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Lanthanides extraction processes in molten fluoride media: Application to nuclear spent fuel reprocessing

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ABSTRACT

This paper describes four techniques of extraction of lanthanide (Ln) elements from molten salts in the general frame of reprocessing nuclear wastes; one of them is chemical: the *precipitation* of Ln ions in insoluble compounds (oxides or oxyfluorides); the others use electrochemical methodology in molten fluorides for extraction and measurement of the progress of the processes: first *electrodeposition* of pure Ln metals on an inert cathode material was proved to be incomplete and cause problems for recovering the metal; electrodeposition of Ln in the form of alloys seems to be far more promising because on one hand the low activity of Ln shifts the electrodeposition potential in a more anodic range avoiding any overlapping with the solvent reduction and furthermore exhibit rapid process kinetics; two ways were examined: (i) *obtention of alloys* by reaction of the electroreducing Ln and the cathode in Ni or preferably in Cu, because in this case we obtain easily liquid compounds, that enhances sensibly the process kinetics; (ii) *codeposition* of Ln ions with aluminium ions on an inert cathode giving a well defined composition of the alloy. Each way was proved to give extraction efficiency close to unity in a moderate time.

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1. Introduction

Since the beginning of the nineties, the reprocessing of nuclear wastes has become a priority for most of the nations using nuclear energy for electricity production. Partitioning and transmutation (P&T) concepts offer the possibility to reduce the volume and the long-term radiotoxicity of nuclear wastes, by recycling of the radiotoxic elements (U and higher actinides Np, Pu, Am, Cm). In these concepts, the separation of the actinides (An) from the fission products is crucial. For this purpose, different pyrochemical separation techniques have been and continue to be investigated, and most of them involve fluoride or chloride molten salt solvents [1]. Molten salts meet indeed a lot of requirements regarding the management of nuclear materials, including neutronic properties (low neutron cross-section for the solvent components, radiation stability) and chemical properties (high solubility of fuel components).

Electrorefining is the most developed pyrochemical separation process used in the USA for sodium-cooled fast breeder reactor metallic fuels in the Integral Fast Reactor (IFR) concept. In this process, uranium is separated from the bulk of fission products by electrolysis in a molten salt electrolyte onto a solid inert cathode, and further developments aim to simultaneously recover U, Pu and the minor An by electrorefining onto a liquid Cd cathode, leaving fission products in the salt phase [2]. Pyroprocessing technologies also appear suitable for recovering and recycling An from spent fuels from Light Water cooled Reactors (LWR), provided that a first step of fuel reduction into metal is performed [3]. For this purpose, various separation systems are also being developed such as reductive extraction of An into a molten Al solvent in fluoride media [4] and electrodeposition or codeposition of An onto solid Al cathodes in a molten chloride salt [5].

On top of these P&T concepts, the Molten Salt Reactor, which is one of the six nuclear reactors concept evaluated in the frame of the Generation IV Forum [6], requires an online processing of the fuel in order to remove fission products and particularly Ln which have a poisonous effect on the nuclear reactions taking place in the core of the reactor.

In order to ensure a longer lifetime of the salts used in the above-mentioned pyrochemical processes, it is required to remove the lanthanides (Ln) from the salts after the selective extraction of the An. It is proposed in this paper to describe, among a general panel of techniques, a special scope on chemical and electrochemical processes aiming at removing Ln from a selected

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fluoride molten salt. The four following techniques consist in using selective properties to extract Ln in a solid form, either as pure element or as a compound or an alloy:

(1) Electrodeposition of pure metals;
(2) Precipitation of insoluble oxygenated compounds (oxides or oxyfluorides) by addition of lithium oxide in the fluoride melt;
(3) Electrodeposition of alloys or intermetallic compounds by reaction of the reducing ion with the substrate (Ni or Cu);
(4) Electrodeposition by co-reduction with aluminium on an inert W cathode.

These techniques were developed in the same fluoride melt (i.e. $LiF–CaF_2$ eutectic), in order to perform the extraction of the elements Nd, Sm, and Gd, which are the main Ln present as fission products in nuclear spent fuels. The Ln content in the melt was monitored by electrochemical techniques.

2. Experimental

- The cell was a cylindrical refractory steel vessel, closed by a stainless steel lid with circulating water for cooling and placed under inert argon atmosphere (LINDE U quality, less than 5 ppm O_2) from which moisture and oxygen are removed using a purification cartridge (Air Liquide) [7,8].
- The salt mixture was placed in a vitreous carbon crucible (Carbone LorraineV25 grade) inside the vessel.
- The electrolytic bath was composed of 200 g of a eutectic LiF/CaF_2 (Merck 99.99%) mixture (79/21 molar ratio). Solutes were introduced into the bath in the form of fluoride salt pellets: SmF_3 (Merck 99.99%), GdF_3 (Merck 99.99%), NdF_3 (Merck 99.99%) and AlF_3 (CERAC 99.99%). Oxide additions were realized by introduction of Li_2O powder (Merck 99.99%) into the media.
- Experiments were performed in the temperature range 800–920 °C.
- Molybdenum, tantalum, tungsten and copper wires (Goodfellow purity 99.99%, 1-mm diameter) were used as working electrodes. Molybdenum, tantalum and tungsten are inert with the studied elements whereas copper can form alloys with them in the temperature range considered.
- The auxiliary electrode was a vitreous carbon (Carbone LorraineV25 grade) rod with a large surface area (2.5 cm^2). The potentials were referred to a platinum wire (0.5-mm diameter) acting as a quasi-reference electrode (QRE) $Pt/PtO_x/O^{2-}$ sensitive to the oxide content in the bath [9].
- Cyclic voltammetry and square wave voltammetry were used for the investigation of the reduction process of the Sm, Gd, and Nd ions, and performed with an Autolab PGSTAT30 potentiostat/galvanostat controlled by a computer using the GPES 4.9 software.
- Techniques for the characterization of reduction products: after the electrolysis runs, the surface of the cathodes was observed by scanning electron microscope (LEO 435 VP) and analysed with an EDS probe (Oxford INCA 200).

