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A computational tool for selective pyrochemical processes based on molten salts in nuclear industry

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Abstract

In the framework of the development of pyrochemical techniques for future nuclear systems, we propose to investigate the development of computational tools in order to optimise the control of chemical parameters for pyrochemical processes (electrodeposition, oxide selective precipitation, liquid/liquid reductive extraction). This paper discusses how potential–oxoacidity diagrams can be automatically constructed and gives illustrative examples on how these diagrams may help in the choice and the optimisation of pyrochemical processes.

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1. Introduction

The development of pyrochemical techniques for future nuclear systems is currently under investigation. Salts are generally chloride or fluoride mixtures. Molten salt mixtures could be used either as a medium for the reprocessing of spent fuels, or as a fuel itself in the case of a Molten Salt Reactor (MSR) concept. MSR is a concept of nuclear reactor in which the fuel, composed of a thorium fluoride dissolved in a molten fluoride mixture, is liquid and circulates continuously through the core. One of the main advantages of the concept is the on-line reprocessing the fuel by deviation of a small part of the salt in a dedicated reprocessing unit. The major difficulty is the extraction of lanthanides, necessary because of their high neutronic cross-section in the thermal neutron spectra. Our work deals only with fluoride mixtures, since chloride salts are not suitable for MSR application (chloride salt are not adapted to the thermal spectra of neutrons in the core).

Such innovative reprocessing methods can be rationally conceived via a thermodynamic analysis based on a deep understanding of the actinide and lanthanide chemistry in these media [1]. In that field we are engaged for some years in a large research programme, including the development of computational helps for the prediction of chemical reprocessing of nuclear fuels and wastes. In comparison to existing aqueous technologies, the number of controlling parameters is much higher in the case of molten salt technology and most of them are generally unknown (activity coefficients in different phases, formation of mixed compounds together with the solvent, etc.). Our studies are devoted both to the prediction and the assessment of reprocessing processes involving separation steps such as, e.g., liquid/liquid reductive extraction or electrolytic extraction via liquid or solid metallic cathodes. We therefore have focussed our activities on the thermodynamic selectivity and efficiency of these elementary steps.

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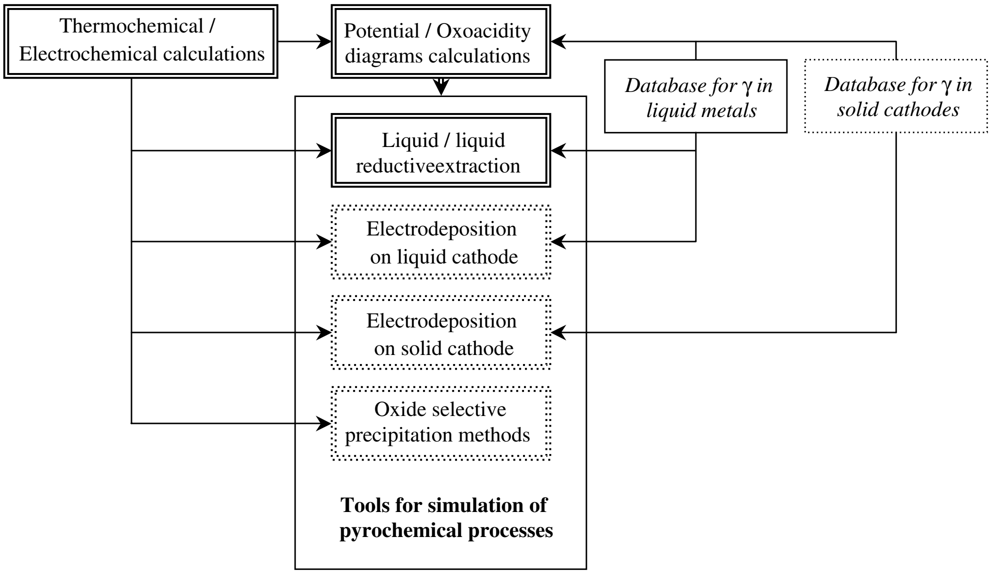

Fig. 1. General structure and objectives of computational helps. In dash lines: currently in progress.

