SORPTION OF URANIUM ON FIBROUS CERIUM(IV) HYDROGENPHOSPHATE

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ABSTRACT

The uranium sorption properties of fibrous cerium(IV) hydrogenphosphate (f-CeP) in acid solutions were examined under different conditions in order to elucidate its applicability as a new medium of uranium-sorption/fixation for radioactive liquid wastes processing. From chemical and thermal analyses, the chemical composition of the f-CeP used was proved to be $Ce(HPO_4)_2 \cdot 3.4H_2O$. The cation-exchange capacity of the f-CeP was 4.2 meq/g. The plot of logarithmic distribution coefficients for uranyl ions against pH gave a straight line with slope of +2, indicating the occurrence of $UO_2^{2+}/2H^+$ exchange on the f-CeP. Selectivities for uranyl ion and various metal ions at pH 2 were increased in the response order; $Mg^{2+} < Co^{2+} < Na^+ < Ca^{2+} < Sr^{2+} < Ba^{2+} < K^+ < Rb^+ < Cs^+ < Eu^{3+}, UO_2^{2+}, Am^{3+}$. The temperature dependence of uranium uptake below 85°C was very small and the sorption data obtained within the temperature range followed the Freundlich sorption equation. The X-ray photoelectron spectroscopy Ce 3d spectrum observed after sorbing uranium showed that a part of tetravalent cerium in the f-CeP was converted to the trivalent state. At temperatures above 100 °C, the structure of the f-CeP after sorbing uranium collapsed, and some uranium phosphates and their hydrates were formed. Based on above results, two types of mechanisms (ion-exchange/formation of uraium phosphates) for the uranium sorption on the f-CeP were proposed.

INTRODUCTION

Concerning processing and disposal of radioactive wastewater, for development of diverse radioactive nuclide sorbent materials, a fixing medium is one of the important tasks. Especially, because actinides having a long half life seem to show superior attenuation, development of a sorption/fixation medium, and efficient processing and disposal, they are treated importantly in the literature, with several studies having been done by using several inorganic ion-exchangers (1).

One of these, fibrous cerium(IV) hydrogenphosphate, is superior in handling qualities, chemically stable, and also has the property of large cation-exchange capacity (2). Also, by heating the structure, it is easily transformed into cerium orthophosphate. On the other hand, cerium orthophosphate is a main component of monazite. Even if natural monazite contains actinides such as thorium and uranium, those radioactive nuclides release less dangerous radiation, remaining stable for a long time (3). Knowledge about those above natural monazites indicates the possible use of fibrous cerium(IV) hydrogenphosphate as an actinide sorption/fixation medium. Though there are several reports especially concerning ion-exchange for fibrous cerium(IV) hydrogenphosphate (2, 4), there are none concerning actinides.

In this periphery of relevant literature, from the above views on research work concerning sorption of actinides by fibrous cerium(IV) hydrogenphosphate, we test uranium's sorption from acid solutions under several reaction conditions. Also from results obtained, we considered uranium's sorption mechanism.

EXPERIMENTAL

Preparation

All reagents were of analytical grade and were used without further purification. Fibrous cerium(IV) hydrogenphosphate (abbreviated as f-CeP) was prepared according to the literature (5); f-CeP sample was obtained by adding 500 cm^3 of 0.1 M (M = mol/dm^3) $Ce(SO_4)_2 \cdot 4H_2O$ solution (in 0.5 M H_2SO_4) slowly to a well-stirred 500 cm^3 of 5 M H_3PO_4 solution at 90 °C until the molar ratio of P/Ce in the mixed solution became fifty. After aging for 4 h under the same temperature, the precipitate was washed with distilled water until free of sulfate ions, air-dried at 60 °C for 24 h, powdered and finally stored in a sealed vessel over saturated NH_4Cl solution (Humidity: 79% at 25 °C) at a constant vapor pressure of water. The *d* -values (Found: 1.12; 0.547; 0.372 nm) of three main peaks from a X-ray powder diffraction pattern of the fibrous product having 20-50 nm width matched with those (1.095; 0.535; 0.370 nm) of the fibrous cerium(IV) hydrogenphosphate reported, $Ce(HPO_4)_2 \cdot nH_2O$ (5). Chemical analysis gave a P/Ce molar ratio of 1.99 (Found: Ce, 31.21 ; P, 13.72 wt%). From the weight loss at 550 °C by thermal analysis, the water content was 20.22 wt %. Thus the chemical composition was proved to be $Ce(HPO_4)_2 \cdot 3.4H_2O$.