3. Results and discussion

3.1. Electrodeposition of pure Ln on an inert cathode

Lanthanides are reactive elements and their equilibrium potentials are either close to the one of solvent cations or less negative; thus the fluorides solvent exhibiting the widest electrochemical window in the cathodic sense had to be selected. For this purpose, a previous examination of standard equilibrium potentials of the possible solvent cations, according to data on the decomposition energy of fluoride compounds gathered by Barin [10] led to select as solvent the eutectic mixture $LiF–CaF_2$, which exhibits an optimized electrochemical window and a moderate melting temperature (760 °C) [11].

Cyclic voltammograms of Fig. 1 show up first the closeness with the solvent reduction (Li^+/Li) of the Nd^{III} (Fig. 1a) and Gd^{III} (Fig. 1b) reduction potential in their respective metallic phase, while the Sm^{III} reduction (Fig. 1c) proceeds in two successive steps (Sm^{III}/Sm^{II} and Sm^{II}/Sm) with only the first one observable within the electrochemical window.

Accordingly, more detailed studies on the Nd^{III}/Nd system [12] and Gd^{III}/Gd system [13] let us to conclude, using as well thermodynamic as experimental data, that the extraction of Nd and Gd by electrodepositing them on an inert cathode cannot

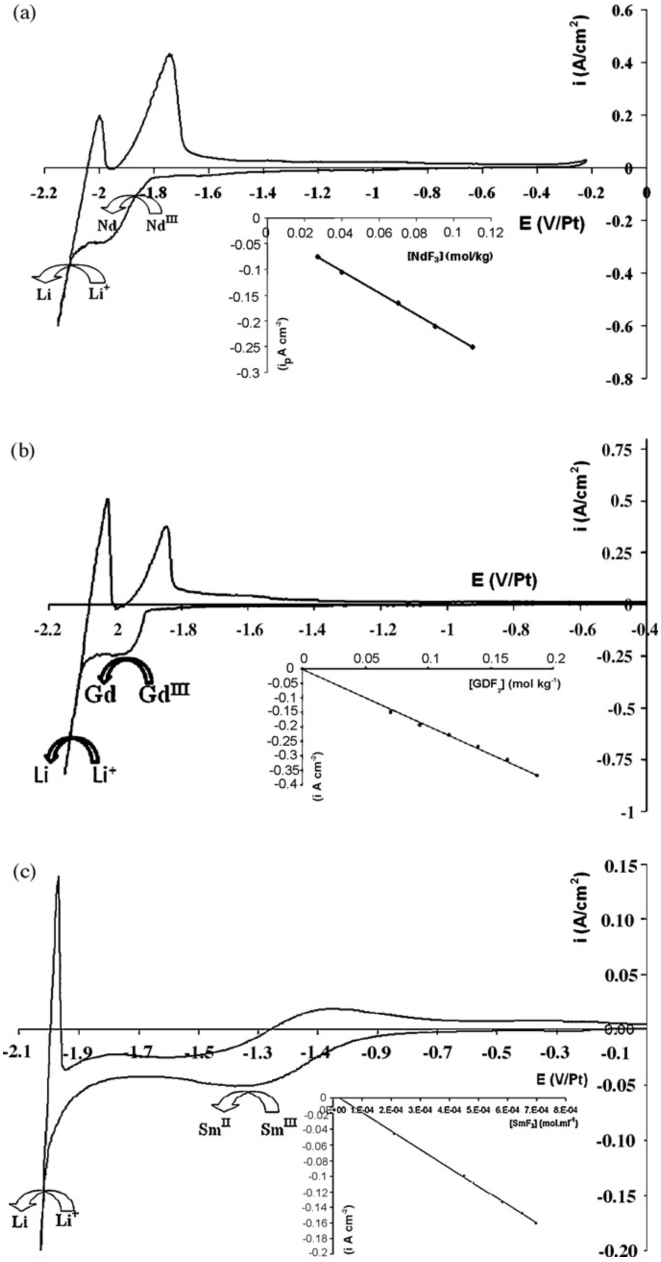

Fig. 1. Cyclic voltammograms of $LiF–CaF_2–LnF_3$ (0.1 mol kg^{-1}) system on Mo electrode at 0.1 V/s and T = 840 °C. Inset: linear relationship between the LnF_3 reduction peak current density and the NdF_3 content in the melt at 0.1 V/s. (a) Ln = Nd; (NdF_3 = 0.100 mol kg^{-1}) = 0; (b) Ln = Gd; (GdF_3 = 0.200 mol kg^{-1}); (c) Ln = Sm (SmF_3 = 0.253 mol kg^{-1}).

proceed with a yield efficiency close to 100% as required for recycling the solvent; obviously, Sm cannot be extracted by this method.

Moreover, first experiments aiming at extracting Nd and Gd have shown a poor adherence and a dendritic form of the electrodeposited metal, falling apart in the molten solution, making its recovery too difficult.

Nevertheless, it is expectable that electrodeposition of pure Ln elements on an inert electrode is feasible in the overall reprocessing treatment in view of a partial extraction.

3.2. Oxygenated compounds precipitation

The addition of oxide ions in molten fluorides baths containing metallic ions leads easily to the formation of stable metal oxyfluorides and according to the oxoacidity diagrams, the precipitation of oxides [10].

