Possible routes for pyrochemical separation: Focus on the reductive extraction in fluoride media*

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Abstract: Molten salts (MSs) such as fluoride or chloride salts at high temperature (400–800 °C) are solvents known for their high solvation power and electroactivity range. Rare earths, lanthanides, actinides, and refractory metals can be dissolved, treated, and purified in MSs. The properties of these solvents are particularly interesting for nuclear spent-fuel reprocessing. The pyrochemical separation and extraction of solutes can be performed using several methods taking into account the effects of redox and/or acidity. This paper is focused on the reductive extraction method performed by contacting a liquid metal (LM) containing reductive species and an MS. The analytical model developed to calculate the efficiency of such a method is detailed in this paper. To apply this model, one essential point is the establishment of a database related to the redox and solvation properties of solutes in MSs. The approach retained to propose a database based on the analysis of both thermochemical data of pure compounds and experimental measurements reported in the literature is described in this paper in the case of lanthanides in fluoride MSs. The use of the database to calculate efficiency as a function of process parameters is given in this paper as well as the comparison between two reducing agents considered.

Keywords: actinides; inorganic chemistry; lanthanides; molten salts; nuclear energy; redox properties; reductive extraction.

INTRODUCTION

The reprocessing of spent nuclear fuel consists in separating actinides (including the fissile material) from fission products (FPs). In most generation IV concepts, actinides are separated from the spent nuclear fuel and re-introduced into the reactor core while FPs are sent to waste storage. The molten salt reactor (MSR) is one of the six concepts retained by the generation IV forum in 2001. The particularity of such a concept is the use of a liquid fuel (a molten salt, MS), which is both fuel and coolant. In this particular case, the use of a pyrochemical treatment of spent fuel is obvious. Concerning future fast reactors (containing high amounts of actinides) or current nuclear power plants [(reacteur à eau pressurisée (REP) or European pressurized reactor (EPR)] containing UOX or mixed-oxide (MOX) fuel, a pyrochemical treatment of spent fuel can be of interest either to replace Plutonium URanium EXtraction (PUREX) or to be the continuation of PUREX (after extraction of U and Pu) for the separation of minor

actinides (especially Am and Cm, which are responsible for the long-term radiotoxicity in the waste storage [1]) from FPs.

The advantages of MS implementation to perform the nuclear fuel treatment are essentially related to a safety increase: no fire risk (because no organic solvent is involved in the process), no explosion risk (no hydrogen formation by radiolysis), and no criticality risk (no neutronic moderator). Another advantage is related to the high power of solvation of MSs, which increases the fuel dissolution rates. The major drawback of MS is the high working temperature, which contributes to increase the corrosion of structural materials when the environment is not well controlled [2].

The pyrochemical separation and extraction of actinides and FPs can be realized using several methods (Table 1) taking into account the effects of redox and/or acidity. Thus, some methods are based on modifications of oxidation states of the elements considered either by the action of selected oxidizing or reducing reagents or by the use of an electrical current. The oxidation generally leads to the formation of a gaseous halide compound (e.g., UF_6 or NpF_6 for fluoride media). This technique has been developed and successfully tested by the Oak Ridge National Laboratory (ORNL) in the United States [3]. The reduction reaction leads to the formation of a metal or an alloy. Metals are obtained by electrochemical reduction on solid and inert cathodes. Experimental studies have been done to study the feasibility of extracting lanthanides from a fluoride MS by electrolysis on inert and reactive cathodes [4]. Then, metal is in its solid state. Reduction can also be performed on a liquid cathode, so-called liquid metal (LM) (e.g., Bi, Ga, Sb, Cd, Al...), either by electrochemical reduction or by chemical reaction using a reducing reagent (such as Li or Th), solvated in the LM solvent. This method was retained for the reprocessing of the salt in the MSBR (molten salt breeder reactor) concept studied by the ORNL [5,6]. In this way, the product of the reduction is a metal solvated by the metallic liquid solvent (LM). Other methods are based on the oxoacido-basic properties (oxide anion exchange power) of the solutes. The control of the amount of oxide ions in the media can lead to a selective precipitation of an oxide which can be subsequently separated from the liquid media. The amount of oxide can be controlled by addition of solid oxide (such as Li_2O) or by addition of a gas such as H_2O. The advantage of using a gaseous reagent is the formation of a gaseous product (e.g., HCl) that does not modify the composition of the MS. The efficiency of this technique has been demonstrated in a chloride media [7].

Table 1 Possible routes to realize selective separation/extraction of solutes from an MS.

Reagent state	Used effects	Methods		Product state
Solute (in fluoride or chloride media) (M^{n+})	**A**- Redox (oxidation state modification)	**A1**- Action of an oxidizing agent F_2, Cl_2 **A2**- Action of an oxidizing electrical current		**Gas** (MF_x)
		A3- Action of a reducing agent, e.g., Li **A4**- Action of a reducing electrical current	Metal (M)	**Solid** **Solute** (in LM solvent)
	B- Acido-basicity (oxide precipitation solubilization)	**B1**- Action of oxide ions donors (e.g., Li_2O) **B2**- Action of gaseous mixtures $H_2O/HF/H_2$		**Solid** (MO_x)

As an example, the reprocessing scheme [8,9] proposed to clean the fuel salt in the concept MSFR (molten salt fast reactor), which has been studied since 2004 in CNRS (France), makes use of most of these techniques to separate the FPs from the fuel salt. After reprocessing, the cleaned salt containing only actinides is back-introduced in the reactor core. In this way, the fuel cycle is closed.

To evaluate a reprocessing scheme, we have to consider firstly the efficiency of all the steps involved in the scheme. In a preliminary step, the efficiency can be calculated theoretically taking into

account the thermodynamical equilibrium. The kinetics of the reactions will be studied in a second step through experimental measurements.

This paper is focused on the reductive extraction between MS and LM. The establishment of the analytical relation of efficiency will be detailed. In this expression, some parameters depend on the intrinsic properties of the solutes in the MS (solvation and redox properties) and others can be controlled by the process operator. One part of the paper is dedicated to the determination of the intrinsic properties of solutes in fluoride media, and a database is established by combining and analyzing experimental measurements published by several authors. The knowledge of the intrinsic properties leads to calculation of the efficiency and the selectivity as a function of the process parameters: the phase volumes, the nature and the concentration of the reducing element.

LIQUID–LIQUID EXTRACTION (REDUCTIVE EXTRACTION)

The aim of this paper is to estimate the feasibility of liquid–liquid extraction technique in a special case: the separation of lanthanides from actinides in the MSFR concept.

The characteristics of the process are:

- The fuel salt is LiF–ThF$_4$ (77.5–22.5 mol %) at 873 K.
- The solvent LM retained for the extraction is Bi.
- The reducing compounds can be either Li or Th.