Determination of Distribution Coefficient

The distribution coefficients of uranium ion (K_d) for f- CeP in several acid solutions (HNO_3; HCl; $HClO_4$; H_2SO_4) were measured at different acid concentrations (0.01~1 M). The equilibration of f-CeP with uranium ion was carried out by a batchwise operation; 0.05 g of f-CeP was immersed in a sealable teflon tube or a glss ample with 10 cm^3 of 10^{-4} M uranium ion solution, which were prepared by adding $UO_2(NO_3)_2 \cdot 6H_2O$ in each acid solution, at a constant temperature ranging from 25 to 130 °C for 168 h, which was found to be sufficient for attaining equilibrium. After cooling to room temperature, the solid was filtered off, and the filtrate was analyzed for uranium ion concentration and pH. The distribution coefficient for the uranium ion was calculated using

$$K_d = (C_o - C)\, V / WC \quad (\mathrm{cm}^3/\mathrm{g}), \qquad \text{(Eq. 1)}$$

where C_o and C represent the initial and final concentration of uranium ion and V and W are volume (10 cm^3) and weight of f-CeP. The distribution coefficients of various nuclides were determined by the same batch method as previously reported (6).

Cation-Exchange Capacity

The cation-exchange capacity of f-CeP sample was determined by the batch method. A mixed aqueous solution (10 cm^3) with a different pH of 0.1 M NaCl-0.1 M NaOH was contacted with 0.1 g of f-CeP sample at 25 °C for 168 h. After the aqueous phase was separated by filtration, the concentration of Na^+ ions in the supernatant was measured by atomic absorption spectroscopy. The uptake amount of Na^+ ions was deduced from the concentration relative to the initial concentration in the solution.

Uptake of Uranium

The equilibration of f-CeP with uranium ion was done by a batchwise operation; 0.05 g of f-CeP was taken into a sealable teflon tube or a glass ample together with 10 cm^3 of 0.08~10 $x10^{-3}$ M uranyl nitrate solution (in 0.1 M HNO_3), and kept at a constant temperature ranging from 25 to 130 °C for 168 h. After cooling to room temperature the solid was recovered by filtration and dried at 60 °C. The filtrate was analyzed in order to determine the amount of uranium ions taken by f-CeP together with the concentration of cerium and phosphorus released from the sample. The solid residues were retained for X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron micrography (SEM) and chemical analyses.

Method of Analysis

The concentrations of uranium, cerium, and phosphorus ions in an aqueous solution were determined using a Seiko Denshi ICP emission spectrometer (model SPS 1500R), the concentration of sodium ions was determined by means of a Hitachi Z-6000 polarized Zeeman atomic absorption spectrophotometer. XRD powder patterns of the samples were recorded using a Rigaku RAD-X diffractometer with Ni-filtered CuKα radiation. A measurement of XPS was carried out using an ULVAC-Phi ESCA 5600Ci spectrometer on which the powdered sample was fixed on a piece of adhesive tape. SEM was performed with a Hitachi S-4100L electron microscope, operating at 15 kV.

RESULTS AND DISCUSSION

Ion-Exchange Capacity

Fibrous cerium(IV) hydrogenphosphate (f-CeP) is a kind of weakly acid type ion-exchanger, and its cation-exchange capacity is different according to different pH when measured in solution (5). Table I shows Na^+ uptake and XRD results of a solid phase f-CeP sample reacting at 25 °C. Use of differing pH is obtained by a mixed solution of 0.1 M NaCl - 0.1 M NaOH . Na^+ uptake increases simply along with increased pH, and no curvature can be seen. This shows that the f-CeP sample's sorption site is only of one kind, and while the f-CeP structural phosphorus atomic peripheral environment is almost uniform, we recognized that short-range order ^{31}P MAS NMR matched measurement results (7). Na^+ uptake in a pH 10.5 solution is 4.2 mmol/g. This value is lower than the theoretical cation-exchange capacity value of 5.1 mmol/g calculated from f-CeP sample structure ($Ce(HPO_4)_2 \cdot 3.\ 4H_2O$). But considering values greater than pH 10, a fair amount of phophorus is dissolved in water by hydrolysis (8), and the above measured value is considered to approximate the theoretical exchange capacity.

For the H^+-type f-CeP sample, *d*-value of the strongest XRD peak is 1.12 nm. At this value, Na^+-exchange occurs according to its increase concomitant with d value's increase. Maximum Na^+-uptake obtained sample *d*-value is 1.37 nm; indicating a 0.25 nm increase compared to the H^+-type f-CeP sample. To explain the crystalline f-CeP structure, the XRD pattern's CuKα 2θ = 8° can be seen to be strongly diffracted by different exchanged ions, and it can be considered that it takes a layer structure (2). Because of this, shown in Table I, Na^+-attached *d*-value increases, and we consider that increase of interlayer distance due to exchange interlayer H^+ of H^+-type f-CeP sample for Na^+ ions occured. On the other hand, XRD intensiry of the strongest peak decreases according to the increased pH, showing a change of f-CeP structure by hydrolysis.

