Journal of Fluorine Chemistry 130 (2009) 18–21

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Potentialities of fluoride-based salts for specific nuclear reprocessing: Overview of the R&D program at CEA

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ARTICLE INFO

Article history:
Received 28 February 2008
Received in revised form 13 June 2008
Accepted 3 July 2008
Available online 23 July 2008

Keywords:
Molten salts
Fluoride
Electrolysis
Extraction
Minor actinides
Reprocessing
ADS
Transmutation

ABSTRACT

Initially studied in the frame of the first French act on radioactive waste management (December 1991), the pyrotechnology is currently assessed by the Nuclear Energy Direction of the Commissariat à l'Energie Atomique (CEA) within the succeeding act (June 2006) as a potential alternative to hydrometallurgy for the reprocessing of targets or dedicated fuels (coming from accelerator-driven systems or ADS) considered for the minor actinides transmutation.

The R&D program is mainly focused on the evaluation of the fluoride melts as interesting media for operating separation between the actinides and the fission products. Two separation techniques are currently evaluated; the first one uses the liquid–liquid extraction technique between molten fluoride and liquid metal at high temperature, the second one is based on an electrolytic separation in a molten fluoride melt. Both are promising in terms of separation efficiency. This paper gives an overview of the current studies and presents the last main experimental results.

1. Introduction

The French planning act of 28 June 2006 on Sustainable Management of Radioactive Materials & Waste involves one specific area devoted to Partitioning and Transmutation of Long-lived Radioactive Elements. This act notably requires further investigations conducted with those concerning the new generations of nuclear reactors and the accelerator-driven systems (ADS) dedicated to transmutation of waste, in order to provide by 2012 an assessment of the industrial prospects of those systems and to commission a pilot facility before 31 December 2020.

Among the various techniques of reprocessing, the pyrotechnology is assessed as a potential alternative to hydrometallurgical technology (PUREX process and its analogues), especially in case of the treatment of minor actinides-rich materials. Two possible applications have been identified: (i) reprocessing of targets coming from minor actinides transmutation and (ii) reprocessing of dedicated fuels for ADS. In this latter case, the typical scenario would implement a double strata reactor base: the first stratum uses light-water reactors to produce energy; the second one comprises subcritical transmutation reactors (ADS). The pyrotechnology could be applicable for reprocessing the spent fuel from the second stratum, consisting of actinide oxides dispersed in an inert matrix.

A R&D programme on pyrotechnology has been launched at Marcoule in the late-1990s. It is going on in order to provide the largest quantity of facts before 2012.

Ideally a new pyroprocess should not generate more waste and should be at least as safe and cost effective as the hydrometallurgical processes currently implemented at industrial scale. Therefore, along with experimental research, it is necessary to conduct system studies to devise potential processes and to assess their capability to achieve the assigned objectives. These latter are: (i) to recover all the actinides (>99.9%) present in the process input stream for recycling them, (ii) to ensure sufficient decontamination between actinides and fission products, (iii) to generate the minimum of ultimate waste flows, and (iv) to have suitable confinement of process waste.

Preliminary experimental studies showed that fluoride medium is very attractive in terms of confinement: direct fluoride immobilization into glass matrix up to 15 wt.% has been successfully proved at lab-scale [1]. The physical and chemical

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doi:10.1016/j.jfluchem.2008.07.011

properties of the product are compatible with an industrial-scale melting process such as La Hague vitrification process. These promising results drove us to assess more extensively the potentialities of fluoride melts for separating the actinides from the fission products.

2. Separation assessment results

An alpha laboratory has been equipped in the Atalante facility (Marcoule, France) and the design of a hot cell for performing tests on irradiated materials is currently under consideration. Two main separation techniques are currently evaluated; the first one is named chemical reductive extraction and consists in using molten fluoride–liquid metal extraction technique at high temperature, the second one is based on an electrolytic separation in a molten fluoride melt.