Principle of the reductive extraction method

The principle of the method is described Fig. 1. The left part of the figure presents the reductive extraction principle using a solvent metal (LM) in which a reducing element R is introduced. R can be metallic Li or Th. The right part of the figure presents the back-extraction of the element M by an electrochemical method, this method being retained in the reprocessing of the MSFR concept. In this way, the use of two different pools of Bi leads to oxidization of M in the MS at the anode and to a reduction of the reducing element from the MS to the LM in order to recover the solvent metal composition. It is obvious that the reducing compound has to be a component of the melt and has to be reducible in the melt.
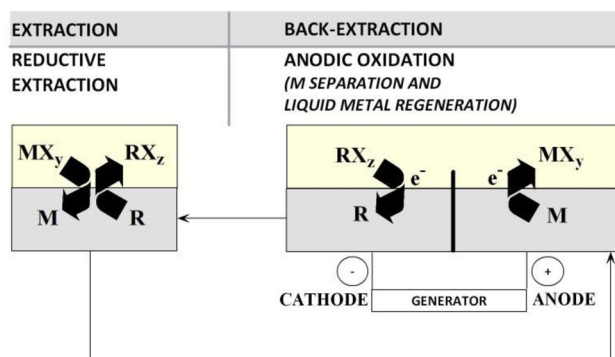

Fig. 1 *Left*: Principle of reductive extraction of an element M from an MS to a solvent LM containing a reducing compound R. *Right*: Principle of anodic oxidation of the element M (contained in the LM) and LM regeneration by reducing the reducing agent from the MS to the LM.

The particularity of the reprocessing scheme proposed for MSFR treatment, which has already been described [8,9], is to use the same technique to extract actinides in the first step (step 1) and lanthanides in the second one (step 2). During the first step, actinides have to remain with high efficiency and good selectivity against lanthanides. During the second step, lanthanides have to be extracted with high efficiency. The nature of the solvent metal chosen for the two steps is Bi. Therefore, the achievement of the two extraction steps requires an optimization of the process parameters for each step. A scheme of these steps is given in Fig. 2.
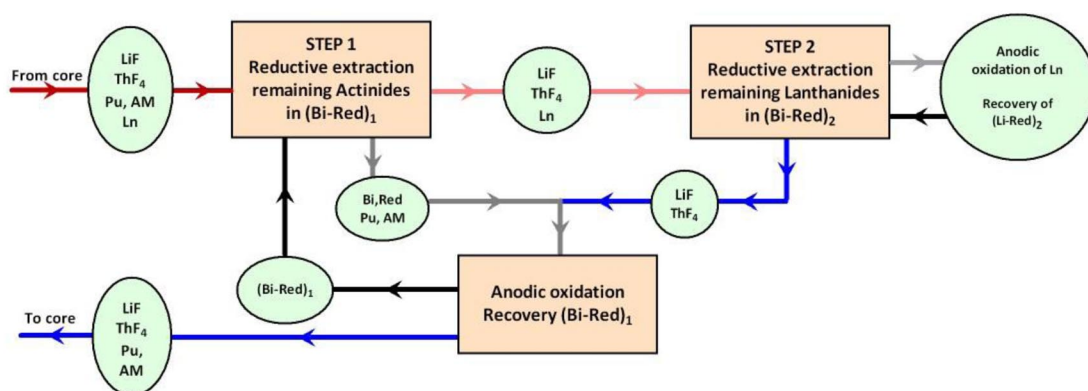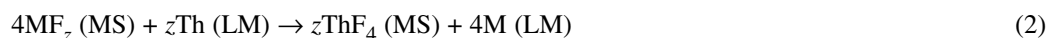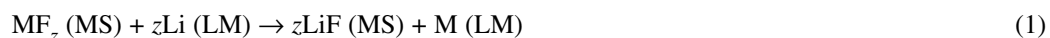

Fig. 2 Part of the reprocessing scheme with steps 1 and 2 retained for the MSFR fuel salt treatment.

Moreover, the technique retained for the back-extraction of actinides is the anodic oxidation of the Bi pool containing actinides. This oxidation has to be performed in the cleaned LiF–ThF$_4$ MS. During this step, the MS is reduced and the metallic solvent regenerated. The reduction of LiF–ThF$_4$ media on bismuth electrode leads to the reduction of both Th and Li, the solubility of Th in Bi being rather low (0.1 mol %) [10–12]. Therefore, the behavior of Li and Th as reducing agent is studied and described in this paper.

Analytical description: Efficiency equation

The liquid–liquid extraction between a molten fluoride salt and a solvent metal is due to the two following reactions depending on the nature of the reducing element:

$$MF_z \ (MS) + z Li \ (LM) \rightarrow z LiF \ (MS) + M \ (LM) \tag{1}$$

$$4 MF_z \ (MS) + z Th \ (LM) \rightarrow z ThF_4 \ (MS) + 4 M \ (LM) \tag{2}$$

Li or Th (in their metallic state) are introduced in the LM (Bi) to react with MF_z. This reaction depends on the redox potential difference between the two redox systems LiF/Li and MF_z/M and on the solvation of the elements in the fused salt and in the solvent metal.

The equilibrium constants of reactions 1 and 2 are, respectively,

$$K(\text{Li}) = \frac{a(\text{LiF})^z \, a(\text{M})}{a(\text{LiF})^z \, a(MF_z)} \tag{3}$$

$$K(\text{Th}) = \frac{a(\text{ThF}_4)^z \, a(\text{M})^4}{a(\text{Th})^z \, a(MF_z)^4} \tag{4}$$

The terms $a(X)$ are the activities of the different compounds involved in the equilibria 1 and 2. M (which represents the element M), Li, and Th are in their metallic state, and MF_z, LiF, and ThF_4 are the elements in their oxidation states, respectively, $(+z)$, $(+I)$, and $(+IV)$ dissolved in the fluoride MS. The fluorides are dissolved in the MS and the metals in the metallic phase of Bi.

