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Extraction and Separation of Neptunium(IV), Plutonium(IV) and Americium(III) by Bidentate Organophosphorus Extractant

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This paper summarized the extraction and separation of Np(IV), Pu(IV) and Am(III) with dihexyl-N,N-diethyl carbamyl methylene phosphonate (DHDECMP)-diethyl benzene (DEB) in nitric acid medium.

The distribution ratio of Np(IV), Pu(IV) and Am(III) was studied as a function of a number of parameters such as concentration of nitric acid, salting-out reagents in the aqueous phase, contact time, and temperature. Stripping and separation of Np(IV), Pu(IV) and Am(III) from pregnant organic phase were studied. The suitable stripping and separation conditions were obtained. The enthalpy changes ΔH_{Np}, ΔH_{Pu} and ΔH_{Am} associated with their extraction process were estimated individually. The composition of extracted complex of Np(IV), Pu(IV) and Am(III) was determined.

Effect of Contact Time and Temperature. The experiment shows that equilibrium for all extracted species is reached in approximately 30 seconds of contact. The distribution ratios of Np(IV), Pu(IV) and Am(III) decrease with increase of temperature, while the effect of temperature on distribution ratio(D) of nitric acid is negligible. Consequently, the extraction process of the metallic ions is considered as an exothermic and it is not desired to increase temperature during extraction. In the plot of logD *vs.* 1/T(K) the straight lines were obtained. According to the slope of line and the Van't Hoff equation:

$$\Delta \lg D/\Delta(1/T) = -\Delta H/2.303R,$$

the enthalpy changes ΔH associated with extraction process were estimated as follows:

$\Delta H_{Np} \simeq -3.7$Kcal/Mol

$\Delta H_{Pu} \simeq -7.9$Kcal/Mol

$\Delta H_{Am} \simeq -7.6$Kcal/Mol

Effect of Concentration of Nitric Acid. The effect of nitric acid concentration in aqueous phase on extraction of trivalent and tetravalent actinides was investigated. The distribution ratios of Pu(IV), Np(IV) and Am(III) increase with concentration of nitric acid, so it is capable of extracting these actinides in higher concentration of HNO_3. The data on the distribution ratios of these elements in 3 *M* HNO_3 medium are as follows:

$D_{Np(IV)} = 221$

$D_{Pu(IV)} = 101$

$D_{Am(III)} = 2.2$

Effect of Concentration of theExtractant. The distribution ratios(D) of these elements increase with DHDECMP concentration. The logarithmic plots of D_{Np}, D_{Pu} and D_{Am} *versus* DHDECMP concentration are straight lines with slopes of 2.0, 1.9 and 2.9 respectively. Therefore, the extraction reaction for Np(IV), Pu(IV) and Am(III) with DHDECMP can be expressed as:

$$Np^{4+}_{aq} + 4NO^-_{3\,aq} + 2DHDECMP_{org} \rightleftharpoons Np(NO_3)_4 \cdot 2DHDECMP_{org}$$

$$Pu^{4+}_{aq} + 4NO^-_{3\,aq} + 2DHDECMP_{org} \rightleftharpoons Pu(NO_3)_4 \cdot 2DHDECMP_{org}$$

$$Am^{3+}_{aq} + 3NO^-_{3\,aq} + 3DHDECMP_{org} \rightleftharpoons Am(NO_3)_3 \cdot 3DHDECMP_{org}$$

Effect of Concentration of Salting-out Reagent. The experiment shows that the distribution ratios(D) of trivalent and tetravalent actinides increase obviously with concentration of $Al(NO_3)_3$ and $NaNO_3$ in aqueous phase. When the concentration of $Al(NO_3)_3$ is equal to 1.5 *M* in 3 *M* HNO_3 aqueous phase, the distribution ratios for Np(IV) and Am(III) are 1.15×10^3 and 10 respectively.

Back-Extraction. The stripping condition of Np, Pu and Am from the organic phase were investigated. It is shown that the Am(III) can be recovered quantitatively after twice stripping with 0.01 *M* HNO_3. With (0.05–0.2 *M*) HNO_3–0.05 *M* $H_2C_2O_4$ for Pu(IV), Np(IV) to be stripped or with (0.05–0.2 *M*) HNO_3–0.05 *M* $Fe(NH_2SO_3)_2$ for Pu(IV) to be stripped, the back-extraction percentage is more than 97 after twice contacts.