We have first to determine the relevant stability constants deduced from the corresponding thermochemical data. For that purpose, powerful commercial software such as, e.g., FACTSAGE [2] or HSC[1] can be used.

In order to have an integrated computational tool (adapted to the subsequent analysis of pyrochemical separations), we have preferred to develop a code working with a set of independent databases (depending on the nature and composition of melt and metallic solvents), favouring the further development of computational routines dedicated to separation steps for specific pyrochemical treatments. The scheme of Fig. 1 gives an overview of all the planned routines. Liquid/liquid reductive extraction routines have been already computed and results have been presented [3].

This work deals with the first part of our task, i.e., the development of thermochemical routines in order to automatically establish relevant potential–oxoacidity diagrams from which the basis of new processes can be conceived. This paper describes the thermodynamic models used in calculations, the methods we used to solve and to draw diagrams, and an example of interpretation is given.

2. Potential–oxoacidity diagrams: general considerations

Potential–oxoacidity diagrams represent the stability areas of compounds in a molten salt depending on (i) the electrochemical potential (y-axis) and (ii) the amount of oxides (x-axis). The electrochemical potential can be controlled in a salt by different means, including the control of the relative amounts of multivalent soluble compounds, the control of the composition of the cover gas and the use of a solid or liquid electrode. The oxoacidity can be controlled by a gas bubbling technique or by addition of a fixed amount of a strong oxide donor.

Oxides are present in the melt under the form of solvated O^{2-} anions. The diagram should be built using the activity of O^{2-} anions in the molten salt, but its interaction with the components of the fluoride mixture are generally unknown, therefore thermochemical calculations cannot be performed. To draw the diagram, the activity of oxides can be represented by the activity of an oxide compound. In order to have a common reference for a larger number of mixtures as possible, we decided to use the most used component in molten mixtures for nuclear applications, i.e., LiF and its oxide Li_2O.

The electroactivity and oxoacidity domains greatly depends on the molten salt composition. The upper limit is the oxidation of O^{2-} to O_2, in the main part of the oxoacidity domain, except on the very oxoacidic side, where the limitation comes from the oxidation of F^- to F_2 (but it does not appear on the diagrams presented in this paper, since we have limited the oxoacidity range).

The lowest electrochemical potential in the melt is reached when the first cation M of the solvent began to be reduced. These limits can be estimated from the thermochemical data, by writing the corresponding chemical equations:

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[1] HSC Chemistry is a commercial software including a thermochemical database, developed and sold by Outukumpu, Finland. See http://www.outokumpu.com/hsc for more details.

$$Li_2O + F_2\ (g) = 1/2O_2\ (g) + 2LiF \tag{1}$$

$$M + x/2F_2\ (g) = MF_x \tag{2}$$

Using the Nernst equation for the reactions (1) and (2), the limits of the diagrams for a given molten salt mixture are given by Eqs. (3) and (4):

$$E = \frac{\Delta G^r_{(1)}}{2F} - 2303\frac{RT}{2F}\log\frac{a_{Li_2O}}{a^2_{LiF}}, \tag{3}$$

$$E = \frac{\Delta G^r_{(2)}}{nF} - 2303\frac{RT}{nF}\log a_{MF}. \tag{4}$$

In which, $\Delta G^r_{(1)}$ and $\Delta G^r_{(2)}$ are the Gibbs energies of reactions (1) and (2), F is the Faraday's constant and R is the ideal gas constant. The activity of LiF is estimated by using the Raoult's law. Since the oxidation of fluorine anions into gaseous fluorine is the reference for the calculation of all equilibrium potentials, this potential is $E(F_2(0.1\ MPa)/F^-) = 0$ V.