Table I. Na^+-uptake as a function of pH and XRD measurement results for the solid phase reacted at 25 °C.

pH	Na^+-uptake (mmol/g)	XRD[1] *d*-value (nm)	R.I.[2]
2.60	0.86	1.29	100
3.68	1.58	1.29	85
6.17	2.40	1.27	95
8.21	3.94	1.29	83
9.28	4.06	1.33	75
10.29	4.15	1.33	75
10.51	4.21	1.37	70

[1] Measurement was carried out for the strongest XRD peak of f-CeP. [2] Relative intensity.

Chemical Stability (Acid Resistance)

We can believe that f-CeP has especially stable characteristics in a water solution where reducing agents and complexing agents do not exist. However, even if put in an acidic solution, Na^+ uptake of the sample's XRD strongest line diffraction strength ratio was seen to have a slight decreasing tendency by f-CeP (Table I). This evidence suggests that f-CeP has effects when put in water even if the water is slightly acid. For that, we examined various kinds of inorganic acids to test the f-CeP sample's chemical stability. From an initial concentration at 25 °C of from 0.01 to 1 M, four kinds of inorganic acid solutions were prepared in which an f-CeP sample was placed. Amounts of cerium and phosphorus released from f-CeP sample were measured and shown in Table II.

Table II. Chemical stability of f-CeP sample in several inorganic acid solutions.

Acid	Concn. (M)	Ce dissolved (mol/g)	Ce dissolved (wt %)	P dissolved (mol/g)	P dissolved (wt %)
HCl	0.01	0.00	0.0	0.37	7.2
	0.1	0.01	0.2	0.31	6.0
	0.5	0.03	1.1	0.31	6.0
	1.0	0.17	6.8	0.47	9.3
HNO_3	0.01	0.00	0.0	0.40	7.8
	0.1	0.01	0.2	0.34	6.6
	0.5	0.02	0.9	0.34	6.8
	1.0	0.06	2.4	0.41	8.0
$HClO_4$	0.01	0.00	0.0	0.33	6.4
	0.1	0.01	0.3	0.28	5.5
	0.5	0.02	0.7	0.27	5.2
	1.0	0.05	1.9	0.27	5.3
H_2SO_4	0.01	0.00	0.0	0.32	6.3
	0.1	0.03	1.2	0.41	8.1
	0.5	0.41	1.6	1.23	24.1
	1.0	1.37	5.4	2.44	48.0

Acid solution = 10 cm^3; f-CeP sample = 0.05 g; contact time = 168 h; temperature = 25 °C.

No matter which acid is considered, concentration of dissolved cerium and phosphorus amounts were increased. Excluding the case of sulfuric acid, we confirmed that cerium amounts remain below 0.1 M and in mild acid solutions, cerium shows almost no dissolution, while phosphorus amounts show comparatively larger amounts of from 6% to 8%. Tendency was seen for dissolved amounts of both components to increase in the following order: $HClO_4<HNO_3$, $HCl<H_2SO_4$. Also viewing relations of both components' proportions in solution, excepting sulfuric acid, we understood that in all cases cerium rates increased quickly with phosphorus rates, but in no case was the amount of cerium larger. Of the acids used, sulfuric acid has the high ability to complex forming with several kinds of metal and it is thought that cerium is drawn out from the structure of the f-CeP sample, forming a complex with SO_4^{2-} (8).

Distribution Coefficient

Uranium's distribution coefficients K_d were measured in the four inorganic acid solutions and their relations to pH are shown in Figure 1. Generally, by H^+ type ion-exchanger's properties, we know that from the low concentrate metal ion solution ($<10^{-3}$ M), metal ion exchange effects progress in an ideal case according to the following formula:

$$\log K_d = C - n \log [H^+], \qquad \text{(Eq. 2)}$$

where K_d is the uptake ion distribution coefficient, n is the valence of uptake ions, and C is a constant (9). That is to say, the second equation expresses the logarithmic distribution coefficient which, when plotted against pH, inclines with uptake ions' valence. A straight line relation, if it exists, shows that the uptake reaction is an ion exchange reaction.