In both cases, the process begins with a series of head-end operations on the fuel assemblies to obtain an oxide powder that is fine enough (50–100 μm) for the subsequent operations (possibly a reductive distillation above 1000 °C for caesium removal and then hydrofluorination). During the head-end treatment, some or all of the gaseous or volatile fission products (Kr, Xe, I, Br) are released and must be collected and trapped for disposal as an ultimate waste form. After the hydrofluorination step, the resulting powder is dissolved in a fluoride melt whose nature and composition are depending on the separation technique.

2.1. Chemical reductive extraction

After the dissolution step, the actinides and the non-volatile fission products are present in the fluoride melt as fluorides. Only the platinum group fission products are preferentially at the metallic state and could be preliminarily digested by suitable metallic solvent such as zinc. The rare earths (Ln) are the most awkward fission products to be separated from the actinides (An).

The chemical reductive extraction of any trivalent element M(III) (actinide or rare earth) from the fluoride melt to a liquid metallic solvent by an *ad hoc* reducing agent R (Fig. 1) can be described by the following equilibrium:

$$\mathrm{MF}_{3(\text{fluoride melt})} + \mathrm{R}_{(\text{metallic solvent})} \Leftrightarrow \mathrm{RF}_{3(\text{fluoride melt})} + \mathrm{M}_{(\text{metallic solvent})} \tag{1}$$

For a given element M at the temperature T(K), the distribution coefficient ($D_M = x_M/x_{MF_3}$) is:

$$D_M = K_M^o(T)\frac{a_R}{a_{RF_3}}\frac{\gamma_{MF_3}}{\gamma_M} \tag{2}$$

where $K_M^o(T)$ is the thermodynamic constant of the equilibrium calculated from the free enthalpies of formation of the pure species involved (reference state being the pure compound in the liquid state, except for RF_3 for which the reference state is the pure solid), x_M is the weight (or molar) fraction of M in the metallic solvent, x_{MF_3} is the weight (or molar) fraction of MF_3 in the salt, γ_{MF_3} and γ_M are, respectively, the activity coefficient (weight or molar scale) of MF_3 in salt and of M in the metallic solvent, a_R and a_{RF_3} are, respectively, the chemical activity of R in the metallic solvent and of RF_3 in the salt.

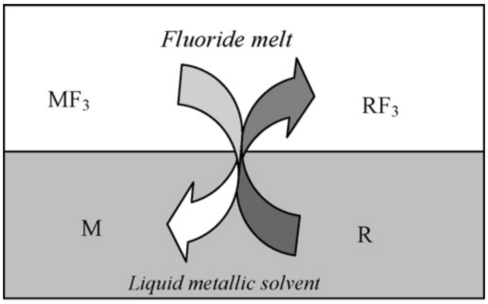

Fig. 1. Chemical reductive extraction diagram.

According to the Eq. (2), for a given RF_3 content, D_M is directly depending on the (γ_{MF_3}/γ_M) ratio. As An(III) and Ln(III) have close ionic radii, they will be similarly solvated in the saline melt and therefore will have comparable γ_{MF_3} activity coefficients [2].

To optimize the An/Ln separation (i.e., to increase the separation factor ($S_{An/Ln} = (D_{An}/D_{Ln})$)) this is necessary to increase the (γ_{An}/γ_{Ln}) ratio. It is representing the difference of solvation for the actinide and the rare earth in the metallic solvent. Previous studies compiled by Lebedev [3] and our experimental results (Fig. 2) show the interest of aluminium as metallic solvent for increasing this ratio. Cerium and plutonium were selected for representing the rare earths and actinides, respectively.

Other studies from CEA have also shown its interest as a selective reducing agent for actinide fluorides [4]. Thus, liquid aluminium is very attractive in terms of actinides/rare earths separation; the distribution coefficients of actinides and rare earths have been measured in LiF–AlF_3 (85–15 mol%)/AlX (X = Cu or Al) system at 830 °C (Table 1).

According to Table 1, actinides and rare earths (Ce, Nd, Sm and La) are distributed in two separated groups. Firstly, plutonium, americium and curium, having similar distribution coefficients, could be co-extracted. Secondly, their separation from rare earths should be easily reached thanks to their high separation factors (SF > 1000).

The difference between the distribution coefficients obtained by using AlCu and pure Al is mainly due to the variation of the mole fraction of Al in the metallic solvent; besides a probable and little variation of γ_{Al} should also be taken into account to explain that difference (copper being not totally inert).