Oxide ions react with Ln elements to give oxyfluorides, as reported for Nd by Stefanidaki et al. [14], who mentioned the formation of Nd oxyfluoride $NdOF_5^{2-}$, electroactive in the voltage range comprised between the Nd^{III} reduction and the solvent reduction.

Square wave voltammetry (SWV) was proved in our earlier works to be a sensitive method to measure the composition in the electroactive species of fluoride baths containing oxide ions [7,15,16].

More particularly, previous work, concerning tantalum cations (TaF_7^{2-}) in fluorides, demonstrates that the addition of oxide ions decreases the content of TaF_7^{2-} to form first electroactive tantalum oxyfluorides and then insoluble oxides with excess addition [16].

Fig. 2 compares the square wave voltammogram performed in the LiF–CaF_2–NdF_3 (4a) and Lif–CaF_2–GdF_3 (4b) mixtures, before and after addition of a small amount of Li_2O, evidences that the decrease of the peaks of NdF_3 and GdF_3 resulting from their reaction with O^{2-} ions is not balanced by the increase of another electrochemical signal, except a small shoulder of intensity unchanged with the amount of Li_2O, which thus we cannot explain by the formation of a novel electroactive species, that should indicate that an insoluble compound is produced by this reaction.

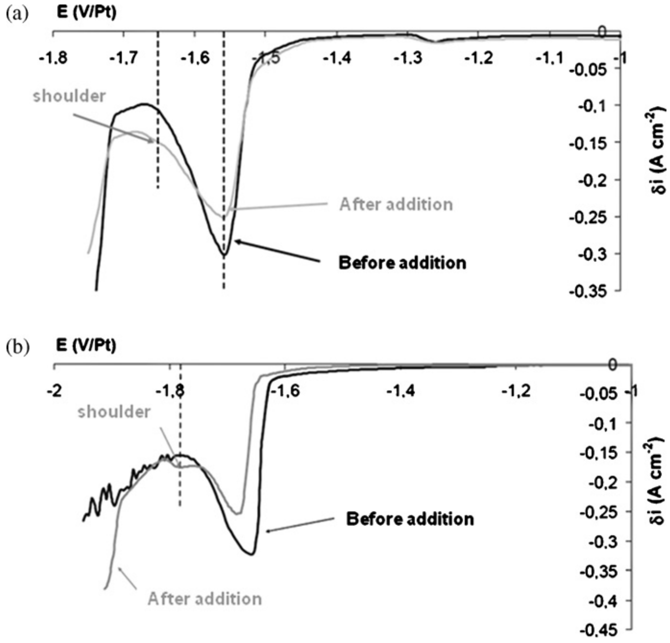

Fig. 2. Square wave voltammogram of the LiF–CaF_2–LnF_3 before and after addition of Li_2O; T = 800 °C; WE: Mo; potential reference: Pt; f = 9 Hz; (a) Ln = Nd; addition of 37 mg of Li_2O (1.23×10^{-3} mol); (b) Ln = Gd; addition of 40 mg of Li_2O (1.233×10^{-3} mol).

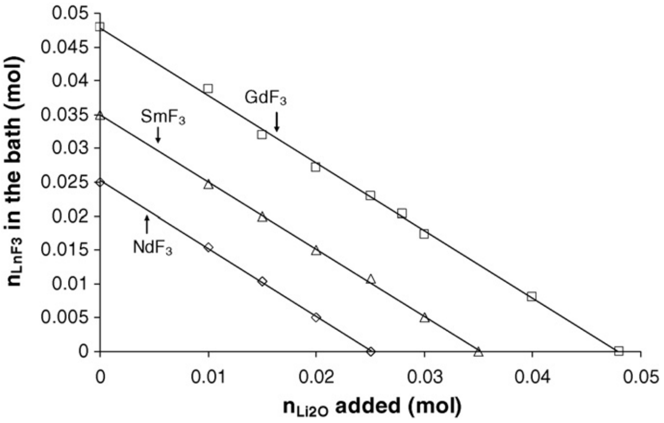

Fig. 3. Variation of LnF_3 content in the bath vs. oxide content added.

In order to know whether an oxide Nd_2O_3 or Gd_2O_3 is the reaction product, we plotted in Fig. 3 the variation of the content in Ln fluoride in the bath (deduced from the peak current of the SWV which is linear with the content in electroactive species) with the addition of Li_2O for Nd, Gd and Sm systems; surprisingly, the slope of the straight lines, observed in Fig. 3 is -1 and not -0.66 as expected for the formation of the above-mentioned oxides, taking into account the stoichiometry of the Ln oxides.

We noticed too that all the Ln ions initially in the bath precipitated at the end of the treatment; Fig. 3 reports as well similar results with samarium, for which we observe the decrease of the Sm^{III}/Sm^{II} peak after addition of Li_2O.

The nature of the reaction product between Ln fluorides and oxide ions is surely questionable: on one hand, Stefanidaki's results with Nd, cited above [14], showed the formation of a soluble and electroactive oxyfluoride, elsewhere identified by Raman spectrometry by the same authors [17]; on the other hand, Elizarova observed in mixtures of gadolinium fluoride and lithium oxide dissolved in a molten fluoride solvent the formation of the insoluble compounds GdOF [18]. Accordingly, our results of Fig. 3 for Nd, Gd and Sm, should rather be coherent with the formation of an insoluble product, expressed as:

$$Ln^{III} + F^- + O^{2-} \rightarrow LnOF \quad (1)$$

According to these results, subject to further verifications, the chemical precipitation of insoluble compounds can participate to the whole treatment for reprocessing nuclear spent fuel. The technique joins up with other works dealing with the extraction of actinides and Ln by chemical precipitation of oxides with a large excess of oxides [19].