Efficiency definition

Efficiency and selectivity are the most important parameters to estimate the feasibility of an extraction process. The efficiency $\mu(M)$ can be defined as the ratio of the mole of M in the metallic phase over the total number of mole of M in the two phases:

$$\mu(M) = \frac{n(M)}{n(M) + n(MF_z)} \tag{5}$$

or

$$\frac{1}{\mu(M)} = \frac{n(M) + n(MF_z)}{n(M)} = 1 + \frac{n(MF_z)}{n(M)} \tag{6}$$

Then

$$\mu(M) = \frac{1}{1 + n(MF_z)/n(M)} = \frac{1}{1 + 10^{\lambda(M)}} \quad \text{with } \lambda(M) = \log\frac{n(MF_z)}{n(M)} \tag{7}$$

The potential of the LM pool at equilibrium E_{LM} is given both by two redox systems LiF/Li_{Bi} or ThF_4/Th_{Bi} and by the redox system of the element M, MF_z/M_{Bi}. Nernst relations are used to express the potential relations as follows:

When the reducing element is Li:

$$E_{LM} = E°_{Li} + \frac{m}{z}\log\frac{a(LiF)^z}{a(Li)^z} = E°_{Li} + \frac{m}{z}\log\frac{x(LiF)^z}{x(Li)^z} + \frac{m}{z}\log\frac{\gamma(LiF)^z}{\gamma(Li)^z} \tag{8}$$

When the reducing element is metallic Th:

$$E_{LM} = E°_{Th} + \frac{m}{4}\log\frac{a(ThF_4)}{a(Th)} = E°_{Th} + \frac{m}{4}\log\frac{x(ThF_4)}{x(Th)} + \frac{m}{4}\log\frac{\gamma(ThF_4)}{\gamma(Th)} \tag{9}$$

and for the element M

$$E_{LM} = E°_{M} + \frac{m}{z}\log\frac{a(MF_z)}{a(M)} = E°_{M} + \frac{m}{z}\log\frac{x(MF_z)}{x(M)} + \frac{m}{z}\log\frac{\gamma(MF_z)}{\gamma(M)} \tag{10}$$

Then, the efficiency can be expressed as a function of the redox potential and of the solvation properties in the two phases. The final expressions are given below.

When the reducing agent is Li, by combining the relations 7, 8, and 10:

$$\mu(M/Li) = \frac{1}{1 + 10^{\lambda(M/Li)}} \quad \text{with} \tag{11}$$

$$\lambda(M/Li) = \frac{z}{m}\left(E°_{Li} - E°_{M}\right) - \log\Gamma_{M/Li} + \log\frac{\gamma(M)}{\gamma(Li)^z} + z\log\frac{x(LiF)}{x(Li)} + \log\frac{n(MS)}{n(LM)} \tag{12}$$

in this relation, $n(MS)$ and $n(LM)$ are, respectively, the number of moles of MS and of LM.

The term $\Gamma_{M/Li}$ represents the solvation in the MS. The expression of $\Gamma_{M/Li}$ in the case of Li as reducing element is

$$\log \Gamma_{\text{M/Li}} = \log \frac{\gamma(\text{MF}_z)}{\gamma(\text{LiF})^z} \tag{13}$$

When the reducing agent is Th, the following relations are established by combining relations 7, 9, and 10:

$$\mu(\text{M/Th}) = \frac{1}{1+10^{\lambda(\text{M/Th})}} \quad \text{with} \tag{14}$$

$$\lambda(\text{M/Th}) = \frac{z}{m}\left(E^\circ_{\text{Th}} - E^\circ_{\text{M}}\right) - \log \Gamma_{\text{M/Th}} + \log \frac{\gamma(\text{M})}{\gamma(\text{Th})^{z/4}} + \frac{z}{4}\log \frac{x(\text{ThF}_4)}{x(\text{Th})} + \log \frac{n(\text{MS})}{n(\text{LM})} \tag{15}$$

with

$$\log \Gamma_{\text{M/Th}} = \log \frac{\gamma(\text{MF}_z)}{\gamma(\text{ThF}_4)^{z/4}} \tag{16}$$

In relations 12 and 15 giving the efficiency of extraction, two kinds of parameters have to be distinguished.

- The parameters that are constants depending on redox and solvation properties: the standard potential and the activity coefficients in the two phases: E° and γ.
- The parameters that can be used to control and adjust the extraction process are the mole fraction of Li (or Th) in the LM, the volumes (or the number of moles) of the two phases, $n_{(\text{LM})}$ and $n_{(\text{MS})}$.

One remark concerning the mole fractions of LiF and ThF$_4$ has to be done. These parameters are involved in relations 12 and 15 and depend on the choice of the MS composition. As it will be demonstrated below, the activity coefficients of all the elements depends on the composition of the MS. Therefore, the activity coefficients in the metallic phase depend on the nature of the solvent metal.

The calculations of efficiency given below have been realized for the system LiF–ThF$_4$/Bi using estimations of activity coefficients given in the literature. For different melt composition and for the use of another LM, new calculations would have to be done.

Database establishment (lanthanides and actinides)

The calculations of the theoretical efficiency of extraction need the knowledge of the parameters involving in relations 12 and 15. Some of these parameters are redox standard potentials, and others are activity coefficients. This paper will present the database established to calculate the extraction efficiencies for two kinds of elements: lanthanides and actinides.

Analysis of bibliographic measurements

Extraction experiments have been performed by several authors using a BeF$_2$-based fluoride MS and different LM (especially Bi, Zn, and Cd). Distribution coefficients have been measured for several elements, several LMs, and various MS composition.

The only common points between these papers are the temperature of 873 K and the reducing element, which is always metallic Li.

The first part of this paper is the estimation of solvation data based on the combination of standard potentials—given in some thermodynamical database—activity coefficients in solvent metal experimentally measured and experimental distribution coefficients.

Distribution coefficient equations

The authors report in their paper the ratio of experimental distribution coefficients. The distribution coefficient is defined by the following relation:

$$\log\frac{D(\mathrm{M})}{D(\mathrm{Li})^z} = \log\frac{x(\mathrm{M})\,/\,x\!\left(\mathrm{MF}_z\right)}{x(\mathrm{Li})^z\,/\,x(\mathrm{LiF})^z} \tag{17}$$

A relation can be established combining relations 8 and 10 between the experimental measurements and a conditional potential $E^{\circ*}$, which depends on the activities of the elements in the MS.

The expression of $E^{\circ*}$ is

$$E^{\circ}{}^{*}{}_{\mathrm{M}} = E^{\circ}{}_{\mathrm{M}} + \frac{m}{z}\log\frac{\gamma\!\left(\mathrm{MF}_z\right)}{\gamma\left(\mathrm{LiF}\right)^z} = E^{\circ}{}_{\mathrm{Li}} + \frac{m}{z}\left[\log\frac{D(\mathrm{M})}{D(\mathrm{Li})^z} + \log\frac{\gamma\left(\mathrm{M}\right)}{\gamma\left(\mathrm{Li}\right)^z}\right] \tag{18}$$

In these relations, $E^{\circ*}$ depends on the activities of the elements in the metallic phase through the terms $\gamma(\mathrm{M})$ and $\gamma(\mathrm{Li})$ [$\gamma(\mathrm{M})$ and $\gamma(\mathrm{Li})$ being, respectively, the activity coefficients of M and Li in the metallic phase]. The potential $E^{\circ*}$ is expected to be not dependent on the nature of the metallic phase. To validate this calculation, $E^{\circ*}$ has been calculated combining experimental measurements performed using various LMs and activity coefficients reported in the literature for these LMs. Table 2 gathers the data available used to realize this comparison.

Table 2 Comparison of conditional potentials calculated for various solvent metals.