2.2. Electrolytic separation

An alternative route (without aluminium) could be necessary if troubles occur in the subsequent step of the process where the actinides have to be recovered from the liquid aluminium (several options are currently evaluated).

One possible route is based on the electrolytic recovery on inert solid cathode, from which the actinides could be easily separated, mechanically for instance. A first rough assessment of such a technique necessarily goes through preliminary electrochemical

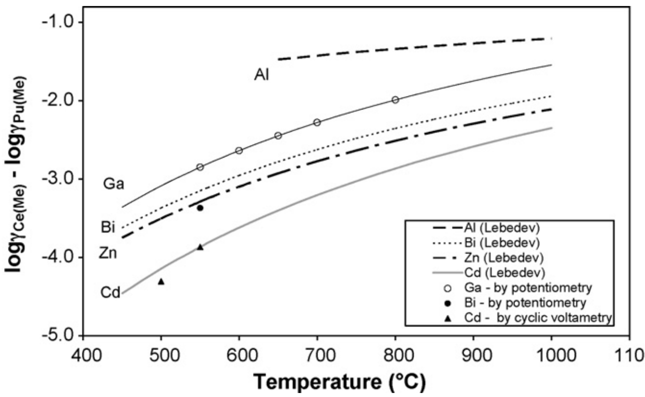

Fig. 2. Capability of various metallic solvents for Pu/Ce separation (activity coefficient γ_M expressed in molar fraction scale with pure solid as reference state).

Table 1
Weight distribution coefficient (D_M) and separation factor ($S_{Am/M}$) in LiF–AlF$_3$ (85–15 mol%)/AlX (X = Cu or Al) at 830 °C [2,5]

Element	AlCu (78–22 mol%)		Pure Al	
	D_M	$S_{Am/M}$	D_M	$S_{Am/M}$
Pu	197 ± 30	0.73 ± 0.21	273 ± 126	0.78 ± 0.47
Am	144 ± 20	1	213 ± 30	1
Cm	–	–	185 ± 31	1.15 ± 0.35
Ce	0.142 ± 0.01	1014 ± 213	0.162 ± 0.02	1315 ± 289
Sm	0.062 ± 0.006	2323 ± 488	0.044 ± 0.004	4954 ± 1139
Eu	<0.013	>11000	<0.03	>7100
La	<0.06	>2400	0.03	7100

studies in fluoride electrolytes of interest. These studies are very few on actinides [6–10]. Furthermore, to our knowledge, no electrochemical data in molten fluorides has ever been published on minor actinides. Preliminary basic research showed that LiF–CaF$_2$ (77–23 mol%) melt appeared to be a potential electrolyte for (U, Pu)/rare earths separation [6]. A more complete evaluation requires further studies on minor actinides (Np, Am and Cm) and comparison with the rare earths. Here are presented the electrochemical behaviour of americium in the molten LiF–CaF$_2$ eutectic on inert solid electrode and the determination of the deposition potential difference between Am and Nd.

2.2.1. *Experimental*

The experimental set-up is presented (Fig. 3). Experiments were realized in an Inconel alloy cell. The top of the cell is cooled by circulating water and the cell is placed under inert argon atmosphere. The cell presents three entries for electrodes and one on the side for gas flow. A sluice equipped with argon flow allows introducing solutes or an electrode without any air entry in the cell. The salt was put in a graphite crucible coated with pyrolytic carbon (SGL CARBONE) itself contained in a boron nitride crucible (MCSE). In order to reduce the amount of solvent, a clover shape crucible limited to the electrodes space was used.

Fig. 3. Electrochemical cell in the glovebox (Atalante facility, Marcoule, France).

The molten LiF–CaF$_2$ eutectic (77–23 mol%) was prepared with LiF (Aldrich, 99.99+%) and CaF$_2$ (Merck, 99.95%). NdF$_3$ (Aldrich, 99.99%) was used as solute. AmF$_3$ was prepared by Am(III) precipitation in aqueous solution with HF addition. Before its use, the salt was firstly heated under vacuum up to 700 °C and after under argon atmosphere up to the working temperature. It was then dehydrated by $HCl_{(g)}$ bubbling.

