The challenging separation of adjacent Am(III) and Cm(III)

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INTRODUCTION

The production of nuclear waste, in particular, the spent nuclear fuel, that employs a too long period of time to be disposed of. In recent years many efforts have been made to develop innovative nuclear Fuel Cycles to separate TRU elements from SNF in order to reuse them in new fuel and reduce long-term radiotoxicity and heat load of nuclear waste. It is evident that it cannot attend such a long time to dispose of nuclear waste, and so it is necessary to find a suitable solution. To date, the only process at an industrial level to approach the closure of the cycle is the PUREX process, through which it is possible to extract U and Pu from the spent fuel, thus reducing the volume of radioactive inventory by recycling a portion.

1. IMPROVEMENT OF Am/Cm SELECTIVITY

In the AmSel process, the separation of Am(III) from Cm(III) is achieved by coextraction of trivalent lanthanides and actinides by TODGA and the subsequent selective stripping of Am(III) by the water-soluble SO4-Ph-PBTz [1]. The first attempt was to introduce in the organic solvent 2,6-Bis(2-ethylhexyl)-1H,1,2,3-triazol-4-ylpyridine (PTEH), a lipophilic ligand showing a preference for Cm [2]. Some liquid-liquid extraction tests were performed with [Eur(III)], Am(III) and Cm(III), representative of Lanthanides and Actinides families, respectively, and exploring:
1. different PTEH concentrations in kerosene/1-octanol 90/10 vol.%(organic phase);
2. different concentrations of nitric acid and SO4-Ph-PBTz in the aqueous phase, with the addition in some cases of ammonium nitrate.

The experimental campaign aimed to find an optimal working condition for both the ligands under which they could express their maximum selectivity. Unfortunately, the results obtained so far did not enable to find an effective working condition. Sulfonated BTzTP appears to be a stronger extractor than PTEH and it was not possible to find an optimal nitric acid concentration of the aqueous phase even with the addition of the ammonium nitrate to increase nitrate concentration. Further attempts are still in progress.

CONCLUSIONS

The results achieved in the present research work will surely be useful for making progressions in solving the spent nuclear fuel management challenges.

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REFERENCES


However, the relevant breakthrough towards fuel reprocessing lies in the Miner Actinides removal. To this purpose, several processes have been studied in the last decades and different strategies were proposed. Currently, the most challenging separation is that of Cm from Am, since short-lived Cm isotopes have a high neutron dose and heat load that makes the production and handling of new fuel extremely complicated. Different hydrometallurgical processes are under development, like Americium Selective extraction (AmSel), Extraction of Americium (ExAm) and Lanthanides Und Curium Americium trenning (LCU) process, but none of these have found yet a suitable efficiency for Am recycling. Another important requirement to consider is the development of solvent extraction systems in compliance with the CHON rule, in order to be able to completely inactivate these chemical systems without producing secondary waste at the end of their useful life.

OBJECTIVE

Within this context, my MSc thesis work would like to contribute to the challenging task of identifying effective systems for the separation of Am from Cm. In particular, two main approaches are pursuing:
1. Improvement of the Am/Cm selectivity of the AmSel reference extraction system by introducing a new extractant;
2. Design of new CHON hydrophilic complexing agents for the selective stripping of Am in the AmSel process.

2. DESIGN OF NEW LIGANDS

Starting from a wide literature review, a list of complexing core fulfilling the CHON principle and showing a different affinity for Am and Cm was drafted. Combining these findings with the promising properties of PyTri ligands in both their hydrophilic and lipophilic derivatives (radiochemical stability, high solubility, targeted selectivity), the first idea was to transform the PyTri complexing core in a tetradentate one by replacing the pyridine with a biarylone or a phenanthroline unit. Such idea is under study by means of a combined approach that would exploit the advances achieved in computational chemistry [3] and experimental investigations. To this purpose, Density Functional Theory (DFT) calculations are in progress to investigate the affinity of the selected cores for Am, Cm and Eu cations. DFT calculations provide a correlation between electron density and the energy of the molecule under study. Thus, thanks to the DFT analysis it could be possible to understand what is the more stable complex formed with Am or Cm, and so understand what is the most promising ligand with respect to the purpose. At the beginning, simulations will be performed with the three different metal ions (Eu, Am and Cm) and without the lateral chains, replaced by a methyl group to simplify the computational calculations. Lateral chains will be selected in order to confer high solubility in water or in organic solvent to the complexing core under study and they will be introduced in the DFT calculations afterwards. Exploiting computational calculations previously done on PyTri ligands [4], the adopted procedure can be subdivided into the following steps:
1. Graphical representations of the component forming the complexes, i.e., the ligand, the metal ion (Eu, Am, and Cm), and nitrate anions;
2. Geometry optimization for all the considered metal-ligand complexes, with the presence of nitrate anions;
3. DFT calculations using Gaussian16 to find the energy of each singular component and of the whole complex, thanks to which is possible to calculate the differences between the complex total energy, minus the energy of individual components, to predict what is the most stable complex.

The theoretical evaluations will be supported by synthesizing the most promising structures to experimentally assess their solubility and selectivity.