3. Operating flow sheet of the computational routine

All computational routines have been developed with Labview 7.0. The operating flow sheet of our tool is presented in Fig. 2 and shows three major steps for the whole calculation process:

1. Selection of compounds – database for Gibbs energies of pure compounds
   The main parameters of the calculation are chosen, including the studied element, the temperature and

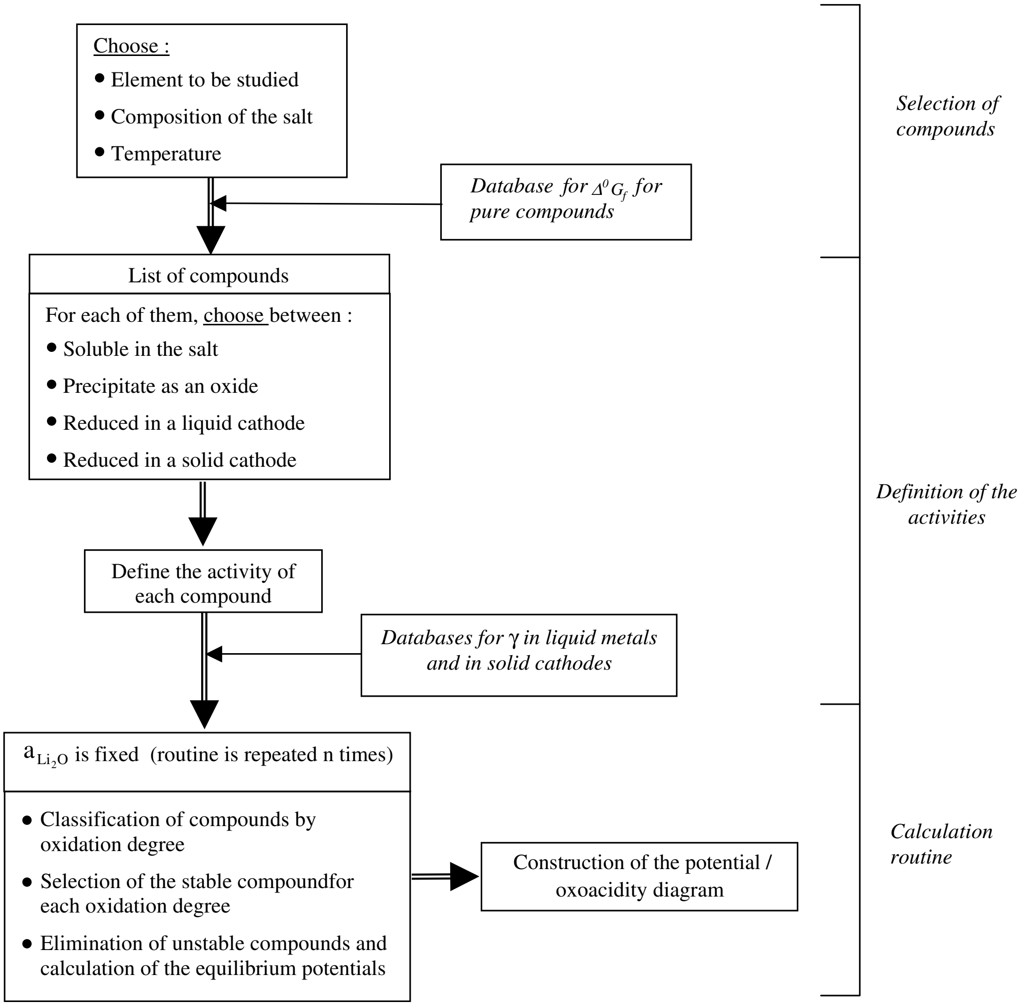

Fig. 2. Operating flowsheet for the calculation of the potential–oxoacidity diagram.

the molten salt composition. All the available compounds are selected and their thermochemical data are extracted from the database, i.e., the enthalpy H, the entropy S, the reference temperature, and the heat capacity C_P, calculated by a four parameters law $C_P = A + B\cdot T + C/T^2 + D\cdot T^2$. Each user can compute or provide his own database. For this study, data come from the HSC Chemistry version 5.1 database.[1]