In order to avoid any disturbance of the other measurements, the temperature of the salt was measured at the end of the experiment.

Electrochemical measurements (cyclic voltammetry (cv) and square-wave voltammetry (sqw)) were performed with an Autolab PGstat30. The working electrode was a 1-mm ∅ tungsten wire (Goodfellow, 99.9%) sheathed with Al$_2$O$_3$ tube (SCERAM, 99.7%). The auxiliary electrode was a 5-mm ∅ graphite rod (Graphitec, >99.99%). The potentials were measured and referred to a 0.5-mm ∅ platinum wire (Goodfellow, 99.95%) immersed in the molten electrolyte, acting as a quasi-reference electrode Pt/PtO$_x$/O^{2-} [11]. Efforts were done to replace as far as possible alumina materials by boron nitride ones.

2.2.2. *Results and discussions*

Fig. 4 shows cyclic voltammetries on W electrode in a LiF–CaF$_2$–AmF$_3$ solution ([Am] = 1.55 × 10^{-2} mol kg^{-1}) at 780 °C. During the electrode potential cathodic sweep, two main peaks appear: Ic at −1.84 V vs. Pt and IIc at −2.26 V vs. Pt. The second one is related to the solvent reduction (Li$^+$/Li). Peak Ia is characteristic of a stripping peak [12]. From the elements present in the salt we associated Ic to the Am(III)/Am(0) reduction. The peak potential (+0.5 V vs. Li$^+$/Li) is consistent with the Am(III)/Am(0) equilibrium potential (+0.51 V vs. Li$^+$/Li). It has been calculated from Li(I) and Am(III) molar fractions and thermodynamic data of pure compounds at 780 °C [13]. However, there is an overpotential of 500 mV between reduction and oxidation peaks, which is a quite important value for

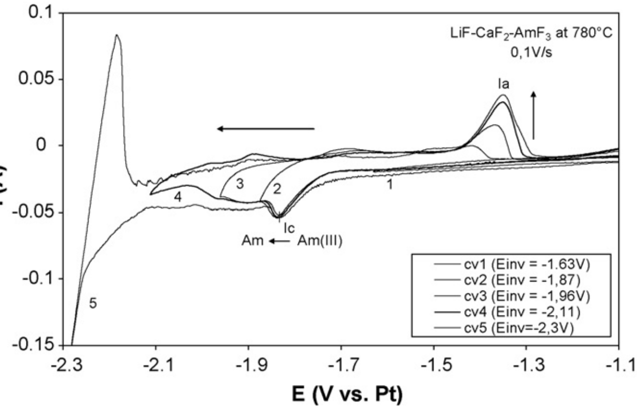

Fig. 4. Cyclic voltammetries on W electrode (S_{WE} = 0.16 cm^2) in LiF–CaF$_2$–AmF$_3$ ([AmF$_3$] = 1.55 × 10^{-2} mol kg^{-1}) at 780 °C, $v = 0.1$ V/s; Pt reference electrode, CE: graphite.

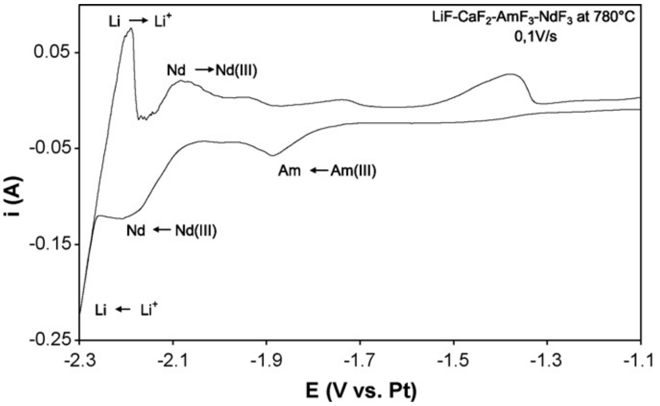

Fig. 5. Cyclic voltammetry on W electrode (S_{WE} = 0.16 cm^2) in LiF–CaF$_2$–AmF$_3$–NdF$_3$ ([AmF$_3$] = 1.55 × 10^{-2} mol kg^{-1}, [NdF$_3$] = 4.7 × 10^{-2} mol kg^{-1}) at 780 °C, $v = 0.1$ V/s; Pt reference electrode, CE: graphite.

