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Separation of Americium by Liquid-Liquid Extraction using Diglycolamides Water-Soluble Complexing Agents

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Abstract

Recycling americium (Am) alone from spent nuclear fuels is an important option studied for the future nuclear cycle (Generation IV systems) since Am belongs to the main contributors of the long-term radiotoxicity and heat power of final waste. Since 2008, a liquid-liquid extraction process called EXAm has been developed by the CEA to allow the recovery of Am alone from a PUREX raffinate (a dissolution solution already cleared from U, Np and Pu). A mixture of DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-(hexyloxy)ethyl)-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) in TPH is used as the solvent and the Am/Cm selectivity is improved using TEDGA (*N,N,N',N'*-tetraethyldiglycolamide) as a selective complexing agent to maintain Cm and heavier lanthanides in the acidic aqueous phase (5M HNO_3). Americium is then stripped selectively from light lanthanides at low acidity (pH=3) with a polyaminocarboxylic acid. The feasibility of sole Am recovery was already demonstrated during hot tests in ATALANTE facility and the EXAm process was adapted to a concentrated raffinate to optimize the process compactness. The speciation of TEDGA complexes formed in the aqueous phase with Am, Cm and lanthanides was studied to better understand and model the behavior of TEDGA in the process. Some Ln-TEDGA species are extracted into the organic phase and this specific chemistry might play a role in the Am/Cm selectivity improvement. Hence the hydrophilicity-lipophilicity balance of the complexing agent is an important parameter. In this comprehensive study, new analogues of TEDGA were synthesized and tested in the EXAm process conditions to understand the relationship between their structure and selectivity. New derivatives of TEDGA with different N-alkyl chain lengths and ramifications were synthesized. The impact of lipophilicity on ligand partitioning and Am/Cm selectivity was investigated.

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Keywords: americium, curium, liquid-liquid extraction, diglycolamides

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1. Introduction

The French Act of June 28th 2006 has defined several strategies to totally or partially reprocess minor actinides from spent nuclear fuels in Generation IV systems. One of these strategies would involve the recovery of americium alone from a PUREX raffinate (already cleared from U, Np and Pu) and leave curium with vitrified wastes dedicated to a future deep geological repository. Separating americium alone from those final waste would allow the reduction of their long term radiotoxicity but also heat emissions, leading to a significant minimization of the surface needed for repository.[1, 2] Moreover, curium recycling would be difficult to implement due to its very significant neutron emissions which would require very thick shielding at any step of the fuel cycle. In order to recover americium from a PUREX raffinate, two main challenges have to be accomplished: the separation of Am from all the lanthanides AND curium. In order to prove the feasibility of this separation, the CEA has developed a hydrometallurgical process, called EXAm (Extraction of Americium),[3,4] using a mixture of two extractants: DMDOHEMA (*N,N′*-dimethyl-*N,N′*-dioctyl-2(2(hexyloxy)ethyl)-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) diluted in hydrogenated tetrapropylene (TPH) diluent.

The key step of this process is the first "extraction/scrubbing" section where the americium/curium separation is achieved using TEDGA (*N,N,N',N'*-tetraethyldiglycolamide) complexing agent in the acidic aqueous phase (4-5 M HNO_3). Americium is co-extracted in the organic phase with lighter lanthanides (Ln) and some fission products (Fe, Mo, Ru, Pd). Hence additional steps are necessary to separate Am from those elements. In this paper we will only focus on the chemistry of the first main "extraction-scrubbing" section where the Am/Cm separation takes place, focusing on the role of TEDGA in the separation between Am and Cm and evaluating the impact of structural modifications on the diglycolamide ligand (DGA).

Nomenclature

TEDGA	*N,N,N',N'*-tetraethyldiglycolamide
EXAm	Extraction of Americium Process
DMDOHEMA	*N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-(hexyloxy)ethyl)-malonamide
HDEHP	di-2-ethylhexylphosphoric acid
TPH	hydrogenated tetrapropylene
DGA	diglycolamide
Ln	Lanthanides
An	Actinides
SF	Separation Factor

2. Highlights on the EXAm process chemistry with TEDGA

2.1. Previous work

The Am/Cm separation is very challenging since both elements have very close physico-chemical properties. The DMDOHEMA extractant has a low selectivity for Am versus Cm ($SF_{Am/Cm}$= 1.6). Hence, the water soluble complexing agent TEDGA was added into the feed solution and in the scrubbing aqueous phase to improve the Am/Cm selectivity ($SF_{Am/Cm}$= 2.5). TEDGA has a higher affinity for heavy lanthanides and curium, maintaining them preferentially in the aqueous phase, while light lanthanides and americium are extracted by the EXAm solvent in the organic phase.

Although TEDGA is a water-soluble complexing agent, its partial transfer to the solvent during the extraction process has to be taken into account. According to a recent complexation study,[5] TEDGA would form preferentially 1:1 and 1:2 complexes with lighter lanthanides in the aqueous phase, and such complexes are extractable into the organic phase, while heavier lanthanides and Cm should mainly form non-extractable 1:3 species. In order to better characterize the impact of this specific TEDGA chemistry on Am/Cm separation, a new series of batch extraction experiments was performed and modelled.