	La	Ce	Nd	Sm	Er	Li	Ref.
log($D(\mathrm{M})/D(\mathrm{Li})^z$) (Zn)	9.75 ± 0.47	10.0 ± 0.17	10.4 ± 0.23	6.38 ± 0.12	10.0 ± 0.61		[13]
log($D(\mathrm{M})/D(\mathrm{Li})^z$) (Cd)	9.45 ± 0.49	9.93 ± 0.14	9.78 ± 0.08	5.37 ± 0.25	7.75 ± 0.12		[13]
log($D(\mathrm{M})/D(\mathrm{Li})^z$) (Bi)	7.13 ± 0.20	7.67	7.66 ± 0.30	4.65 ± 0.17	5.85 ± 0.26		[13]
log γ(M) (Zn)	–9.24	–8.93	–8.97	–10.46	–6.85	–1.91	[14]
log γ(M) (Cd)	–6.99	–6.61	NA	NA	NA	–2.30	[14]
log γ(M) (Bi)	–11.77	–11.03	–10.78	–11.73	–8.61	–4.08	[14]
z (valence)	3	3	3	2	3		
$E^{\circ*}$ (Zn)	–5.15 ± 0.03	–5.12 ± 0.01	–5.10 ± 0.01	–5.54 ± 0.01	–4.94 ± 0.04		
$E^{\circ*}$ (Cd)	–4.98 ± 0.03	–4.93 ± 0.01	–	–	–		
$E^{\circ*}$ (Bi)	–5.08 ± 0.01	–5.0		–4.99 ± 0.02	–5.42 ± 0.01	–4.97 ± 0.02	

NA: not available. Several values of activity coefficients are reported in the literature but measured at a temperature lower than 873 K.
The distribution coefficients are measured for the system LiF–BeF_2/Bi–Li at 873 K.
The conditional potential values $E^{\circ*}$ are calculated using $E^{\circ}{}_{\mathrm{Li}} = -5.52$ V/F_2.

The value of $E^{\circ}{}_{\mathrm{Li}}$ is calculated from the Gibbs enthalpy of the following reaction:

$$\mathrm{LiF} \rightarrow \mathrm{Li} + 1\,/\,2\,\mathrm{F}_2\left(\mathrm{g}\right) \tag{19}$$

The Gibbs enthalpy is given by

$$\Delta G^{\circ} = 1\,/\,2 * G^{\circ}(\mathrm{F}_2) + G^{\circ}(\mathrm{Li}) - G^{\circ}\left(\mathrm{LiF}\right) = -nF\Delta E^{\circ} = nF\,(E^{\circ}{}_{\mathrm{F2}} - E^{\circ}{}_{\mathrm{Li}}) \tag{20}$$

where $E^{\circ}{}_{\mathrm{F2}}$ and $E^{\circ}{}_{\mathrm{Li}}$ represent, respectively, the standard potentials of the redox systems $\mathrm{F}_2(\mathrm{g})/\mathrm{F}^-$ and LiF/Li. Considering the redox system $\mathrm{F}_2/\mathrm{F}^-$ as the reference, the Gibbs enthalpy of the chemical reaction is given by

$$\Delta G^{\circ} = -nFE^{\circ}{}_{\mathrm{Li}} \tag{21}$$

Therefore, standard potential values (given against fluorine reference) can be calculated from the database of pure compounds.

The value of $E^{\circ}{}_{\mathrm{Li}}$ calculated by this way using HSC Chemistry 5.0 database [15] is –5.52 V/F_2.

Conditional potentials $E^{\circ*}$ have been calculated for several elements from experimental measurements obtained in the three systems LiF–BeF$_2$/Zn–Li, Cd–Li, and Bi–Li at 873 K (Table 2). The comparison of these values shows good agreement especially for Cd and Bi solvents. The conclusion is that the method proposed for the determination of conditional potentials from the experimental measurements in metallic solvents reported by Lebedev [14] leads to potential values with good accuracy.

Solvation properties in molten salts

Now the database establishment will be focused on systems using Bi solvent. Some experimental data [13,16,17] have been obtained for various MS compositions of LiF–BeF$_2$ and LiF–BeF$_2$–ThF$_4$. From the calculation of $E^{\circ*}_M$ (relation 18), it is possible to deduce the term log $\Gamma_{M/Li}$, which characterizes the solvation of MF$_z$ in a given solvent. The relation is

$$\log \Gamma_{M/Li} = \log \frac{\gamma(MF_z)}{\gamma(LiF)^z} = \frac{z}{m}\left(E^{\circ*}_M - E^{\circ}_M\right) \tag{22}$$

By combining relations 18 and 22, values of log $\Gamma_{M/Li}$ have been calculated from experimental measurements reported in the literature as a function of the mole fraction of LiF in the MS. The values of E°_M are calculated in the same way as E°_{Li} considering the Gibbs enthalpy of the following reaction:

$$MF_z \rightarrow M + z/2\ F_2(g) \tag{23}$$
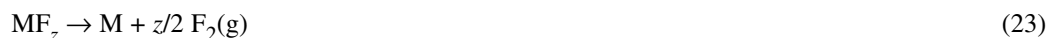
The standard potential is calculated using the Gibbs enthalpy of pure compounds of the database HSC Chemistry 5.0, and the values are given against the reference system F$_2$(g)/F$^-$.

$$\Delta G^{\circ} = z/2 * G^{\circ}(F_2) + G^{\circ}(M) - G^{\circ}(MF_z) = -zF\Delta E^{\circ} = zF\ (E^{\circ}_{F2} - E^{\circ}_M) \tag{24}$$

$$E^{\circ}_M = -\frac{\Delta G^{\circ}}{zF} \tag{25}$$

All the data used for the calculations of log $\Gamma_{M/Li}$ (by combining relations 18 and 22) are given in Table 3. Experimental results reported for some elements such as Eu, Np, Cm, Ra, and Cf are not considered because either activity coefficients in Bi or redox potential values are not available. Concerning Am, the activity coefficient in Bi is chosen equal to the activity coefficient of Pu in Bi. Indeed, a similar behavior have already been observed for Pu and Am in a metallic solvent of Al [18].

The variation of log $\Gamma_{M/Li}$ as a function of x(LiF) is reported in Figs. 3a and b. A linear variation is observed whatever the element considered. The slope measured depends on the valence of the element considered, and the following general relation can be deduced from the analysis of the straight lines of Fig. 3:

$$\log \Gamma_{M/Li} = a_M - 3.5 * z * x(LiF) \tag{26}$$

The term a_M is deduced from the fit of the straight lines given in Fig. 3 for the elements considered in the Table 3. For the other elements, an extrapolation was done using one experimental data {one point [x(LiF) – log $\Gamma_{M/Li}$]} and the characteristics of the straight line (eq. 26) can be deduced for several elements.