3.3. Extraction of Ln elements by electrodeposition of alloys

Compared to the electrodeposition of Ln ions on an inert metal, this method offers the following advantages:

- It shifts the electrodeposition potentials of the Ln metal towards more anodic potentials that can be named "depolarisation", since the activity of the alloyed metal is less than one. If the alloy is an intermetallic compound, depolarisation can be of several hundreds of millivolts, which prevents from the codeposition of the solvent metals [20].

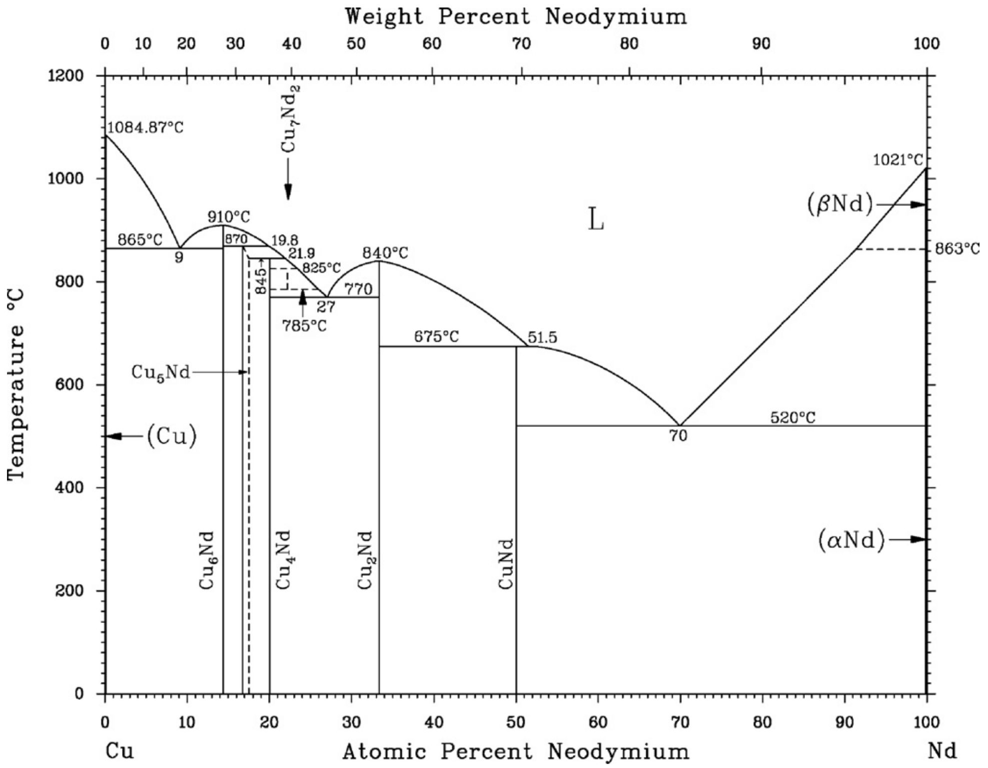

Fig. 4. Binary Cu/Nd phase diagram (copyright of Ref. [10]).

- Binary systems of Ln with elements such as copper, nickel and aluminium (three metals commonly handled in molten fluorides) exhibit a lot of intermetallic compounds or eutectic compositions in a liquid state within the working temperature range (700–900 °C). The possibility of yielding a liquid alloy at the cathode is a real asset because it prevents from the drawbacks mentioned above about the cathodic formation and growth of a pure solid phase and moreover it keeps unchanged during the electrolysis the substrate/electrolyte interface.

We describe here two techniques we use for obtaining these alloys: (i) the reaction of the element deposited with the cathodic material (reactive cathode method) and (ii) the co-reduction of Ln ions with aluminium ions leading to an Al–Ln alloy on an inert cathodic material.

3.4. Reactive cathode method

Even if other authors propose also cobalt [21], classically the cathode material can be nickel or copper, since these metals react easily and rapidly with Ln to give intermetallic compounds identified on the binary diagrams [22] and are more easily available than Co. A typical example of binary diagram is shown for the copper–neodymium system in Fig. 4.

In earlier works, we have developed the technique for alloying copper and/or nickel with each of the Ln investigated here: Sm/Ni, Gd/Ni and Cu, Sm/Ni and Cu, Nd/Ni and Cu [11,23,24]. In previous work [20] we demonstrated that the kinetic of the alloy layer growth is controlled by the intermetallic diffusion within the surface alloy layer. As a consequence, during the electrolysis time, the process rate slows down significantly if the alloy is a solid phase. For this reason, copper can be preferred to nickel as a cathode material since it leads more easily, in our temperature range, to liquid surface compounds which fall down in the crucible and keep the surface of the cathode free of diffusion layer. As observed by Nourry [24], liquid alloy formation enhances sensibly the overall extraction kinetics of each of these Ln:

- Depolarisation effect can be evidenced in Fig. 5 by comparing the voltammograms of fluoride solutions of the elements, each of them drawn successively on a reactive (Cu) and on an inert electrode (Mo or Ta): this figure exhibits for the copper cathode significant cathodic currents before the equilibrium potentials of Nd (Fig. 5a) and Gd (Fig. 5b) and in the case of Sm between the Sm^{III}/Sm^{II} system and the solvent reduction. We see that the depolarisation estimations, reported in Fig. 5a and b, exceed widely the potential shift from the solvent reduction, needed by a complete extraction of Nd and Gd, while in the case of Sm (Fig. 5c), the use of a copper cathode makes its extraction thermodynamically possible.
- The identification of the intermetallic compounds of each binary diagram associated with their standard potential and Gibbs energy can be realized by measurement of emf of galvanic cell, symbolized as follows:

$$\mathrm{Ln/LiF{-}CaF_2, LnF_3/Ln_xCu, Ln_yCu} \qquad (2)$$

where the anodic reaction is the Ln dissolution and the cathodic one, the change of metallic phase:

$$\mathrm{Ln_xCu} + (\mathrm{y}-\mathrm{x})\mathrm{Ln}^{n+} + (\mathrm{y}-\mathrm{x})\mathrm{ne}^- \rightarrow \mathrm{Ln_yCu} \qquad (3)$$

with $n = 3$ for Nd and Gd and $n = 2$ for Sm.