Clearly in Figure 1, the logarithmic distribution coefficient of uranium and the slope when plotted against pH show approximately a +2 straight line relation which we recognize in this experiment's pH area as the uranium species in liquid - uranyl (UO_2^{2+}) (10): we can reason that Figure 1 exhibits the uranium uptake reaction between the liquid's UO_2^{2+} 1 mol and the f-CeP sample's H^+ 2 mol ion-exchange reaction. From inside the nitric acid solutions of different concentration, the measured f-CeP samples' various distribution coefficient measurement results are shown in Table III. In the solution for this experiment, ^{152}Eu and ^{241}Am exist as trivalent (11). These trivalent ions in solution of approximately pH 2 still showed a comparatively large distribution coefficient of 10^4 magnitude. Also, the distribution coefficient's logarithm shown in Table III, when plotted against HNO_3 concentration logarithm, gives a straight line correlation for both cases and valence numbers correspond, suggesting that both of these ions' uptake is an ion-exchange reaction. From Figure 1, Table III and results formerly reported (4), we surmised the f-CeP selection order of various kinds of ions according to Eq. 2 around pH 2 where Eq. 2 can be formulated. As a result, we can see that the decreasing order of character selection tendency is: Am^{3+} , UO_2^{2+} , Eu^{3+} > Cs^+ > Rb^+ >K^+, > Ba^{2+} > Sr^{2+} > Ca^{2+} > Na^+ > Co^{2+} > Mg^{2+}. Selection order of UO_2^{2+} is high, and even more than the other two

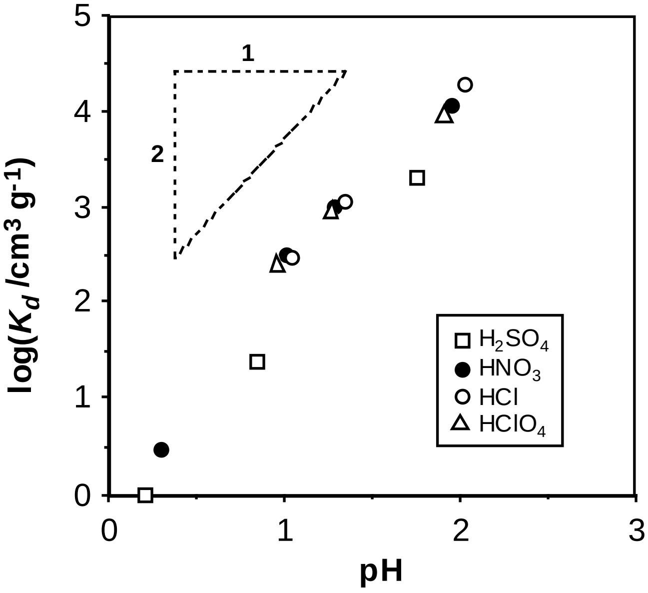

Fig. 1. Uranium ion log K_d as a function of pH.

trivalent ions, Am^{3+} and Eu^{3+} and their equivalents, we have found that f-CeP has peculiarly high selection character for UO_2^{2+}.

Table III. Various nuclides' K_d comparison for f-CeP sample at different HNO_3 concentrations.

$[HNO_3]$ (M)	K_d (cm^3/g) ^{22}Na	^{60}Co	^{85}Sr	^{137}Cs	^{152}Eu	^{241}Am
10^{-2}	46	25	3.9×10^2	4.9×10^3	1.3×10^4	3.8×10^4
10^{-1}	12	<1	3	5.3×10^2	1.7×10^2	82
1	2	<1	<1	44	<1	2

Solution = 7 cm^3/ initial concn. = 10 ppm (Am = 2.1×10^{-9} M); f-CeP sample = 0.07 g; contact time = 168 h; temperature = 25 °C.

Temperature Dependence of Distribution Coefficient

Reaction temperature and distribution coefficient of UO_2^{2+}, post reaction solution pH, and released concentrations of cerium and phosphorus are arranged in Table IV. Cerium concentration is extremely low, though some relation to temperature change is apparent. The distribution coefficient is independent of temperature to 65 °C, but from 80 °C to higher temperatures, phosphorus concentration increases apace. That is to say that the distribution coefficient decreases from 85 °C to 105 °C while phosphorus concentration increases: the distribution coefficient increased with temperature to 115 °C, and phosphorus concentration

Table IV. Distribution coefficient temperature dependence of uranyl ion on f-CeP sample and cerium and phosphorus concentrations released from the f-CeP sample.