Table 4 reports all the terms a_M calculated, either by linear regression of the straight lines of Fig. 3 or by extrapolation using one point. The experimental measurements performed by Moriyama [13] in LiF–BeF$_2$ (66.7–33.3 mol %) was used for the values extrapolation of Gd, Tb, Dy, Sm, and Er.

Table 4 reports also the value of log $\Gamma_{M/Li}$ calculated using relation 26 for the melt composition LiF–ThF$_4$ (77.5–22.5 mol %) corresponding to the MSFR concept, the activity coefficients of the elements M in Bi [14,19], and the redox potentials calculated from eq. 25. These data will be used to calculate the extraction efficiencies.

Table 3 Calculation of log $\Gamma_{M/Li}$ as a function of the composition of the MS.

	Log $\chi(M)_{Bi}$ [4]	$E°_M$ (V/F$_2$)	x(LiF)	41**	50**	51**	56.9*	56.9**	60**	65**	66*	66.7**	69.2*	70**	72*	75*
La	−11.77	−5.12	log[D(La)/D(Li)^z]			8.40	8.234	8.23	7.83	7.32		6.92	6.770		6.628	6.367
			log $\Gamma_{La/Li}$			1.94	1.77	1.77	1.37	0.86		0.46	0.31		0.17	−0.09
Ce	−11.03	−5.08	log[D(Ce)/D(Li)^z]			8.76			8.04	7.53						
			log $\Gamma_{Ce/Li}$			2.35			1.63	1.12						
Nd	−10.78	−5.06	log[D(Nd)/D(Li)^z]										7.041		6.801	6.616
			log $\Gamma_{Nd/Li}$										0.53		0.29	0.10
Th	−7.18	−4.76	log[D(Th)/D(Li)^z]	13.44	12.44		10.979		11.16	10.16	9.731		9.437	9	9.082	8.652
			log $\Gamma_{Th/Li}$	5.02	4.02		2.56		2.74	1.74	1.31		1.02	0.58	0.66	0.23
Pa	−6.13	−4.36	log[D(Pa)/D(Li)^z]			15.82					13.304	13.32	12.758		12.467	12.298
			log $\Gamma_{Pa/Li}$			−0.79					−3.31	−3.29	−3.85		−4.15	−4.31
U	−3.93	−4.54	log[D(U)/D(Li)^z]								11.43		11.337		11.056	10.856
			log $\Gamma_{U/Li}$								2.72		2.63		2.35	2.15
Pu	−8.08	−4.66	log[D(Pu)/D(Li)^z]										10.316		9.979	
			log $\Gamma_{Pu/Li}$										−0.43		−0.76	
Am	−8.08	−4.69	log[D(Am)/D(Li)^z]										9.968		9.865	
			log $\Gamma_{Am/Li}$										−0.43		−0.53	

*Experimental data from ref. [16]; MS: LiF–BeF$_2$ (56.9–43.1 and 66–34 mol %) and LiF–BeF$_2$–ThF$_4$ (69.2–19.4–11.4, 72–16–12, and 75–13–12 mol %) at 873 K.
**Experimental data from ref. [17]; MS: various composition of LiF–BeF$_2$ at 873 K.
$E°$(M) are calculated from relation 25 using HSC Chemistry database [15].
Log $\Gamma_{M/Li}$ are calculated by combining relations 18 and 22.
The conditional potential values $E°*$ are calculated using $E°_{Li}$ = −5.52 V/F$_2$ [15].
The activity coefficient of Li in Bi at 873 K: log γ(Li)$_{Bi}$ = −4.08 [14].

Table 4 Values of a_M, log $\Gamma_{M/Li}$, and log $\Gamma_{M/Th}$ for x(LiF) = 77.5 mol % (calculated from relation 26), log γ(M)$_{Bi}$ (from refs. [14,19]), and $E°_M$ (from relation 25) for several elements at 873 K.

Element	La	Ce	Nd	Sm	Gd	Tb	Dy	Er	Th	Pa	U	Pu	Am
a_M	7.63	7.86	7.87	3.74	8.52	9.62	8.26	9.06	10.74	6.05	9.87	6.82	6.93
Log $\Gamma_{M/Li}$ for x(LiF) = 77.5 mol %	–0.51	–0.28	–0.27	–1.69	0.38	1.48	0.12	0.92	–0.11	–4.8	1.73	–1.32	–1.21
Log $\Gamma_{M/Th}$ for x(LiF) = 77.5 mol %	–0.43	–0.20	–0.19	–1.63	0.46	1.57	0.20	1.01	0	–4.69	1.82	–1.24	–1.13
Log γ(M)$_{Bi}$	–11.77	–11.03	–10.78	–11.73	–10.06	–9.59	–9.62	–8.73	–7.18	–6.13	–3.93	–8.08	–8.08
$E°_M$ (V/F$_2$)	–5.12	–5.08	–5.06	–5.34	–5.11	–5.14	–5.09	–5.09	–4.76	–4.36	–4.54	–4.66	–4.69

The activity coefficients γ(M)$_{Bi}$ are calculated from ref. [14] except for Tb and Dy [19].
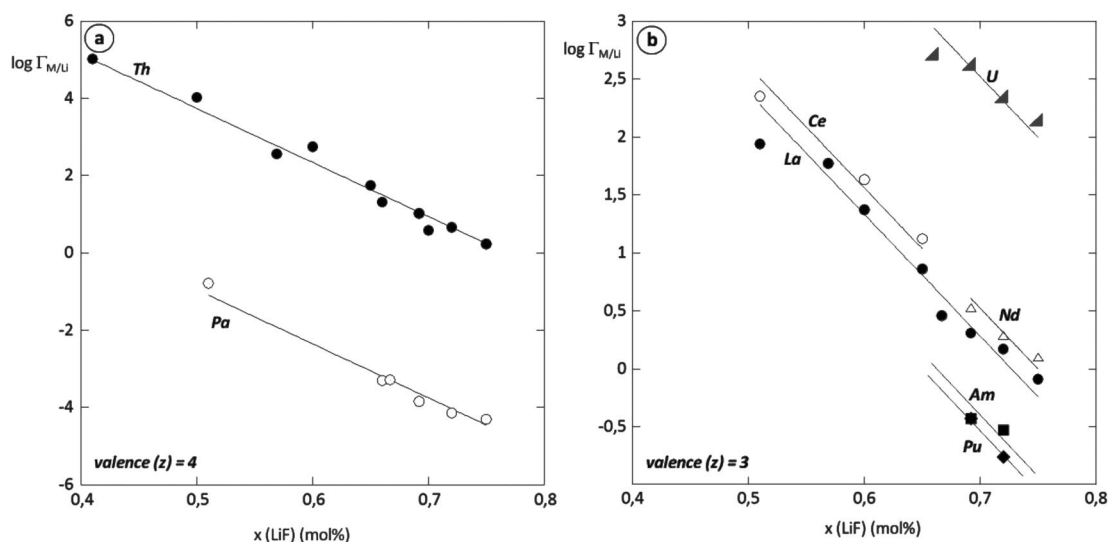
Fig. 3 Variation of log $\Gamma_{M/Li}$ as a function of x(LiF) calculated from analysis of the experimental results of Ferris [16] and Moriyama [17]. (a) For valence 4 elements; (b) For valence 3 elements.