The cells were prepared by electrodepositing a small amount of pure Ln on the copper cathode and afterwards keeping the electrode in the molten salt without depolarisation in such a way that the intermetallic diffusion yields one by one all the compounds of the diagram at the cathode surface. During this time, the potential of the sample measured vs. the Ln anode is the emf of the cell (2). The recording of the potential–time relationship

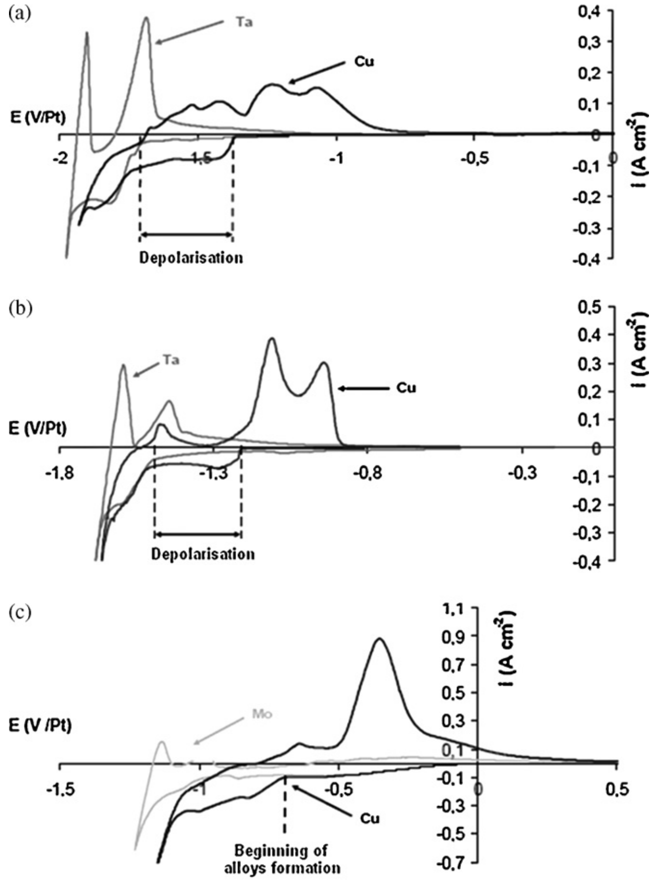

Fig. 5. Comparison of the cyclic voltammograms of the LiF–CaF_2–LnF_3 system on inert (Ta) and reactive (Cu) electrodes; at T = 800 °C and 0.1 V/s; auxiliary electrode: vitreous carbon; potential reference: Pt. (a) Ln = Nd ([NdF_3] = (0.12 mol/kg); (b) Ln = Gd; (0.14 mol/kg). (c) Ln = Sm ([SmF_3] = (0.22 mol/kg).

exhibits plateaus. The potential of each plateau is the emf of the cell (2); more details on the measurement method of Gibbs energy of alloys will be found in Refs. [20,25]. As an example, Table 1 deals with the Gibbs Energy of the Nd–Cu compounds. We can notice that the thermodynamic stability of these compounds increases with the copper content. A similar evolution of the data is observed with the other Ln–Cu compounds [24].

Extraction electrolysis can be performed either at constant current or at constant potentials:

- At constant current (intensiostatic electrolysis), low intensities are preferable but the cathode potential must be controlled in such a way that the precipitation of pure Ln can be prevented. Fig. 6 shows the cross-section of alloy layers of Cu–Nd (Fig. 6a), Cu–Gd (Fig. 6b) and Cu–Sm (Fig. 6c) prepared by short electrolysis runs (2 h maximum) at 840 °C. The thick layers (about 200 μm) of surface alloys, observable in this figure indicate a high kinetic of the intermetallic diffusion and is promising for the extraction process. The great heterogeneity of the layer composition is explained by the change of the surface compound produced on the surface during electrolysis, due to a saturation effect in the underlying diffusion layer.