2. Definition of the activity of each compound
   The activity is defined, depending on the state of the compound, i.e., pure solid, dissolved in the salt or dissolved in a liquid metal. For the elements dissolved in molten salt, activity coefficient (that vary from 1 to 10) and concentration are given by the user. For the elements dissolved in liquid metals, the activity is calculated from its molar fraction in the liquid metal and its activity coefficient γ, calculated from a separate database (vary from 10^{-14} to 10^{-6}). We assumed $\log\gamma = A + B/T$, where γ stands for the activity coefficient and T for the temperature. The activity coefficient model is sufficient in this case, because the amount of reduced element in the liquid metal phase is generally low (few mol.%). We use in this study data reported by Lebedev [4] and estimated at the saturation point of the element in the liquid metal phase. It has been demonstrated that the error made by taking the activity coefficient at the saturation point is low [5].
3. Calculation routine of the potential–oxoacidity diagram
   The main principle of the algorithm is to divide the diagram into vertical lines. For each of them, the oxoacidity potential is then fixed and the routine eliminates the unstable compounds and calculates the equilibrium potentials, based on the following general equation of the possible reactions:

$$\begin{aligned} &l\cdot \mathrm{M}^1_x\mathrm{M}^2_i\mathrm{O}_j\mathrm{F}_k - i\cdot \mathrm{M}^1_y\mathrm{M}^2_1\mathrm{O}_m\mathrm{F}_n + (i\cdot m - l\cdot j)\cdot \mathrm{Li_2O}\\ &\quad + 2\cdot(l\cdot j - i\cdot m)\cdot \mathrm{LiF} + (i\cdot y - l\cdot x)\cdot \mathrm{M^1F}\\ &\quad + \left(i\cdot m - l\cdot j - \frac{l\cdot k - i\cdot n + i\cdot y - l\cdot x}{2}\right)\cdot \mathrm{F_2}\ (\mathrm{g})\\ &\quad = 0 \end{aligned}$$

   The increment between each line is given by the user and represents the precision of the calculation. A value of 0.01 is largely sufficient and gives very short calculation times.

At the end of the calculation process, the routine gives a set of lists of compounds and equilibrium potentials, corresponding to a vertical grid of the diagram. Based on these data, a routine draws the diagram via the graphic interface.

4. Examples

In the frame of the development of future nuclear systems, pyrochemical treatment of fuels is under consideration for solid fuels reprocessing, e.g., for Gas Fast Reactors fuels, or for on-line reprocessing of the MSR fuel. In this latter case, the activity of oxide compounds is very low in the reactor part to avoid the precipitation of UO_2, but it can be controlled independently in the reprocessing unit if needed, especially in the case of a batch reprocessing process.

For both applications, a two-step process is foreseen, corresponding (i) to the selective extraction of actinides to be reprocessed and sent back to the reactor (i.e., a dedicated burner or the core of a MSR) and (ii) to the extraction of lanthanides from the molten salt, for purification of the salt. Either for the spent solid fuels reprocessing or for the on-line treatment of the MSR fuel, all pyrochemical techniques can be used, including liquid/liquid reductive extraction, electrolysis on solid or liquid cathode and oxide selective precipitation, etc. All these techniques are based on either on electrochemical reactions or on oxoacidic–oxobasic reactions. As an example of the kind of information could be derived from potential–oxoacidity diagrams, we interpret the diagrams presented in Fig. 3 for Pu, U and Ce in 40 mol.% LiF/60 mol.% NaF ($T_m = 925$ K), calculated at 953 K, assuming that the activity of dissolved compounds in the salt is 1 and mole fraction of element reduced in liquid cathode is 1 mol.%. We assumed that the activity of LiF and NaF are equal to their respective molar fractions in the mixture (Raoult's law). In this case, sodium is the more reducible cation in the mixture and is limiting the electroactivity domain of the salt, whereas Li^+ is the more oxoacidic compound and is limiting the oxoacidity domain at $a_{Li_2O} = 1$.