To calculate the efficiencies μ(M/Li) and μ(M/Th) (respectively, from relations 11 and 14) as a function of the process parameters, the term log $\Gamma_{M/Th}$ has to be defined. Considering relations 13 and 16, the following relation is established:

$$\log \Gamma_{M/Th} = \log \Gamma_{M/Li} - \frac{z}{4} \log \Gamma_{Th/Li} \tag{27}$$

with

$$\log \Gamma_{Th/Li} = \log \frac{\gamma(ThF_4)}{\gamma(LiF)^4} \tag{28}$$

Table 4 reports the values calculated for log $\Gamma_{M/Th}$ for x(LiF) = 0.775.

Extraction efficiency calculations

Table 4 gathers all the data needed to calculate the efficiency of the reductive extraction in the systems LiF–ThF$_4$/Bi–Li and LiF–ThF$_4$/Bi–Th using relations 11 and 14. The values considered for the redox potential $E°_{Li}$ and the activity coefficient log γ(Li)$_{Bi}$ are, respectively, –5.52 V/F$_2$ [15] and –4.08 [14]. The mole fractions of LiF and ThF$_4$ are, respectively, 77.5 and 22.5 mol %.

Influence of the mole fraction of the reducing agent in Bi and of the ratio of liquid phase mole number

The influence of the concentration of the reducing agent in the solvent metal (expressed in mole fraction) is studied considering that the ratio of the number of mole n(MS)/n(LM) is equal to 1.

Case of the reducing agent is Li

Figure 4 shows the extraction efficiency as a function of the mole fraction of Li in Bi for a phase mole ratio equal to 1. This figure shows a selectivity between the extraction of actinides and lanthanides for a mole fraction of Li in Bi close to 10^{-3}. We observe also that for high concentrations of Li in Bi (typically 10 mol %), the extraction will be efficient for all the elements, and therefore the selectivity required during the first extraction stage (actinides extraction) will not be achieved.
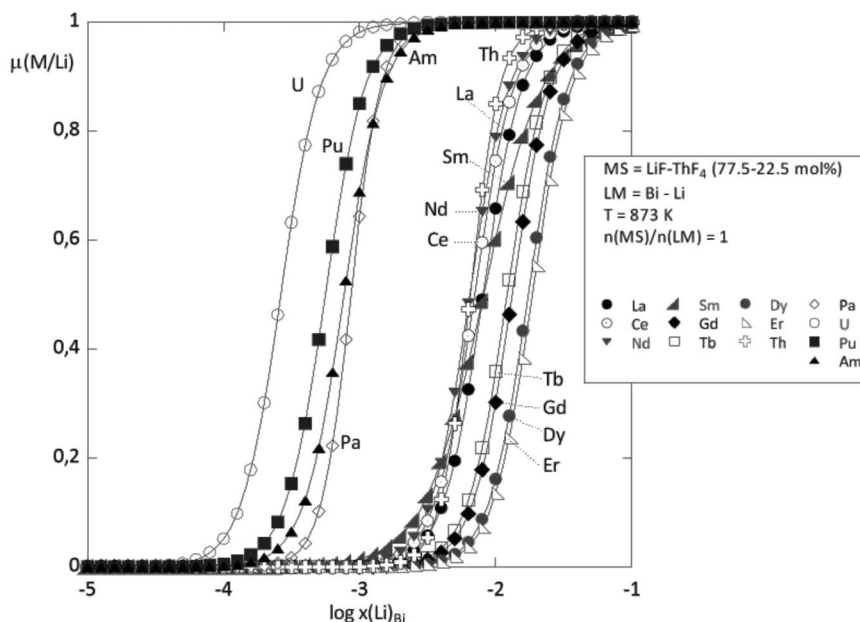
Fig. 4 Extraction efficiency calculated for various elements between LiF–ThF$_4$ and the metallic solvent Bi–Li as a function of log x(Li)$_{Bi}$.

Consequently, using these curves, it will be possible to define, in agreement with the neutronic constraints, some optimized process parameters to perform both the two successive extractions: low amounts of Li in Bi to achieve the first step and high amounts of Li in Bi to achieve the second step.

The selectivity is defined by

$$\log S_{M2/M1} = \log D(M_2) - \log D(M_1) \tag{29}$$

By combining relations 8, 10, 13, and 17, it can be observed that the selectivity of extraction between two elements M_1 and M_2 (with valence, respectively, equal to $z1$ and $z2$) is not dependent on the process parameters. The following relation can be established:

$$\log S_{M1/M2} = \frac{z1}{m}\left(E^{\circ}_{M1} - E^{\circ}_{Li}\right) - \frac{z2}{m}\left(E^{\circ}_{M2} - E^{\circ}_{Li}\right) + \log \frac{\Gamma_{M1/Li}}{\Gamma_{M2/Li}} + (z1 - z2)*\log\gamma(Li) +$$
$$\log \frac{\gamma(M_2)}{\gamma(M_1)} + (z2 - z1)*\log \frac{x(LiF)}{x(Li)} \tag{30}$$

Obviously, and considering relation 27, the expression of selectivity when the reducing agent is Th is the following one:

$$\log S_{M1/M2} = \frac{z1}{m}\left(E^{\circ}_{M1} - E^{\circ}_{Th}\right) - \frac{z2}{m}\left(E^{\circ}_{M2} - E^{\circ}_{Th}\right) + \log \frac{\Gamma_{M1/Th}}{\Gamma_{M2/Th}} + \frac{(z1 - z2)}{4}*\log\gamma(Th) +$$
$$\log \frac{\gamma(M_2)}{\gamma(M_1)} + \frac{(z2 - z1)}{4}*\log \frac{x(ThF_4)}{x(Th)} \tag{31}$$

If the valence of the two elements M_1 and M_2 is the same, the selectivity does not depend on the mole fraction of the reducing agent in the metallic phase. On the contrary, when the valence is different, the selectivity will vary with the composition of the metallic phase.

As an example, the logarithm of selectivity calculated using relation 30 for Pu and Nd is equal to 3, which is characteristic of a high selectivity.

The selectivity is the same whatever the value of $x(Li)_{Bi}$. But for $x(Li)$ equal to 10^{-3}, 85 % of Pu is extracted for only 0.37 % of Nd. For $x(Li) = 10^{-1}$, 99.97 % of Nd is extracted and 100 % of Pu. So, in this case, Nd and Pu are both extracted even if the selectivity is high. Therefore, in the case of separation of elements with the same valence, the one selectivity calculation is not a good criterion to define the process parameters, and it is necessary to calculate the extraction efficiency.