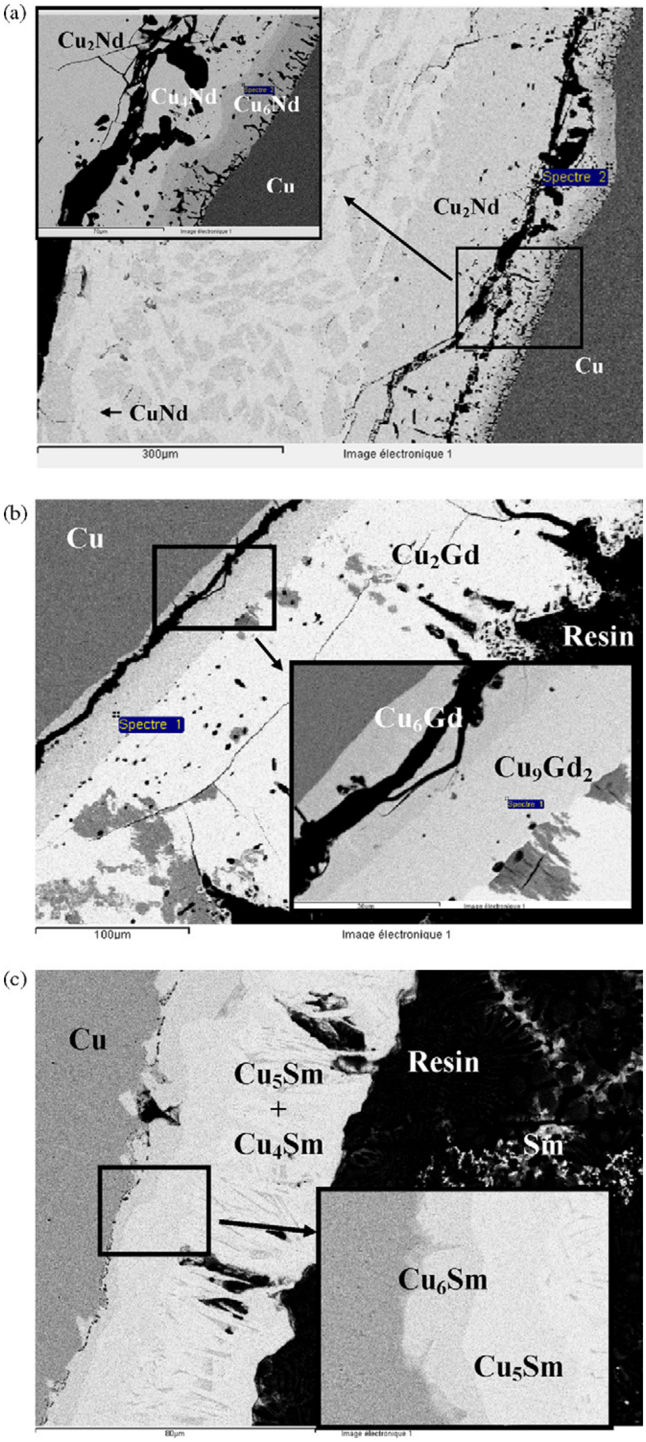

Fig. 6. SEM observation of the cross-section of a copper plate after LnF_3 reduction at T = 840 °C. (a) Ln = Nd (electrolysis time: 2 h; current: 70 mA cm^{-2}); (b) Ln = Gd (electrolysis time: 2 h; current: 32 mA cm^{-2}); (c) Ln = Sm (electrolysis time: 15 mn; current: 110 mA cm^{-2}).

- At constant potential (potentiostatic electrolysis), it is possible to control the composition of the compound produced by the cathodic reaction that leads to more uniform compositions of the alloy layer. According to Table 1, low potentials yield only compounds with a low Ln content while at potentials close to the pure Ln electrodeposition, high Ln contents are obtained in the layer. Moreover, at the most cathodic potentials, we observed first that the process rate is higher and then that the interdiffusion of Cu and Ln in the underlying layer provides a more uniform composition within this layer with states of compounds of increasing Cu content close to the pure copper substrate [24].

Table 1
Energy of formation of copper–neodymium compounds at 840 °C

Compound	ΔG (kJ mol^{-1})
Cu_6Nd	−280
Cu_5Nd	−257
Cu_4Nd	−234
Cu_2Nd	−134
CuNd	−33

Extraction runs were performed by Nourry [24], using the potentiostatic mode with high cathodic potential during the major part of the electrolyses time. The progress in elimination of Ln from the bath was checked first *in situ* by measuring the Ln^{III} peak on SWV recorded periodically on a specific molybdenum working electrode; when the Ln content became very low, this measurement was realized by sampling the electrolyte and titrating by ICP. The results will be detailed in a forthcoming article, but we can give here the following informations:

- The efficiency of the extraction process is more than 99.8%.
- The kinetic of the process is controlled by the intermetallic diffusion at the cathode surface; thus, as observed in the case of electrolyte diffusion, the extraction rate is slowing down during the run for a given cathode area, that is typical of a saturation effect and thus following an exponential law homologous of Cottrell's law [20]. Obviously, the extraction rate can sensibly be enhanced first by using cathodes with extended areas and moreover by promoting the formation of liquid alloys.
- Accordingly, the processing speed is remarkably enhanced by increasing the temperature up to values where the intermetallic compounds are liquid: at 840 °C (solid compounds) 99.8% of extraction rate of Nd is obtained in 150 h on a 1 cm^2 cathode area; at 920 °C (liquid compounds) the same rate is obtained in 50 h for the same surface area. This speed could be significantly enhanced by using cathodes with larger areas.
- The simultaneous extraction of the three elements investigated (Nd, Gd, Sm) here was also successful.

3.5. Co-reduction with aluminium ions

This method consists in extracting the Ln elements in the form of an alloy with aluminium on an inert cathodic substrate. It exhibits some advantages compared to the concept of a reactive cathode:

- It prevents the consumption of the cathodic material.
- As the substrate is inert, no variation of the alloy composition caused by the metallic interdiffusion during the process is expectable.
- It allows eliminating in the same process aluminium ions possibly present in the bath after special a treatment for recovering An by redox displacement of these elements by reactive metals such as Al [4,25]. Indeed, the reductive extraction releases Al^{III} ions in the molten solution which have to be removed afterwards.

We are developing research works on this method for extracting in the same process aluminium with the following Ln: neodymium, samarium and cerium. We present here promising results on codeposition of Al and Nd.