Temp. (°C)	pH	K_d (cm^3/g)	Concn. of released Ce;P Ce (M)	P (M)
25	1.07	407	4.2×10^{-5}	1.4×10^{-3}
45	1.04	403	5.6×10^{-5}	1.6×10^{-3}
65	1.06	413	8.2×10^{-5}	1.8×10^{-3}
85	1.06	369	2.1×10^{-4}	2.7×10^{-3}
105	1.05	298	1.1×10^{-5}	7.4×10^{-3}
115	1.06	382	9.4×10^{-5}	3.3×10^{-3}
130	0.89	63	1.1×10^{-5}	9.8×10^{-3}

rapidly increases thereafter. The distribution coefficient again rapidly decreases to 130 °C and phosphorus concentration jumps markedly. Shown in this way, the completely opposite reaction of the distribution coefficient and liquid phosphorus concentration during temperature change is suggestive that the phosphorous ions in solution were involved in some reaction for which UO_2^{2+} uptake was also participant. To elucidate these points clearly, we performed the following experiment

X-Ray Diffraction Patterns of Post-Reaction Solids

Post reaction solids were measured by XRD, and initial concentration of UO_2^{2+} was increased 100 times while the distribution coefficient and uptake amount in the reaction solution were each measured together at the different temperatures of 25, 55, 105, and 130 °C. Post reaction solid XRD patterns, the UO_2^{2+} uptake amount, liquid pH, dissolved cerium and phosphorus concentration, and *d*-values of the XRD strongest peak and diffraction strength change patterns are all shown in Figure 2 and Table V.

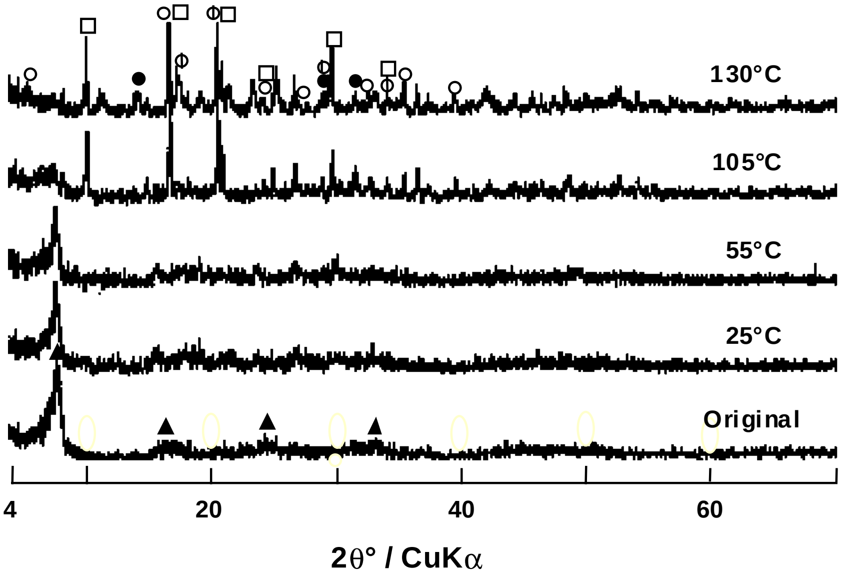

Fig. 2. X-ray diffraction patterns of the products reacted at different temperatures.
Phase: ▲ ,f-CeP; □,Uranyl phosphates ($UO_2HPO_4\cdot 2H_2O$; $UO_2HPO_4\cdot H_2O$; $H_3OUO_2PO_4\cdot 3\text{-}xH_2O$); Φ,$CeP_2O_7$.● ,$Ce(PO_4)$; ○ ,$CeH_2P_2O_8\cdot 1.33H_2O$;

As shown in Figure 2, XRD analysis of f-CeP in the post reaction solid shows the strongest peak at low reaction temperature and shows decreasing strength with higher temperatures: at 105 °C a weak peak of f-CeP is recognized, but at 130 °C, it disappear as the f-CeP structure completely collapses. On the other hand, at 105°C, several kinds of uranyl hydrogenphosphate ($UO_2HPO_4\cdot 2H_2O$; $UO_2HPO_4\cdot H_2O$; $H_3OUO_2PO_4\cdot 3xH_2O$) and furthermore, at 130°C, several kinds of cerium phosphate ($CePO_4$; $CeH_2P_2O_8\cdot 1.33H_2O$; CeP_2O_7) were confirmed. Also, according to high reaction temperatures, uptake increases simply. However, pH of the liquid and the strongest line of relative strength in the XRD decrease inversely (Table V). The *d*-value of the XRD strongest line of the post reaction f-CeP sample showed no change. We recognized that uptake and pH and XRD strongest line relative strength show a strong negative linear correlation with one another (r = 0.999; 0.963). From those results, the sorption of UO_2^{2+} on f-CeP in acidic solution can be seen not just as a simple ion exchange mechanism for the f-CeP interlayer, but that formation of uranyl hydrogenphosphate, which we will write more about shortly, was a complex reaction mechanism that also clearly participated as an uptake mechanism.