Diagrams exhibit three major areas:

1. Oxobasic media (high activities of Li_2O)
   In this area, all the compounds are precipitated as oxides. This domain should be avoided, unless we envisage to purify the salt completely without any An/Ln separation.
2. Oxoacidic media (low activity of Li_2O)
   In this area, no oxides or oxyfluoride compounds are formed in the salt, and electrochemical potentials do not depend on the activity of Li_2O in the salt. This is the ideal domain to perform electrochemical reductions.
3. Intermediate media
   In this area, some oxides or oxyfluoride compounds are formed. The electrochemical potentials are strongly dependent on the activity of Li_2O. Electroreduction in this area can be interesting in some cases, since it could lead to the reduction of oxyfluoride

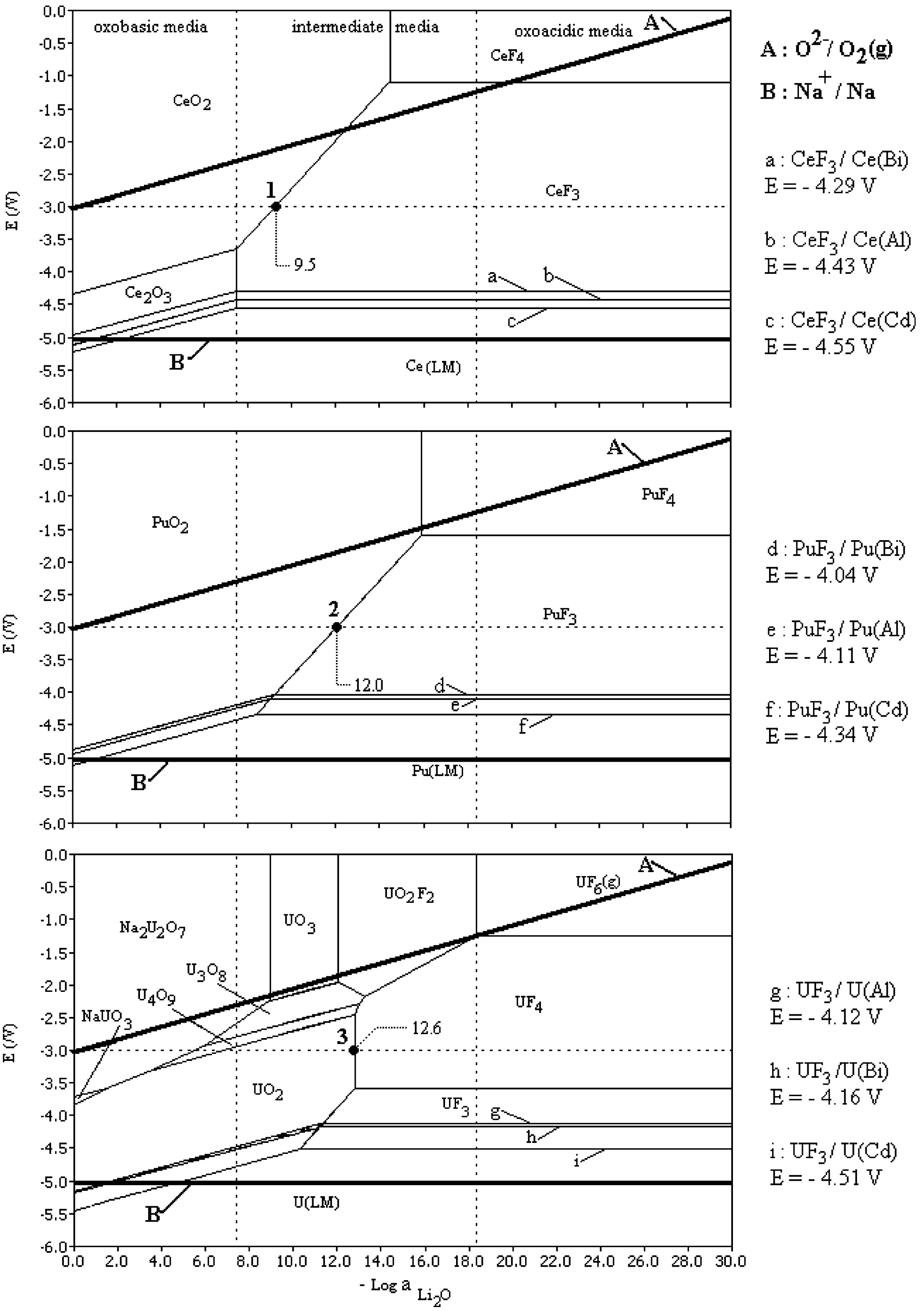

Fig. 3. Potential–oxoacidity diagrams of Pu, U and Ce in 40 mol.% LiF/60 mol.% NaF at 953 K, assuming activities of dissolved compound = 1 and mole fraction of reduced elements in liquid metal cathode = 1 mol.%. The activity of LiF is taken as its molar fraction.

compounds as solid oxides, that could be used directly to refabricate fresh fuels. This domain is also the more interesting one for the selective precipitation of oxides.

4.1. Extraction of U and Pu by electroreduction on a liquid cathode

The behaviour in the presence of liquid Cd, Bi and Al cathodes is compared for Ce, U and Pu (lines a–i in Fig. 3), and the reduction potentials for each compound on each liquid cathode are indicated in Table 1, for the more oxoacidic side of the diagram. As a difference of at least 150 mV is admitted as sufficient to selectively separate two compounds, the use of Cd as a liquid cathode would lead to a selective extraction of Pu (Table 1), whereas the use of Al as a liquid cathode would lead to a co-extraction of Pu and U, with Ce remaining in the mixture. The use of Al as a liquid cathode for An/Ln separation has been evaluated experimentally and results are consistent with our calculations [6].