The influence of phase mole number ratio (equivalent to phases volume ratio) is shown in Fig. 5 for two different concentrations of Li in Bi [log $x(Li)_{Bi} = -1$ and -4]. The influence of the mole fraction of reducing agent on the selectivity of extraction between the two elements Sm and Pa (respectively, of valences 2 and 4) is clearly shown on these curves. For a mole fraction of Li in Bi of 10^{-1} and a mole ratio higher than 1, a high separation factor is observed between Sm and Pa (Fig. 5a). On the contrary, for a mole fraction of Li in Bi of 10^{-4}, the two elements are extracted with the same efficiency (Fig. 5b).
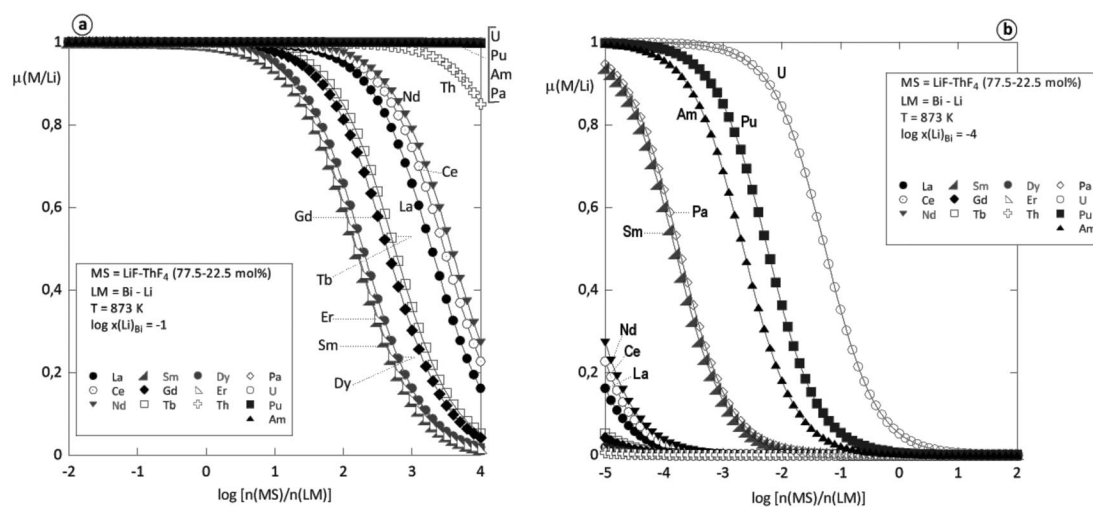

Fig. 5 Extraction efficiency calculated for various elements between LiF–ThF$_4$ and the metallic solvent Bi–Li as a function of log $n(MS)/n(LM)$. (a) $x(Li)_{Bi} = 10^{-1}$; (b) $x(Li)_{Bi} = 10^{-4}$.

The selectivity $S(Pa/Sm)$ has been calculated as a function of the mole fraction of reducing agent (Li or Th) in the metallic phase (Fig. 6). The selectivity increases with the mole fraction of reducing agent in Bi. That is in agreement with relations 30 and 31. The highest selectivity is obtained with Th for the highest concentration of reducing agent in Bi.
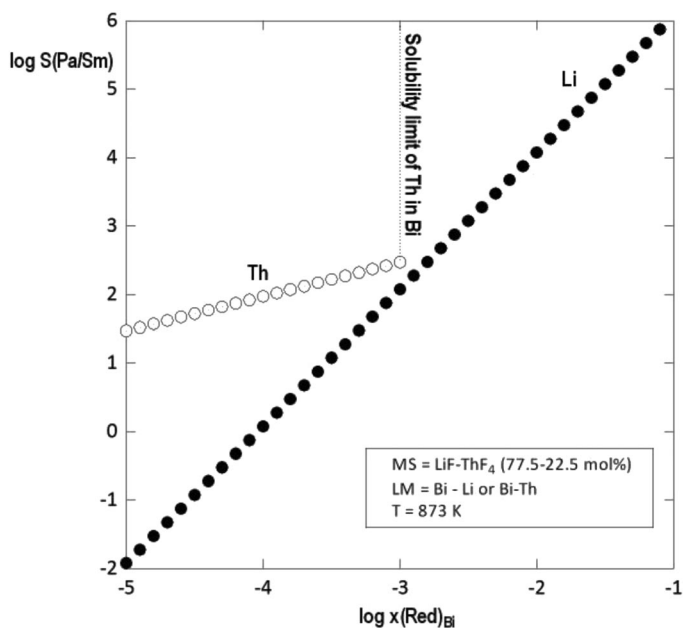
Fig. 6 Selectivity (Pa/Sm) as a function of the mole fraction of reducing element (Li or Th) in Bi.

Case of the reducing agent is Th

Figure 7 presents the efficiency calculated for various elements as a function of the mole fraction of Th in Bi for a ratio $n(MS)/n(LM)$ equal to 1. It clearly appears that, because of the low solubility of Th in Bi, the extraction of lanthanides cannot be achieved in these conditions.
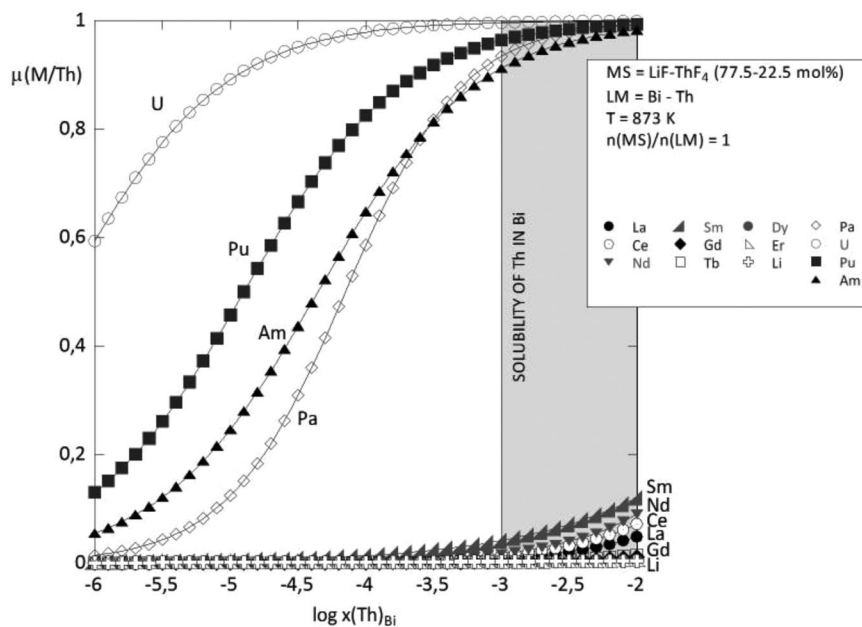

Fig. 7 Extraction efficiency calculated for various elements between LiF–ThF$_4$ and the metallic solvent Bi–Th as a function of log $x(Th)_{Bi}$ for a ratio $n(MS)/n(LM)$ equal to 1.