First we observe that the binary diagram Al–Nd of Fig. 7 exhibits lots of intermetallic compounds. For each of these compounds, we can associate an equilibrium potential associated with the simultaneous reduction of the different ions in the melt, obviously more anodic than the equilibrium potential of pure neodymium, as demonstrated by the following Nernst equations [26]:

$$E_{\mathrm{Nd^{III}/NdAly}} = E^{0}_{\mathrm{Nd^{III}/Nd}} + \frac{RT}{3F}\ln\left[\frac{a_{\mathrm{Nd^{III}}}}{a_{\mathrm{Nd}}(\text{in NdAl}_y)}\right] \tag{4}$$

$$E_{\mathrm{Nd^{III}/NdAly}} = E^{\mathrm{equ}}_{\mathrm{Nd^{III}/Nd}} - \frac{RT}{3F}\ln a_{\mathrm{Nd}}(\text{in NdAl}_y) \tag{5}$$

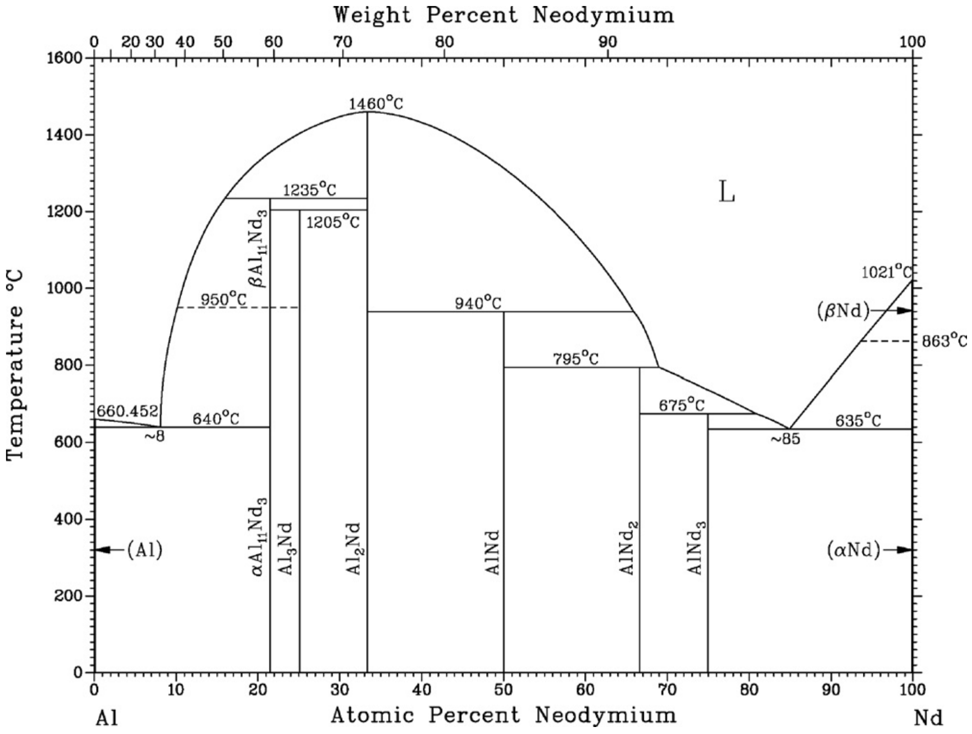

Fig. 7. Binary Al/Nd phase diagram (copyright of Ref. [10]).

As a_{Nd} is less than one in the alloy, E^{eq} ($Nd^{III}/NdAl_y$) is more positive than E^{eq} (Nd^{III}/Nd).

The electrochemical behaviour of a fluoride solution containing Al and Nd ions can be compared on the square wave voltammogram of Fig. 8 with the individual behaviour of Al (grey line Al) and Nd (grey line Nd).

Fig. 8 displays the formation of intermetallic compounds at the potentials of peaks 1a (almost superimposed with the pure Nd peak), 2a, 3a and 4a (almost superimposed with the pure Al peak).

Short electrolysis runs at each of these peak potentials allow the associated compounds deposited on the cathode to be identified by SEM examination and EDS analysis of the cathodic sample quenched out of the cell after electrolysis; we can see in Fig. 9 that (i) the reduction products are not adherent on the substrate; (ii) each of them has a homogeneous composition:

$$E(\text{vs.Pt}) = -1.33\,\text{V} : Al_{11}Nd_3; E = -1.49\,\text{V} : Al_3Nd; E = -1.69\,\text{V} : AlNd_2; E = -1.88\,\text{V} : AlNd_3.$$

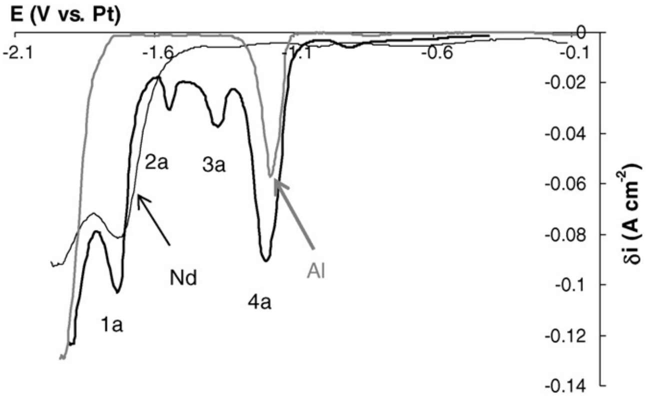

Fig. 8. Square wave voltammogram of the LiF–CaF_2–AlF_3–NdF_3 system compared to LiF–CaF_2–AlF_3 and LiF–CaF_2–NdF_3 systems on Ta electrode at T = 800 °C and 0.1 V/s; auxiliary electrode: vitreous carbon; potential reference: Pt.