Separation of Americium from Neptunium or Plutonium by Back-Extraction. Experiments show that the Am(III) was quantitatively stripped from the organic phase with 0.05–0.2 M HNO_3, while most of the Np(IV) and Pu(IV) is remained in the organic phase (Table I). From Table I it can be seen that the separation factor of Am and Np or Am and Pu is more than 50. Consequently, this method may be applied to separating Am from Pu(IV) and Np(IV).

TABLE I. Stripping Data for Am, Np and Pu.[a]

Stripping solution		0.05 M HNO_3	0.2 M HNO_3
Back-Extraction Percentage	Am	74	71
	Pu	1.0	1.3
	Np	1.2	1.2
Separation factor	Am/Pu	74	54
	Am/Np	61	59

[a] Organic phase: 30 Vol% DHDECMP-DEB pre-equilibrated with 3 M HNO_3 solution containing ^{239}Np, ^{239}Pu and ^{241}Am tracer. Temp.: 30 °C ± 1 °C. Contact time: 5 min.

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Investigation of Transport Processes of Actinides by Use of an Analytical Ultracentrifuge for Optimizing the Purex-Process

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Transport data of Actinides in relevant solutions are urgently needed to optimize the electrochemical techniques introduced quite recently into the purex process. Therefore an Analytical Ultracentrifuge has been used for the determination of diffusion coefficients of $Th(NO_3)_4$, $Pu(NO_3)_4$, $Np(NO_3)_4$, NpO_2NO_3, $NpO_2(NO_3)_2$, $PuO_2(NO_3)_2$ and $UO_2(NO_3)_2$ in aqueous HNO_3 solutions and partially in TBP (30%)-Dodecane-mixtures at 25 °C in the concentration range from 10^{-2} M to 10^{-1} M, applying Schlieren-, absorptions- and Rayleigh-Interference optics combined with laser techniques. In the $Th(NO_3)_4$–HNO_3–H_2O system which stood for the tetravalent actinides, it was shown that the apparent diffusion coefficient ($D_{app} = 5{,}8 \times 10^{-6}$ cm^2 s^{-1}) equalled the main diffusion coefficient ($D_{main} = 6{,}3 \times 10^{-6}$ cm^2 s^{-1}), proving that the cross term could be neglected. An analytical ultracentrifuge can also be used for investigating and determining the kinetics and distributions of extraction processes.

Moreover diffusion coefficients of $UO_2(NO_3)_2 \cdot 2TBP$ in pure dodecane, pure TBP and TBP-dodecane mixtures (30%/70%) were determined within the concentration range from 5×10^{-3} M to 5×10^{-2} M. The obtained results plotted against concentration give straight lines.

In pure dodecane the diffusion coefficient of $UO_2(NO_3)_2 \cdot 2TBP$ was found to be 3×10^{-6} cm^2 s^{-1}, this value decreasing for 10% by adding 30% TBP.

The diffusion coefficients were compared with electrochemical transport data, obtained earlier from conductance and transference measurements, also with limiting ionic conductances of Am^{3+} and Cm^{3+}, found quite recently.

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Lanthanide Orthophosphate Ceramics for the Disposal of Actinide-Contaminated Nuclear Wastes[†]

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Since the half lives of some of the hazardous, α-active actinide isotopes contained in nuclear wastes are relatively long, severe stability requirements are imposed on the materials that must function as primary containment media in a permanent actinide waste-disposal system. Such materials must maintain a high degree of physical and chemical integrity under a variety of potentially hostile geological environments, including possible hydrothermal conditions. Investigations by McCarthy *et al.* [1] of the stability of borosilicate glasses under hydrothermal conditions led to reservations regarding their suitability as primary hosts for the disposal of nuclear wastes during the desired 10^4 to 10^5 year immobilization period. These concerns, in turn, resulted in renewed interest in alternative materials for the disposal of radioactive wastes.

One approach employed in selecting alternatives to borosilicate glass consisted of a process of examining various mineral systems whose long-term stability was well established geologically. An approach of this type led to the SYNROC concept of Ringwood [2] and also to the decision to investigate the lanthanide orthophosphates that are analogs of the uranium and thorium bearing mineral monazite [3] (La, Ce, $\cdots PO_4$). Geological evidence indicates that monazites have survived various rock-forming and

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