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	Am	74	71
Percentage	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.

E22

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.

E23

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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[†] Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

metamorphic processes in the earth's crust for ~2 X 10^9 years—a time span that exceeds the required stability period for an actinide waste form by a factor of 10^5 to 10^4.

A program consisting of both fundamental and applied studies of the characteristics of lanthanide orthophosphates is currently under way for the purpose of evaluating these materials as primary nuclear waste forms. The investigations carried out in this program range from spectroscopic (EPR, optical, X-ray, *etc.*) studies of doped synthetic single crystals to practical investigations of the formation, sintering, and leaching properties of prototype lanthanide orthophosphate polycrystalline ceramics.

In order to study the solid state properties of mixed lanthanide-actinide orthophosphates, single crystals of lanthanide hosts doped with Cm, Am, Pu, Np, and U were grown using a flux technique. Additionally, since most actual nuclear wastes contain elements other than the actinides, orthophosphate crystals doped with iron group (and other) impurities were prepared and studied using a number of techniques. These fundamental investigations of the properties of mixed orthophosphates have yielded information on the coordination chemistry, valence states, structure, and solid state chemical properties of the actinides as well as such diverse impurity ions as Pb^{3+} and Zr^{3+}. A typical result from this phase of the effort is given in Fig. 1 where the EPR spectra of $^{243}Cm^{3+}$ and $^{244}Cm^{3+}$ in a single crystal of $LuPO_4$ are shown [4].

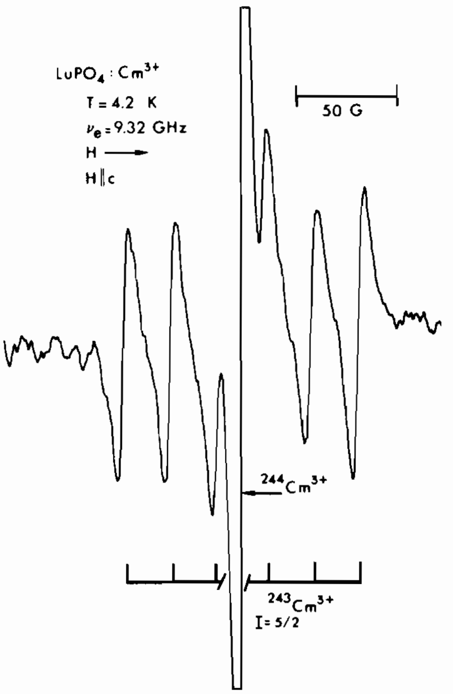

Fig. 1. EPR spectra of trivalent curium 243 and curium 244 impurities in a synthetic crystal of $LuPO_4$. The spectrum was taken at a sample temperature of 4.2 K.

One of the most important criteria in establishing the relative performance of a radioactive waste form is its ability to resist dissolution and corrosion in aqueous media. Accordingly, the 'leaching' characteristics of lanthanide orthophosphate nuclear waste forms are being emphasized in the ongoing investigations. An example of some of the results obtained in this phase of the lanthanide orthophosphate research program is illustrated in Fig. 2. Here a conductivity cell was used to determine the ionic release rate into distilled water for $LaPO_4$ and for borosilicate glass (Frit 21) containing simulated Savannah River Plant wastes and for SYNROC B which did not contain simulated nuclear waste. These results show that after ~100 h at 90 °C, the ionic release rate of the waste-loaded polycrystalline $LaPO_4$ ceramic is ~1000 times lower than that of waste-loaded borosilicate glass and is ~10 times lower than the SYNROC sample that does not contain any nuclear waste simulant [5].

The results of previous and ongoing basic investigations of the solid state properties of lanthanide orthophosphates containing actinide and other impurities will be reviewed along with the current status of the applied studies of complex simulated waste forms.