Table V. Temperature dependence of uranium uptake on f-CeP sample.

Temp. (°C)	U-uptake (mmol/g)	Concn. of released Ce;P			XRD[1]	
		pH	Ce (M)	P (M)	*d*-value (nm)	R.I.[2]
Original	-	-	-	-	1.16	100
25	0.399	1.77	1.3×10^{-5}	2.0×10^{-4}	1.16	80
55	0.456	1.70	1.2×10^{-5}	4.2×10^{-4}	1.16	73
105	0.509	1.64	1.3×10^{-5}	1.4×10^{-3}	1.16	27
130	0.558	1.59	1.1×10^{-5}	6.2×10^{-3}	-	0

Solution = 10 cm^3/ initial concn. = 0.01 M uranyl nitrate; f-CeP sample = 0.1 g; contact time = 168 h. [1] Measurement was carried out for the strongest XRD peak. [2] Relative intensity.

Reaction Conditions and Solid Mineral Elements

In the previous section, we described use of a comparatively high concentration (0.01 M) UO_2^{2+} solution for uptake test results. In this section, this research object is examination of comparatively low concentration solution uptake character. In previous sections, the cases for sorption mechanism have no essentially different uranium and cerium phosphates, and formation conditions proceed in a delicate manner during a reaction where there are very many known compounds from an uncrystallized nature to a crystallized character (5,12). Understanding these reaction conditions and their relation to compound formation is of practical importance. Therefore fixing the ratio of liquid to f-CeP sample at 200 cm^3/g, and UO_2^{2+} initial concentration, and reaction temperature respectively at from 0.08 to 2.1 mM, and from 25 °C to 130 °C range, we can observe changed system reaction conditions and the resultant post reaction solid material. Those measured results are shown in Table VI. In cases where the reaction temperature was below 80 °C to above 115 °C, post reaction solid mineral elements showed great difference. That is to say, below 80 °C, solid mineral composition was dominated by f-CeP. In this temperature region, XRD of f-CeP we did not see a complete change in strongest line *d*-value - both of which were about 1.1 nm; UO_2^{2+} concentration and reaction temperature increases bring decreases in diffraction strength. On the other hand, at reaction temperatures greater than 115 °C, UO_2^{2+} concentration disappears in both cases while from f-CeP, three new compounds: Vyacheslavite (Vy; $UPO_4OH·2H_2O$); cerium phosphate (Cp; $CePO_4$); and phosphorous oxide (P; P_2O_5), are formed. At high temperatures and lower concentrations, Vy and P show high XRD diffraction strength, and Cp shows high diffraction strength, conversely, in a high temperature/high concentration environment. Clearly, from comparison of results in Figure 2, UO_2^{2+} initial concentration differences affect uranium phosphate formation, as we found that at comparatively low UO_2^{2+} initial concentration, Vy is formed.

Table VI. Relation between the initial UO_2^{2+} concentration of the solution and the constituent minerals of the solid phase reacted at different temperatures.

UO_2^{2+} concn. (mM)	U/P molar ratio	Reaction temp. / phase				
		25°C	50°C	80°C	115°C	130°C
0.08	$4.0x10^{-4}$	f-Cp (100)	f-Cp (93)	f-Cp (80)	-	-
0.17	$8.5x10^{-4}$	-	-	-	Vy; Cp; P (58)(29)(51)	Vy; Cp; P (100)(71)(100)
0.25	$1.3x10^{-3}$	f-Cp (83)	-	f-Cp (80)	-	-
0.34	$1.7x10^{-3}$	-	-	-	Vy; Cp; P (58)(57)(62)	-
0.67	$3.3x10^{-3}$	f-Cp (83)	-	f-Cp (76)	-	Vy; Cp; P (61)(100)(59)
1.26	$6.3x10^{-3}$	-	-	-	Vy; Cp; P (35)(71)(28)	-
2.10	$1.1x10^{-2}$	f-Cp (74)	f-Cp (65)	f-Cp (65)	-	Vy; Cp; P (35)(100)(26)

Solution = 10 cm^3/ initial concn. = $0.08\sim2.1x10^{-3}$ M (in 0.1 M HNO_3); f-CeP sample = 0.05 g; contact time = 168 h. Phase: f-Cp, fibrous cerium(IV) hydrogenphosphate ($Ce(HPO_4)_2·nH_2O$); Vy, Vyacheslavite ($U(PO_4)(OH)·2H_2O$; Cp, Cerium phosphate ($CePO_4$); P, Phosphorus oxide (P_2O_5). Numerical values in parentheses show the relative XRD peak intensities of corresponding phases.