Table 1
Reduction potentials (V) of Pu, U and Ce in liquid Cd, Bi and Al at 953 K

	Cd	Bi	Al
Pu	−4.34	−4.04	−4.11
U	−4.51	−4.16	−4.12
Ce	−4.55	−4.29	−4.43

Activity of dissolved compounds in the salt = 1 and 1 mol.% element dissolved in the liquid metal.

For MSR application, the presence of thorium tetrafluoride must be taken into account, since it limits the electroactivity domain. Fig. 4 exhibits the behaviour of Ce in 54.5 mol.% LiF/13.5 mol.% NaF/32 mol.% ThF_4 (T_m = 763 K) on Al, Bi and Cd liquid cathodes at 953 K. The behaviour of thorium from the molten salt solvent is superposed in bold lines (lines C, D and m) and exhibits a very similar behaviour both for Al and Bi cathodes. Cd cathode were not calculated because of a lack of data on the Th/Cd system. From the position in Fig. 4 of lines k and m , and j and m, the selective extraction of Ce by electroreduction is not possible. These evaluations are first approaches that should be completed to take into account the real concentrations of the elements in the melt. The temperature of the process should also be optimised.

4.2. Extraction of (U, Pu) by oxide selective precipitation

In the intermediate area of the diagram, it is possible to play on the oxoacidity of the molten salt to selectively separate the compounds by oxide precipitation. At a electrochemical potential of −3.0 V and an activity of Li_2O at $10^{-12.00}$ (point 2 in Fig. 3), Ce is still soluble in the salt (point 1 is not yet reached), whereas U and Pu are precipitated, respectively, as UO_2 and PuO_2 (points 2 and 3). At this point, the activity of Li_2O required for the precipitation of CeO_2 is more than