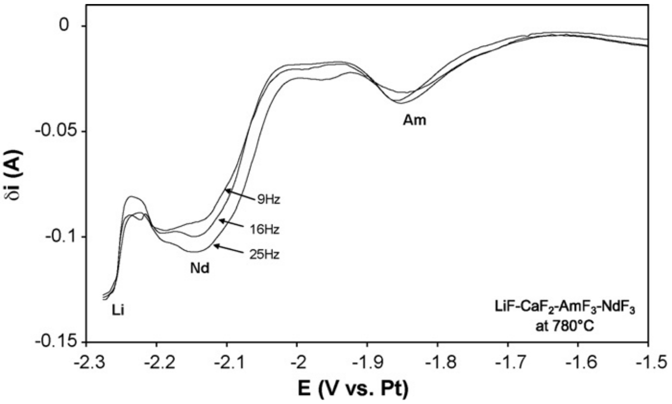

Fig. 6. Square wave voltammetry on W electrode (S_{WE} = 0.16 cm^2) in LiF-CaF$_2$-AmF$_3$-NdF$_3$ ([AmF$_3$] = 1.55 × 10^{-2} mol kg^{-1}, [NdF$_3$] = 4.7 × 10^{-2} mol kg^{-1}) at 780 °C, Pt reference electrode, CE: graphite.

a quasi-reversible or irreversible system. This might be related to the molten bath temperature close to its melting point. This has already been observed [14]. Presence of some oxides on the electrode could also delay the oxidation. Fig. 4 also shows the association of those two previous peaks by cv and reverse scan potential variation. The oxidation peak is increasing when the reverse scan potential gets closer to peak Ic potential.

Thus, the americium (+II) oxidation state is not stable in fluoride medium contrary to the chloride one [14,15]. Consequently, the fluoride melt shifts the equilibrium (3) to the left, which avoids a possible corrosion of americium deposit in case of electrolytic recovery:

$$2\mathrm{Am(III)} + \mathrm{Am(0)} \leftarrow 3\mathrm{Am(II)} \qquad (3)$$

NdF$_3$ was added to the molten bath at the end of the experiment and Fig. 5 shows the measured voltammetry. Neodymium and americium reduction peaks are well separated.

Table 2
Estimated (by sqw) apparent standard potential in LiF-CaF$_2$ (77–23 mol%) at 780 °C

Redox couple	Li(I)/Li	Nd(III)/Nd	Am(III)Am
E'°(V vs. Pt)	−2.28	−2.14	−1.85
E'°(V vs. Li)	0	+0.14	+0.43

sqw = square-wave voltammetry.

Square-wave voltammetries at various frequencies were measured (Fig. 6) in order to estimate apparent standard potentials of the Nd(III)/Nd and Am(III)/Am redox couples.

The peaks were, respectively, attributed to the Am(III)/Am, Nd(III)/Nd and Li(I)/Li redox couples. Under restrictive conditions, the square-wave voltammetry peak potential can be assimilated to the apparent standard potential E'° [16]. Potentials were measured vs. Pt and then referred to the Li$^+$/Li couple (Table 2). The results are consistent with thermodynamic data.

The difference potential between Am(III)/Am and Nd(III)/Nd redox couples in LiF–CaF$_2$ (77–23 mol%) at 780 °C is estimated by sqw to be 290 mV and is theoretically wide enough for achieving Am/Nd quantitative electrolytic separation.

3. Conclusions

This overview shows that fluoride-based salts are promising in terms of An/Ln separation and of confinement of the ultimate process wastes. Spent fluoride melt can be directly confined in a glass matrix and there are two separation techniques theoretically attractive for operating actinides/rare earths separation. All these experimental results encourage us to pursue the evaluation, notably on irradiated materials (transmutation targets or spent ADS fuel) in shielded cell, and possibly at higher scale, to confirm or invalidate these preliminary lab-scale results.

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