Uptake Isotherm

According to XRD measurement results of post reaction solids (Table VI), f-CeP complex diffraction shows no reaction at temperatures below 80 °C, and f-CeP samples' comparative UO_2^{2+} sorption isotherms are exhibited for each temperature in Figure 3. For this experiment's UO_2^{2+} concentration scope the sorption amount has a slight temperature dependent character, and the uptake amount to logarithmic equilibrium concentration is in one straight line relation (r = 0.994). These results are for f-CeP samples below 80 °C against UO_2^{2+} uptake results, and by the following Freundlich sorption formula we can show it simply as:

$log\ A = log\ K + 1/n\ log\ C$ (mol/g), (Eq. 3)

here, A (mol/g), C (mol/dm^3) are each UO_2^{2+} uptake amount and equilibrium concentration. Freundlich constant is defined by n, K which calculated from the slope and intercept of the straight line in Figure 3.

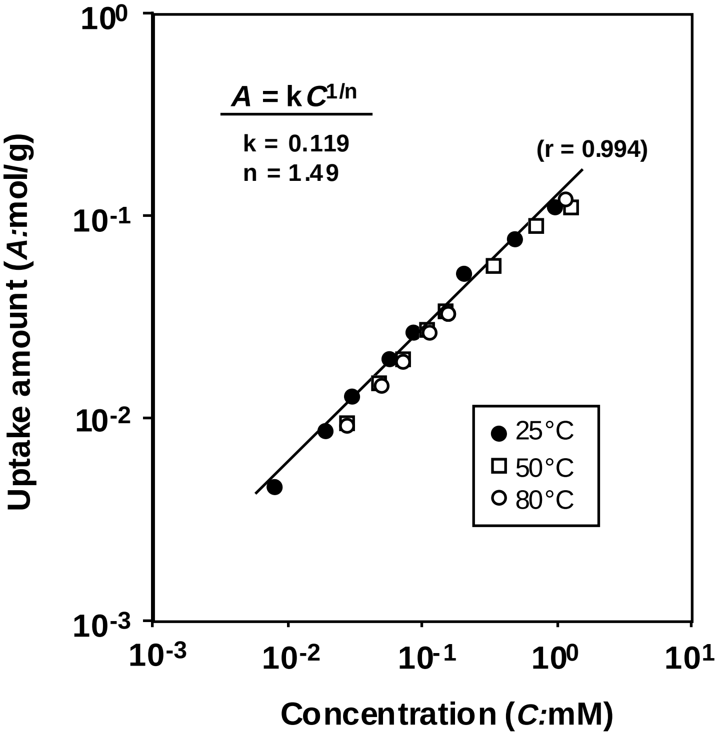

Fig. 3. Freundlich plots for UO_2^{2+} uptake on f-CeP. Conditions are the same as those in Table VI.

XPS Spectra of Ce 3d

We observed both uptake reaction and $CePO_4$ formation under hydrothermal conditions and in the sample (Figure 2, Table VI). In this high temperature uptake process, we found that reduction of a part of tetravalent cerium to trivalent state had occurred. This cannot be confirmed from XRD measurements, but in this manner, cerium's reduction in a low temperature uptake process can also occur. To elucidate this point, a post uptake reaction f-CeP sample was measured by XPS. XPS is a powerful technique for studying a mixed-valence system; especially for tetravalent-trivalent cerium spectographic forms, we can make distinctions. Measuring the same sample in Figure 2, Ce 3d XPS spectograph is shown in Figure 4.

The original f-CeP (U free) sample shows, cerium of tetravalent state and contains chemical combinations in a characteristic pattern. That is to say that each spin-orbit component according to different final states $4f^0$ and $4f^1$ is split (13). The post reaction sample varies according to high temperature reaction - for peak corresponding $4\ f^1$ is uniformly larger, but conversely, $4\ f^0$ peak is smaller, suggesting that this tetravalent cerium has been partially reduced to a trivalent state. Cerium in the f-CeP structure shows existence of a strong reducing agent to reduce tetravalent to trivalent reduction (8). However, suitably strong reducing agents are not used in this study. Especially, UO_2^{2+} uptake still clearly reduces the cerium in a 25 °C low temperature reaction sample. Focusing attention on the f-CeP sample in 100 - 175 °C distilled water and comparing the processed sample, XPS spectography shows remarkable differences from the fact that none can be seen above (7). In the cerium reduction, that UO_2^{2+} does not exist is suggestive of a connection.