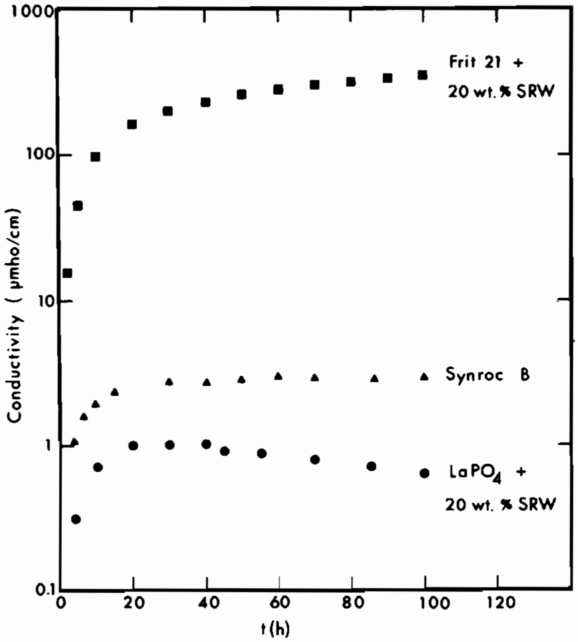

Fig. 2. The conductivity versus time of a distilled water leachant is shown for synthetic monazite, SYNROC B, and borosilicate glass. Both the monazite and glass samples contained simulated waste while the SYNROC B specimen did not. The ionic release rate for the borosilicate glass waste form is clearly much higher than for the lanthanum phosphate (monazite) specimen.

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E24

Pyrochemical Separation of Lanthanide and Actinide Metals[†]

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A highly efficient group separation of lanthanide and actinide metals can be effected by molten salt extraction of the lanthanide fraction(s) from a solution of actinide and lanthanide metals dissolved in molten copper–magnesium alloy. The extraction salt used for this separation is 50 m/o $MgCl_2$, 30 m/o NaCl and 20 m/o KCl, and the composition of the solvent metal alloy is approximately 20 to 30 mass-percent magnesium in copper. At 800 °C, the distribution coefficient (K_d) for +3 lanthanide chlorides varies from 150 to 70 while the distribution coefficient for the +3 actinides varies from 4.5 to 6.0. At 20 mass percent magnesium, the ratio of K_d is about 30 between Cerium (150) and Americium (4.5). With these large differences in K_d, a simple batch extraction can be used to separate Cerium from Americium. The lanthanide elements are extracted into the molten salt phase as the +3 chloride salt and the equivalent mass of magnesium metal is deposited in the immiscible metal alloy phase. After separation of phases which can be performed mechanically after cooling, or by decantation at elevated temperature, the pure lanthanide metal can be recovered from the salt phase by reduction with calcium metal at 800 °C. The lanthanide metal is formed as a high-density-powder bottom-phase, which can be converted to a molten liquid by the addition of zinc. After retorting, the pure lanthanide metals are recovered as metallic sponge.

[†] This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

E25

Actinide Partitioning by HDEHP Solvent Extraction. A Verification of the Process Scheme by Countercurrent Experiments in Hot Cells

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Three HAW partitioning processes have been selected and investigated on a laboratory scale at the JRC-Ispra Establishment (CEC). The purpose of these processes was to demonstrate the chemical feasibility of the actinide separation from HAW in order to reduce the potential long term hazard of vitrified HAW.

Two of these processes (HDEHP and TBP processes) are based on liquid–liquid extraction of actinides from original and concentrated HAW solutions, respectively.

To verify on a larger fully active scale these two process flow sheets, a fruitful collaboration was established between the JRC (Ispra Establishment) and the CEA (CEN-Fontenay aux Roses, France).

For this purpose, on the basis of indications resulting from the previous laboratory investigations at the JRC, continuous countercurrent experiments with mixer–settler batteries were performed in the hot cells of CENFAR laboratories. As a feed solution a fully active HAW raffinate prepared by treatment of high burnt UO_2 fuel specimens (33 GWd/tU) was used.

The present paper deals with the verification of option 1 of the HDEHP process flow sheet and illustrates related experimental results. By means of M–S batteries continuous countercurrent operating conditions were thus applied to the most relevant steps of the HDEHP 1 process scheme, namely:

actinide (U, Pu, Np, Am, Cm) extraction from HAW;

trivalent actinides (Am, Cm) back-extraction from loaded HDEHP, with the aim of verifying the performances and hydraulic behaviour of these two specific process steps under dynamic conditions.

For the remaining process steps (RE and Pu back-extractions, exhausted solvent clean-up) experiments were carried out batch wise.

The reduction of the HAW acidity (denitration) was successfully operated on fully active and rather large (42 litres of HAW) scale according to the experimental conditions indicated by additional exploratory experiments, performed at Ispra.