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ScienceDirect

Procedia Chemistry 21 (2016) 433 – 440

Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Application of the pyrochemical DOS, developed by the CEA, within reprocessing of CERCER transmutation fuel targets

E. Mendes[a]*, T. Ducasse[a], M. Miguirditchian[b], M. Bertrand[a]

[a]*CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, SMCS, LDPS*
[b]*CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, SMCS, LCPE*
F-30207 Bagnols-sur-Cèze, France

Abstract

Pyrochemical technology using high-temperature molten salts and molten metal media presents a potential interest for an overall separation and transmutation strategy for long-lived radionuclides. Within the frame of the two French acts on radioactive waste management, a pyrochemical R&D program was launched at the CEA Marcoule in the late 90's. The second step is the actinides back-extraction, which consists in a liquid/liquid oxidative stripping of the An from aluminium matrix into molten chloride media. The DOS process has been successfully demonstrated for treatment of oxide type fuels within the last years: the core of the process has been already assessed and the studies have shown high selectivity and a quantitative recovery of actinides.
Within the framework of the SACSESS European research program, the pyrochemical activities focused on applications of the DOS process to reprocess CERCER transmutation targets. These particular type of fuels consist of a mixture of minor actinides (MA) oxides diluted in an inert (oxide MgO) matrices. The behaviour of matrices material was first investigated regarding the solubility in the fluoride salt, starting from both oxide powders or sintered pellets. Further investigations focused on the reductive extraction behaviour of Mg in metallic Al. The impact of Mg on the efficiency of An reductive extraction was also studied using uranium simulating the behaviour of MA oxides.

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: Pyrochemistry, Liquid/Liquid extraction, Transmutation targets

* Corresponding author. Tel.: +33-466-796-251; fax: +33-466-796-567.
E-mail address: eric.mendes@cea.fr

1876-6196
Peer-review under responsibility of the organizing committee of ATALANTE 2016
doi:10.1016/j.proche.2016.10.060

1. Introduction

Among the various techniques of nuclear fuel reprocessing, pyrochemical separation technology using high-temperature molten salts and metal media has been studied and developed in order to reprocess nuclear fuel. It represents a potential alternative to hydrometallurgical technology (PUREX process and its analogues), especially in case of the treatment of minor actinides-rich materials[1].

Previous studies showed that fluoride salts are very attractive in terms of confinement since direct immobilization into glass matrix is feasible[2]. Thus, a reference process route was assessed for actinides recovery in fluoride melts consisting in two liquid/liquid extraction steps[3, 4, 5, 6, 7, 8, 9]. The first step is based on the selective actinides reductive extraction by contacting the LiF-AlF_3 salt, containing dissolved spent fuel, with a liquid aluminium phase leading to the following reaction (1):

$$AnF_{3(\text{salt phase})} + Al_{(\text{metal})} \leftrightarrow An_{(\text{metal})} + AlF_{3(\text{salt phase})} \quad (1)$$

Initially, the fuel was planned to be converted into fluoride species prior the reductive extraction (and then introduced inside the salt), using HF fluorination process. Recent studies led to a significant simplification of such process, avoiding any use of HF[10, 11, 12]. Taking advantage of chemical properties of cryolite fluoride salts, particularly its affinity for oxides, the spent oxide fuel is directly dissolved (as fluoride and/or oxifluoride species) inside the fluoride salt while contacting with the aluminium phase (so called Direct Oxide Solubilisation process)[13]. The efficiency of the extraction is given by the distribution ratio $D_{An} = [An]_{metal} / [AnF_3]_{salt}$ (concentrations in g/g) and the selectivity is given by the separation factor $SF_{M/M'} = D_M / D_{M'}$.

The second step of the DOS process is the actinide oxidative back-extraction from the Al matrix. It consists in contacting the liquid Al containing the actinides with a pure molten chloride salt containing the oxidizing agent $AlCl_3$. The process reaction is described by the following equation (2):

$$An_{(\text{metallic solvent})} + AlCl_{3(\text{salt})} \leftrightarrow Al_{(\text{metallic solvent})} + AnCl_{3(\text{salt})} \quad (2)$$

This process was extendedly studied within the last years and lead to an excellent selectivity of the reductive extraction regarding the actinides and a quasi-quantitative back-extraction of the actinides in the chloride salt in a single batch[7, 8, 9]. Within the framework of the SACSESS European research program, the studies focus now on the applications of the DOS process to treat MgO based CERCER and Mo based CERMET transmutation targets. These types of fuels consist of a mixture of minor actinides (MA) oxides diluted in an inert (oxide MgO or metallic Mo) matrices. Since the DOS process was developed for reprocessing oxide type fuels a prior oxidation of Mo into oxide form step must be considered for reprocessing CERMET. Particular attention must be paid on the behaviour of matrices material regarding the solubility in the fluoride salt. Another point to be assessed consists in the reductive extraction behaviour of Mg or Mo in metallic Al. Finally, the impact of Mg and Mo on the efficiency of An reductive extraction must also be addressed.

The present work focusses on application of the DOS process for reprocessing CERCER matrices. The behaviour of MgO was first investigated regarding the solubility in the fluoride salt, starting from both oxide powders or sintered pellets. Further investigations focussed on the reductive extraction behaviour of Mg in metallic Al. The impact of Mg on the efficiency of An reductive extraction was also studied using uranium simulating the behaviour of MA oxides. These investigations were completed by a demonstration of the DOS process on a $Pu_{0.5}Am_{0.5}O_{2-\delta}$-MgO FUTURIX CERCER pellet synthesized at the ATALANTE facility within the framework of Eurotrans program.

2. Experimental

Al, Cu, LiF, AlF_3 and MgO were purchased from Sigma-Aldrich with > 99.99% purity. Al–Cu alloy (78–22 mol%) was prepared by dissolving the suitable quantity of copper in liquid aluminum at 800° C. This operation was performed under argon sparging in a stainless steel reactor using a graphite crucible.