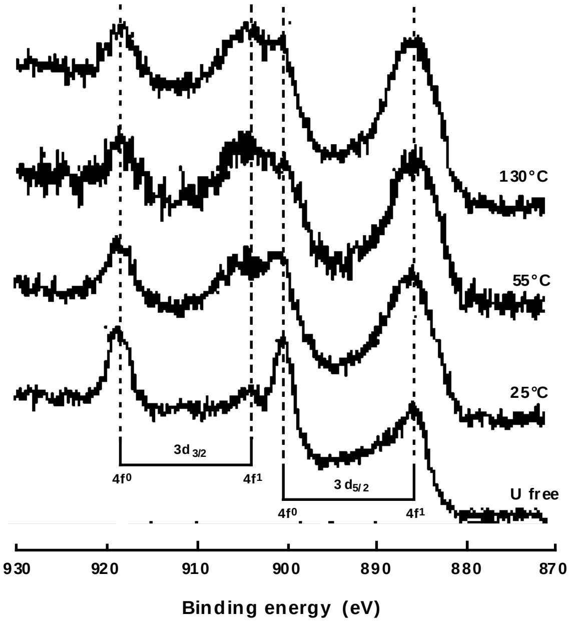

Fig. 4. X-ray photoelectron spectra of Ce 3d for f-CeP samples reacted at various temperatures.

Uptake Mechanism

In our uptake sample at comparatively low temperatures (80 °C), both f-CeP and UO_2^{2+} XRD strongest line *d*-values did not appear to change, and the uptake amount increases with XRD strength of a corresponding peak decrease. Also, in cases where the reaction temperature was high, several kinds of uranium phosphate and cerium phosphate formations were confirmed. From these results, f-CeP- UO_2^{2+} sorption reaction when immersed in an acidic solution is that along with the f-CeP structure collapse, the combination of UO_2^{2+} and phospate ions are released to the liquid which in turn form uranium phosphate in one possible formation mechanism. However, the above results are both taken from post equilibrium samples, and do not explain early mechanisms of the reaction that we seek to explain below. A *d*-value change can be seen when f-CeP inserts between alkali and alkali earth metal ions first, then large alkyl ammonium ions encircle it for an even ion exchange by intercalation (7). From this solution UO_2^{2+}, in an uptake reaction, according to the ion exchange reaction shown below the possibility is high that UO_2^{2+} was extracted. Results

$$Ce(HPO_4)_2 \cdot 3.4H_2O + UO_2^{2+} \longrightarrow Ce((UO_2)_{0.5}PO_4)_2 \cdot 3.4H_2O + 2H^+ \qquad \text{(Eq. 4)}$$

from Figure 1 hold support for this progressive reaction. In this step, one might guess by Figure 4 that inside of the f-CeP structure that cerium was not reduced. But, intercalating UO_2^{2+} between the intercalated f-CeP complex $\{Ce((UO_2)_{0.5}PO_4)_2 \cdot 3.4H_2O\}$, because it is extremely chemically unstable, it is likely that the more stable uranium phosphate will re-crystallize. This recrystallization occurs readily at normal temperatures, so in XRD measurement of post reaction solids, the increased *d*-value of f-CeP was not evident. Also, after recrystallization with emerging with a phosphate group, the structure increased *d*-value of f-CeP complex was not observed. Furthermore, because it is recrystallized along with a phosphate group result, the structure is partially collapsed, and that diffraction strength can be thought to have decreased. Similar irreversible phosphate forming reaction for Sc^{3+}-sorption on f-CeP was found out (14). In its original form, with UO_2^{2+} present in hydrothermal environment, the above reactions are accelerated and due to this f-CeP structure is completely corrupted and several kinds of uranium phosphates and cerium phosphates are probably formed. At somewhat lower temperatures of about 80 °C, UO_2^{2+} in the XRD pattern of a reacted sample, uranium phosphate formations distinctly showing diffracted phosphate could not be confirmed. But, (Figure 2, Table VI), in diffraction angles $2\theta = 15°$ to $35°$, these semi-crystallized bodies probably show some weak diffracted phosphate. So in the latter, recrystallized process, cerium reduction can be thought to have happened. Through that mechanism and from Figure 4 are observed reduction conditions and whether the cerium is from the internal structure or not is presently unclear. Clearer examination of these latter points necessitates further study.

SUMMARY

Examining an acidic solution containing f-CeP yielded the following results on UO_2^{2+} sorption activity and lead to several conclusions. Ions of UO_2^{2+} from f-CeP, in their uptake reactions are assumed to behave in the following manner. Ion exchange from liquid to the solid is a comparatively rapid extractive reaction which proceeds to a comparatively slow uranium phosphate crystallization reaction, the latter recrystallization process partially reduces the cerium (IV) to cerium (III) that occurs with the collapse of the complex. These reactions can progress even at normal temperatures, and UO_2^{2+} concentration progress remains both high and rapidly increasing in tandem with increased reaction temperature.

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