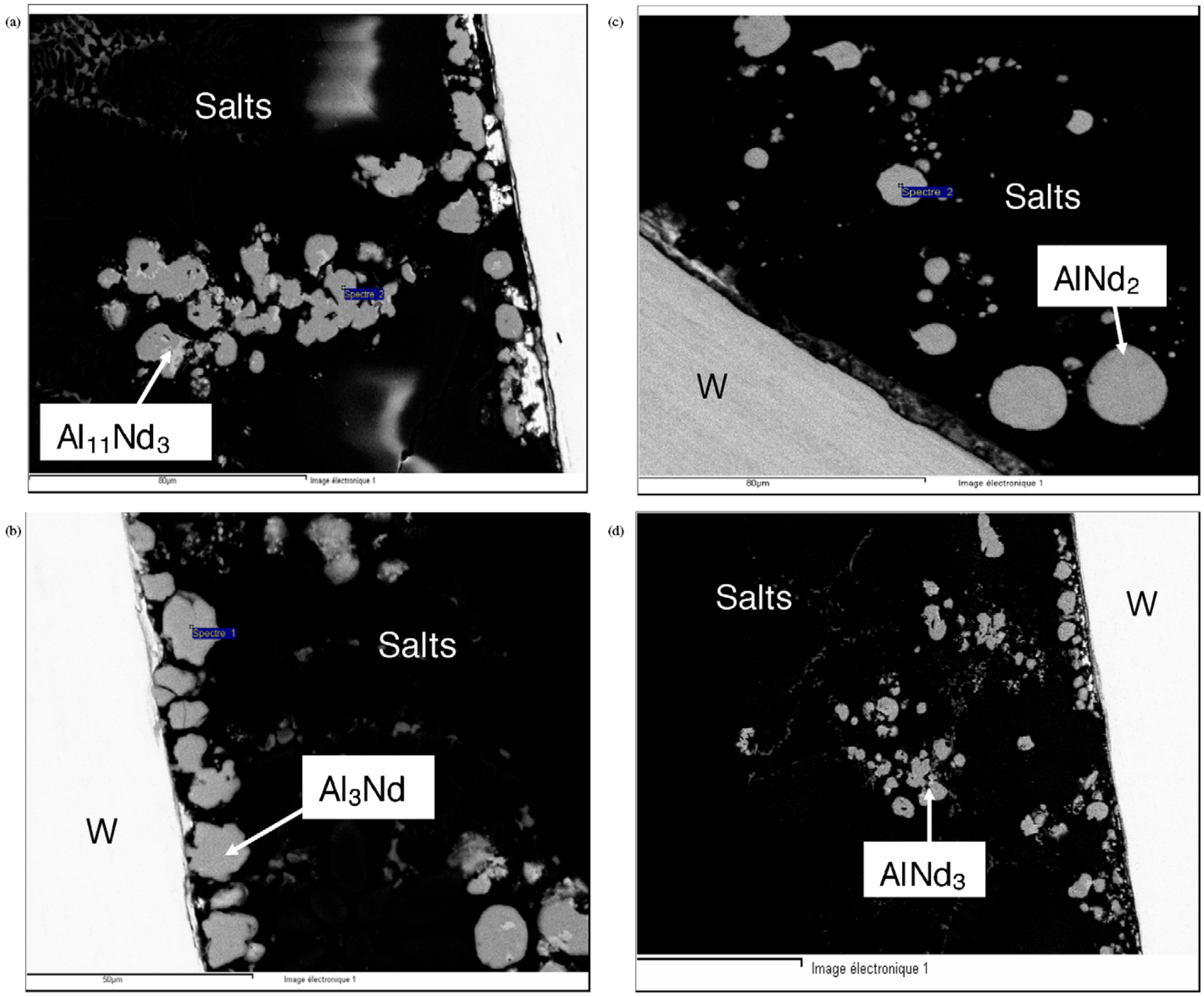

Fig. 9. SEM observation of the cross-section of a tungsten plate after AlF_3–NdF_3 co-reduction at T = 840 °C. (a) Electrolysis time: 1200 s; E_{imp}: −1.33 V; (b) electrolysis time: 1200 s; E_{imp}: −1.49 V; (c) electrolysis time: 1200 s; E_{imp}: −1.69 V; (d) electrolysis time: 1200 s; E_{imp}: −1.88 V.

As predicted by Eq. (5), the Nd content increases with the cathodic potentials.

The extraction process of Nd and Al by codeposition at the potential of the formation of $AlNd_2$ (referred to a reliable NiF_2/Ni comparison electrode insulated with a boron nitride compartment) was attempted at $T = 860\,^{\circ}C$ on a W electrode of large area and using a special device for recovering the reaction product released within the molten salts [26]. The progress of the extraction process was measured by recording periodically cyclic voltammograms of the mixture; a clear decrease of the current in short electrolysis duration was observed; according to these results, detailed in Ref. [26], 95% of Nd was extracted in 50 h on 1 cm^2 cathode area. Similar to the reactive cathode method, this result should be sensibly improved by increasing the electrode area.

The co-reduction method is currently applied to the extraction of other Ln (Ce, Sm) and gives similar results than for Nd: it provides a new and promising technique in the overall program of nuclear waste reprocessing.

4. Conclusion

This article gives informations on the role of the electrochemical processes in molten fluorides in the general program of nuclear spent fuel reprocessing and mostly here for the complete extraction of fission products by their deposition or electrodeposition in a solid form; we can summarize our results as follows:

- Electrodeposition of pure metals on an inert electrode cannot lead to a complete extraction due to the closeness of the redox potentials of these elements with the solvent; nevertheless, this method, simple and practical to use (if a reliable system of recovering on line the electrodeposited metals is set up), can be used as a first extraction step.
- Precipitation of insoluble oxygenated compounds (oxides and/or oxyfluorides) could be a convenient method to eliminate certain elements.
- Electrodeposition of Ln alloyed with other elements (reactive cathode or aluminium co deposited) is proved here to be a promising technique to eliminate Ln elements from molten salts with efficiency close to unity in a relatively short time.

Notice in addition that electrochemical methods were confirmed here to be relevant analysis tools for the *in situ* measurement of the progress of the extraction process.

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