To perform this extraction using Th as the reducing agent, it is necessary to drive the extraction from the MS to the metallic solvent by increasing the volume of the metallic phase. The calculation of efficiency as a function of the phase mole ratio is given in Fig. 8.
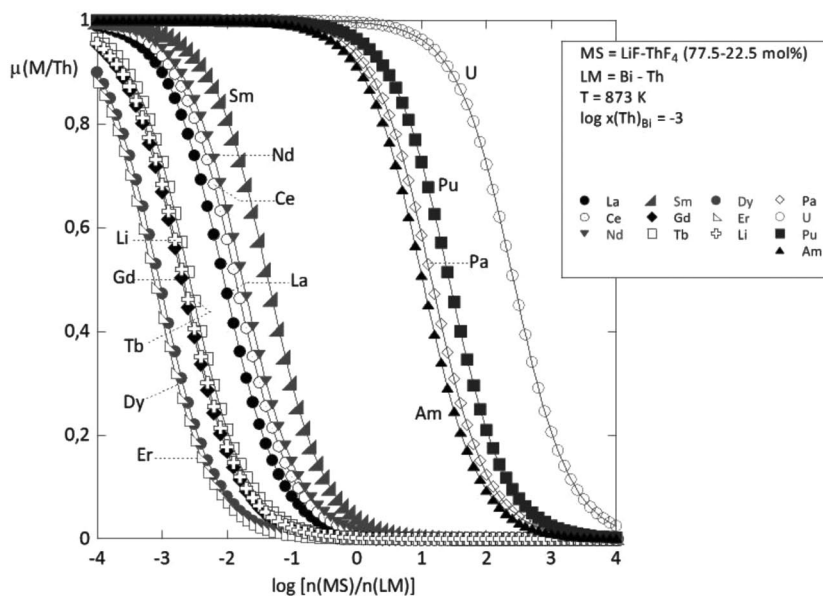

Fig. 8 Extraction efficiency calculated for various elements between LiF–ThF$_4$ and the metallic solvent Bi–Th as a function of $n(MS)/n(LM)$ for $x(Th)_{Bi}$ equal to 10^{-3}, the solubility limit.

The first step of extraction (corresponding to a selective and efficient actinide extraction) can be performed at the solubility of Th in Bi and for a phase mole ratio of 1. The second step (efficient lanthanide extraction) can be achieved by increasing the volume of LM. In this case, the efficiency of lanthanide extraction increases and an optimization of the process parameters can be proposed. In several cases, the efficiency is not very high and it is necessary to do several stages of the extraction to remove all the elements from the MS.

DISCUSSION AND CONCLUSION

This study has shown that the knowledge of selectivity and distribution coefficient is not enough to optimize the parameters of successive reductive extractions to achieve firstly selective and efficient actinide extraction and secondly, efficient lanthanide extraction. The calculation of efficiency leads to a best understanding of the role of the parameters involved in the process.

The relations established combined with the analysis of the experimental results lead to the calculation of the extraction efficiencies for various elements in the systems LiF–ThF$_4$/Bi–Li and Bi–Th. Using these relations, it is possible to optimize the extraction process parameters as a function of the neutronic constraints of the reactor, which assess the level of fuel salt cleaning. Indeed, due to the fast neutron spectrum, the formation of lanthanides in the reactor core is not a major problem (compared to the MSBR concept, which works with a thermal neutron spectrum [5]) for the neutronic point of view, but if the concentration becomes too high, lanthanides will precipitate because of their low solubility in the fuel fluoride melt. Then it is necessary to remove them regularly.

When the reducing agent is Li, it is possible to perform the two extraction steps (actinides and lanthanides) by changing the concentration of Li in Bi in the two steps. The calculations have shown that the extraction is not really improved by changing the ratio of phase volumes.

On the contrary, the use of Th as reducing agent requires one to vary the ratio of phase volume to achieve the extractions because of the low solubility of Th in Bi. The limitation in the concentration of reducing agent is characterized by the impossibility of extracting lanthanides with an optimized efficiency. Therefore, the only possibility is to increase the volume of the metallic phase in order to force the extraction reaction from the salt to the metallic solvent.

Therefore, the extraction parameters for the two extraction steps can be adjusted, whatever the reducing agent considered, by changing the mole fraction of reducing agent in the case of Li and the phase mole ratio in the case of Th.

The extraction efficiency curves calculated and presented in this paper show that it is difficult in only one stage to remove all the actinides and/or all the lanthanides from the MS. To improve the efficiency and to achieve a full extraction will require several extraction stages. It means that the LM after one extraction is cleaned and put back in contact with the MS. Then, after each contact, the concentration of the extracted elements decreases in the MS. The objective is to remove the elements with an efficiency higher than 99.99 % and with a high selectivity (in the case of actinide removal).

The total amount of moles of the element M extracted is given by the following relation:

$$n_{ext} = n_{init} * \{1 - [1 - \mu(M)]^{nbs}\} \tag{32}$$

in which n_{ext} and n_{init} are, respectively, the extracted and the initial number of moles of the element M and "nbs" represents the number of extraction stages.

The number of moles that are not extracted during the process is given by the relation:

$$n_{Next} = n_{init} * [1 - \mu(M)]^{nbs} \tag{33}$$

Combining the relations of efficiency and relation 32, the optimization of the extraction process parameters, nature and concentration of the reducing agent, and number of moles in each phase can be achieved. That can be done taking into account the neutronic constraints of the reactor, which assess the level of fuel salt cleaning.

LIST OF NOMENCLATURE

$a(M)$	activity of the compound M with $a(M) = x(M)* \gamma(M)$
$\gamma(M)$	activity coefficient of the compound M (in LM or MS)
$x(M)$	mole fraction of M in LM or MS
$n(M)$	number of moles of element M in solvent metal
$n(MF_z)$	number of moles of MF_z in the MS
$\mu(M)$	extraction efficiency of M
$E°_X$	standard potential of the element X
z	valence of the element M
m	$2.3RT/F$ with R the ideal gas constant, T the temperature, and F the Faraday constant
$n(MS)$	number of mole of the MS phase ($LiF–ThF_4$)
$n(LM)$	number of moles of the LM phase (Bi)
$E°*_X$	conditional potential
nbs	number of extraction stages
n_{init}	number of moles initially in the MS before the first extraction stage
n_{ext}	number of moles extracted
n_{Next}	number of moles not extracted

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