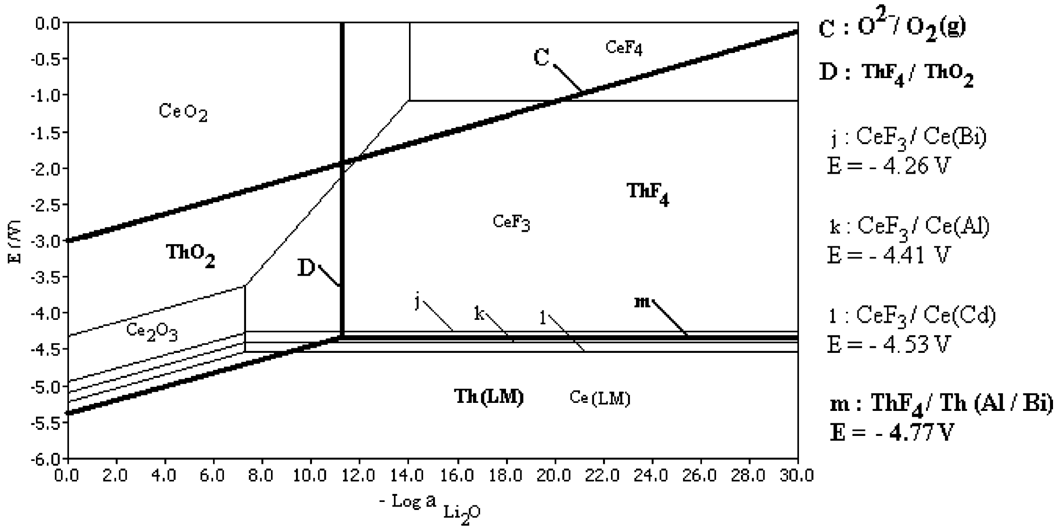

Fig. 4. Potential–oxoacidity diagram of Ce in 54.5 mol.% LiF/13.5 mol.% NaF/32 mol.% ThF_4 at 953 K, assuming activities of dissolved compound = 1 and mole fraction of reduced elements in liquid metal cathode = 1 mol.%. The activity of LiF is taken as its molar fraction. Electroactivity and oxoacidity domains are limited, respectively, by the reduction of Th from the salt (potential calculated taken the activity of ThF_4 as its molar fraction) and the formation of ThO_2.

two orders of magnitude higher (difference between points 1 and 2), so that we can expect the formation of a mixed oxide of U and Pu, i.e., $(U,Pu)O_2$, with Ce remaining in the salt as CeF_3.

As far as MSR application is concerned, the oxoacidity domains is limited by the precipitation of ThO_2 (line D in Fig. 4). As a consequence, we expect a co-precipitation of PuO_2, UO_2 and ThO_2, with Ce remaining in the salt, so that it cannot be precipitated until all the ThF_4 will be converted as ThO_2.

Of course, a realistic analysis has to take into account the real concentrations and activities in the melt to be reprocessed. The value of the operating temperature remains to optimised. Obviously, experiments are necessary *in fine* to validate these approaches.

5. Conclusions

A program has been launched to better understand the chemistry of lanthanides and actinides in molten fluoride mixtures. This program includes the development of computational helps with the aim to give predictive ideas concerning the most promising pyrochemical techniques, with a thermodynamic point of view.

We have shown that a general formulation of chemical equations in a molten salt mixture can be used as a basis for the development of computational routines for the construction of potential–oxoacidity diagrams in molten fluorides. This tool includes basic thermochemical data as well as databases for activity coefficients in liquid metals and melts. Such a structure allows us to further develop simulation tools for specific pyrochemical techniques, including electroreduction on liquid or solid cathodes, oxide selective precipitation or liquid/liquid reductive extraction.

Examples show how it is possible to use these equilibrium diagrams and make a first approach of a process, by optimising the conditions under which the best results may be obtained. We showed that the use of a Cd cathode would lead to a selective extraction of Pu by electroreduction, and the use of Al would lead to a co-extraction of U and Pu. We also show how to optimise the conditions of an oxide precipitation process to optimise its selectivity. Finally, we showed that the presence of thorium in the MSR would lead to significant difficulties for the extraction of lanthanides.

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