for ^{241}Am in 0.1 M HNO_3 , the K_D being 2140 mL/g. The hydrothermally prepared NH_4MoPO was very selective for ^{134}Cs and had a K_D of 23,400 mL/g in 0.1 M HNO_3 , about one-half of that of AMP (44,000 mL/g). Therefore, additional tests for NH_4MoPO and AMP were carried out under more acidic conditions (Table 2, Fig. 5). AMP was very selective for ^{134}Cs even in 14 M HNO_3 , having a K_D of 2900 mL/g. NH_4MoPO does not tolerate such high acid concentrations, and the $^{134}\text{Cs } K_D$ was only 40 mL/g at 14 M HNO_3 . The difference in selectivity could be observed in the H^+ -ion titration (Fig. 3).

The effect of pH on $K_D(^{134}\text{Cs})$ in 0.1 M NaNO_3 for AMP is shown in Fig. 5. It can be seen that the K_D decreased almost linearly from $2.7 \cdot 10^5$ mL/g to 5900 mL/g when the pH fell from 3 (in 0.1 M NaNO_3) to below 0 (in HNO_3).

**Figure 5.** $^{134}\text{Cs } K_D$ as a function of pH for AMP in 0.1 M NaNO_3 and HNO_3 .

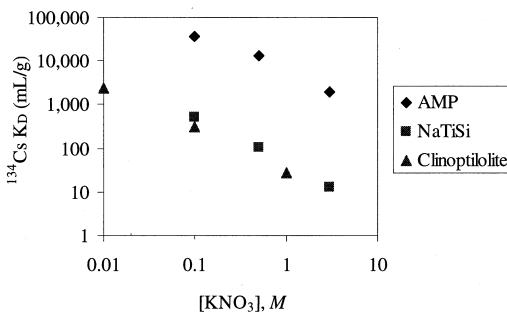


Figure 6. ^{134}Cs K_D as a function of $[\text{KNO}_3]$ for AMP, sodium titanosilicate, and clinoptilolite.

The values for pH points (0.6, (0.9 and (1.14 were obtained with 4, 8, and 14 M HNO_3 . When compared with two other cesium-selective ion exchangers, a crystalline sodium silicotitanate $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4\cdot 2\text{H}_2\text{O}$ and the naturally occurring clinoptilolite (Mud Hills, USA), AMP clearly outperformed them both in the presence of the macro component potassium (Fig. 6). The K_D for AMP was 12,800 mL/g at 0.5 M KNO_3 while it was two orders of magnitude lower for $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4\cdot 2\text{H}_2\text{O}$ (100 mL/g). Sodium interferes with cesium exchange less than potassium does, which is obvious from the fact that the ^{134}Cs K_D s were clearly higher in NaNO_3 than in KNO_3 . AMP was slightly more affected by the presence of macro ion Na^+ than $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4\cdot 2\text{H}_2\text{O}$ (Fig. 7). In 0.5 M NaNO_3 the K_D s were very high for both materials, 639,500 mL/g for $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4\cdot 2\text{H}_2\text{O}$ and 163,600 mL/g for AMP. For clinoptilolite the K_D was only 1000 mL/g under the same conditions.

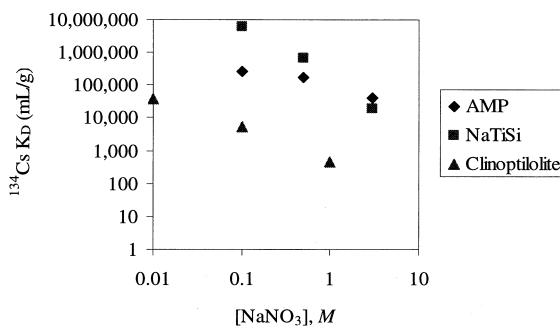


Figure 7. ^{134}Cs K_D as a function of $[\text{NaNO}_3]$ for AMP, sodium titanosilicate, and clinoptilolite.



The $\log K_D$ can also be expressed (7) as in Eq. 2. When the measured K_{DS} are plotted as a function of $\log C_T$ (total ion concentration of solution), the result is a straight line with a slope of $-(z_A/z_B)$ when the sorption is equivalent exchange of ion A for B.

$$\log K_D = (1/z_B) \log(k_{A/B}Q^{2A}) - (z_A/z_B) \log C_T, \quad (2)$$

where z_A and z_B are the charges of the trace and the macro ions, $k_{A/B}$ is the selectivity coefficient, and Q is the capacity. For Cs^+/K^+ exchange, the slopes for AMP, $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ and clinoptilolite are -0.85 , $(1.09$ and -0.96 , respectively, which are close to the theoretical slope of -1 (Fig. 6).

The other materials took up few of the tested radionuclides selectively; the K_{DS} were usually below 1000 mL/g (Table 1). In addition to NH_4MoPO , $KMoPO$ and $NaMoPO$ showed a slight affinity for cesium. $KMoPO$ has a ^{134}Cs K_D of 160 mL/g in $4\text{ M }HNO_3$ and $NaMoPO$ a K_D of 1170 mL/g in $0.1\text{ M }HNO_3$. $NaMoPO$ also appeared to take up ^{236}Pu and ^{241}Am in $0.1\text{ M }HNO_3$; the K_{DS} were 3350 mL/g and 8600 mL/g, respectively. $FeMoPO$ proved to be the material that took up most of the tested nuclides. It has a slight affinity for ^{85}Sr and ^{57}Co in $0.1\text{ M }NaNO_3$ but is more selective for ^{65}Zn , ^{59}Fe and ^{241}Am . Surprisingly, it does not seem to be selective for cesium.

The K_{DS} for ^{110m}Ag are high because of the precipitation of silver in alkaline medium and its adsorption onto the walls of the centrifuge tubes. Therefore, the K_D results for ^{110m}Ag are not accurate.

CONCLUSIONS

In this study, five molybdenum phosphates were prepared hydrothermally. The traditional ammonium molybdenum phosphate, AMP, prepared by cold synthesis was found to be the most cesium-selective material. The hydrothermally synthesized novel NH_4MoPO with a layered structure tolerated high HNO_3 concentrations very well but had somewhat lower ^{134}Cs K_D s than AMP. This material also took up ^{236}Pu and ^{241}Am reasonably well in $0.1\text{ M }HNO_3$. $KMoPO$, the isostructural compound of NH_4MoPO , did not show as high an affinity for cesium but tolerated acidic conditions well. All three materials have about the same H^+ -ion exchange capacity (2.5 - 2.8 meq/g) before dissolving at pH 4-5.

Higher distribution coefficients for some of the molybdenum phosphates prepared in this work might be obtained if the template could be removed from the structure either by very delicate calcination or a chemical process. This could prove especially beneficial in the case of the framework $FeMoPO$ which has already shown reasonable selectivity for actinides ^{236}Pu and ^{241}Am in acidic solution, because the organic template in the pores now blocks the exchanging cations from entering.



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