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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.

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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.

Data on the HAW denitration will be presented with particular reference to the problem of the precipitation of actinides during this process.

A preliminary indication is also given of the areas of the HDEHP 1 process scheme where further experimental investigations are needed.

E26

Recovery of Grams of Americium from Scraps and Analytical Residues by Means of an Extraction Chromatographic Process Using Dihexyl N,N-Diethylcarbamylmethylene Phosphonate (DHDECMP)

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The preparation of americium compounds as well as analytical procedures lead to solid or liquid wastes from which americium must be removed and purified in order to get the oxide to be recycled. The experimental procedure for such a removal depends essentially upon the dissolution medium. Although there is a general tendency for nitric acid media, it is sometimes necessary to treat hydrochloric solutions like those coming from the analytical procedures. In most cases, these solutions are highly acid (from 1 N to 8 N or 9 N) and contain numerous cationic species (Ca, Mg, Al, Na, Li, Fe, Ni, Cr, ...) at great concentrations (10 g/l to 100 g/l). Uranium and plutonium are also present at concentrations up to 100 g/l while the americium concentration is rarely higher than 1 g/l.

If the recovery of uranium and plutonium presents no special difficulty (Purex process, anionic resins, *etc.*) the americium recovery, due to the high acidity of the solution, is a stiffer problem. However some studies [1] have demonstrated that it can be solved using bidentate extractants like the DHDECMP in the case of nitric acid media. Since our waste contains various chloride species, we have studied the extraction of americium from hydrochloric solutions. Even though the extractant appears to be slightly soluble in hydrochloric acid, we successfully removed 4 grams of pure americium from 3.5 liters of liquid waste. The present work describes our main results and the various problems we were faced with.

Americium Extraction in Hydrochloric Acid. The distribution coefficient of americium in the hydrochloric medium was studied and the results were compared with those obtained with nitric acid. One will first notice that at very low HCl concentration the coefficient decreases as the acidity increases. The curve presents a minimum around 0.8 N. This result is very important for practical purposes. At high acidity the coefficient increases but remains smaller than with nitric acid.

Americium Extraction from a Complex Composition Solution. Even though the relatively high solubility of HCl in DHDECMP at high acidities does not give great confidence, we carried on an extraction experiment from a complex solution whose composition is as follows:

Am = 1.16 g/l
Acidity = 0.8 N
Salinity $\simeq$ 100 g/l (mainly Ca^{++}, Li^+, Na^+)
Minor constituants: U, Fe, Ni, Cr at a few g/l
Organic species: TBP, TOPO at unknown but small concentrations

(This solution came from a Purex cycle and has been concentrated by evaporation).

The distribution coefficient of americium between this solution and DHDECMP 0.8 N previously equilibrated with HCl 8.5 N was $D_{Am} = 55$. This results indicates a very strong salting-out effect due to the high salinity of the solution. It gives us confidence to undertake a direct recovery of americium using column chromatography. Therefore we first ran a small scale experiment using a 1.1 cm diameter column filled with 1.5 g of DHDECMP fixed on 3 g of Gas Chrom Q. Through this column we percolated 10 ml of HCl 8.5 N and then a sufficient volume of the americium solution to reach the saturation. (This run was to calibrate a large scale experiment).

The elution step was performed with HCl 0.5 N. The americium balance is as follows:

Americium introduced: 87 mg (±10%)
Americium unfixed: 11 mg (±10%)
Americium recovered during the elution: 70 mg (±10%)

The americium was measured by alpha-spectrometry. Considering the precision of the analysis, the yield appears to be quite good and leads us to run a large scale recovery.

Large Scale Recovery of Americium Using DHDECMP. In order to remove 4 grams of americium contained in 3.5 liters of liquid waste (the same solution was used in the small scale experiment) we filled a column 50 cm high and 5 cm diameter with a 30% DHDECMP–Gas Chrom Q mixture. Then we equilibrated passing through the column a HCl 8.5 N solution under high pressure. Unfortunately, the DHDECMP did not stack on the support but fell down. This problem comes certainly from the solubility of HCl in DHDECMP. To overcome this problem we decided to refill the column with only a 15% DHDECMP–Gas Chrom Q mixture and to stop using a