

Pyrometallurgical Separation Processes of Radionuclides contained in the Irradiated Nuclear Fuel

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Abstract

Faced with the new options for the high level waste management, the "Partitioning and Transmutation (P&T)" of the radio nuclides contained in the irradiated nuclear fuel appear as a promising option from different points of view, such as environmental risk, radiotoxic inventory reduction, economic, etc.

The present work is part of a research project called "PYROREP" of the 5th FWP of the EU that studied the feasibility of the actinide separation from the rest of fission products contained in the irradiated nuclear fuel by pyrometallurgical processes with the aim of their transmutation. In order to design these processes it is necessary to determine basic thermodynamic and kinetic data of the radionuclides contained in the nuclear fuel in molten salt media.

The electrochemical study of uranium, samarium and molybdenum in the eutectic melt LiCl – KCl has been performed at a tungsten electrode in the temperature range of 450 – 600°C in order to obtain these basic properties.

Keywords: Pyrometallurgical process, molten salts, electrochemistry, uranium, samarium, molybdenum, irradiated nuclear fuel, separation & transmutation

Introduction

In the last few years a renewed interest on "Partitioning and Transmutation (P&T)" strategy for the management of high level wastes and advanced nuclear fuels reprocessing is being considering worldwide. This strategy consists of separating some long-lived radionuclides to transmute them into short-lived or even stable isotopes by means of neutronic capture or fission processes, reducing this way the volume of high level nuclear waste and its long term radiotoxicity.

Pyrometallurgical processes appear as a promising option for the reprocessing of the fuels that are being proposed to carry out the transmutation. These fuels will have high contents of Pu and minor actinides and will reach high burn-ups, therefore these processes will allow shorter cooling times due to the high radiation stability of the molten salts media. This type of processes includes, among others, the separation and recovery of the actinides in metallic form by means of electrolysis in molten salts. The molten salt media proposed in the separation studies are mainly fluorides and chlorides of alkali and alkaline-earth metals (Gruppelaar, H. et al. 1998).

In the period 2000 - 2003 the research project called "PYROREP" of the 5th FWP of the EU studied the feasibility of the separation of the radionuclides contained in the irradiated nuclear fuels by pyrometallurgical processes. The main objective was to determine basic thermodynamic and kinetic properties of the different elements of interest in molten salt media necessary to design a separation scheme. This investigation, that was included in the project, deals with the study of the electrochemical behaviour of the elements uranium, samarium and molybdenum in the eutectic melt LiCl – KCl at a tungsten electrode.

Experimental study

The electrolyte selected was the eutectic mixture LiCl – KCl (59% mol LiCl) that was melted in a glassy carbon crucible, placed in a quartz cell inside a furnace as it is observed in Fig. 1 The working temperature was measured with a thermocouple protected by an alumina tube inserted into the melt. The

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electrolyte mixture was heated to dehydrate it at 200°C for a few hours and then melted at 450°C under atmospheric pressure using dry Ar(g). All the experiments were performed under inert Ar atmosphere. Before each experiment the electrolyte was purified to remove moisture and oxide ions content by bubbling HCl gas into the melt.

Solutions of the electroactive species were prepared by direct additions of SmCl₃, MoCl₃ and UO₂. It should be noticed that Mo(III) solutions are unstable, fact that is attributed to the volatilisation of the highest oxidation state molybdenum chlorides (Gabriel, J. C. et al., 1999; Volkovich, V. A. et al., 2003; White, S. H. y Twardoch, U. M., 1987). In the case UO₂ dissolution in the melt was performed by carbochlorination (Cl₂(g) + C(s)).



Fig. 1 Electrochemical cell and experimental device

Analysis of the electroactive species concentration in the molten bath was performed by taking samples of the melt, dissolving them into HNO₃ (1%) and then analysed by ICP-MS.

For the electrochemical studies different transient electrochemical techniques such as cyclic voltammetry and square wave voltammetry as well as convolution analysis of the cyclic voltammograms were used (Bard, A. J. y Faulkner, L. R., 1980).

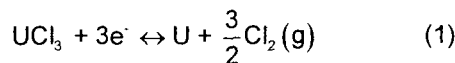
As working and counter electrodes tungsten wires (1 mm diameter) were used. As reference electrode Ag/AgCl was used, which was constituted by a silver wire (1mm diameter) dipped into a Pyrex tube containing a solution of silver chloride in LiCl – KCl (0.75 mol·kg⁻¹). Potentials measured versus the Ag/AgCl couple were converted into potentials versus a Cl⁻/Cl₂(g) reference electrode to make the comparison with the literature values easily (Mottot, Y., 1986).

Basic electrochemical studies

Stable oxidation states and reversibility

Stable oxidation states and reduction mechanism of the metallic ions under study in the eutectic melt LiCl – KCl was investigated by cyclic voltammetry technique. In the case of U it was found that several oxidation states were present into the melt as it is shown in Fig. 2a. In the voltammogram are observed several electrochemical signals in reduction named A, B, C, D and the corresponding signals in oxidation, named A', B', C', and D'. The signal D-D' is associated to a Li-U alloy formation. The signal C-C' corresponds to the U(III)/U(0) system, B-B' to the couple U(IV)/U(III) and finally the signal A-A' corresponds to the system U(VI). Although in this voltammograms is not clearly observed, this peak shows two signals, one that correspond to the reduction of U(VI) in form of UO₂²⁺(VI) into UO₂⁺(V) and a second one very close to it corresponds to the couple UO₂⁺(V)/UO₂. The presence of these oxidation states in the eutectic LiCl-KCl has also been observed by several authors and the electrochemical reactions between these oxidation states has also been measured (Landresse, G. y Duyckaerts, G., 1971; Molina, R., 1961; Uchida, I. et al., 1981).

The number of electrons exchanged in the reduction reaction U(III)/U(0) was also calculated by square wave voltammetry technique being equal to 3. The reduction reaction produced is:



The analysis of the cyclic voltammograms registered at different scan rates on a tungsten electrode indicates that the reduction of the U(III) ions to U(0) presents a quasi – reversible behaviour. Under our experimental conditions it was not feasible to study the redox Sm(II)/Sm(0) system due to the fact that Sm(II) is reduced to Sm(0) at a very negative value close to that of the solvent reduction (Bychkov, A. V. et al., 1998; Plambeck, J. A. 1976). Fig. 2b shows a cyclic voltammogram obtained

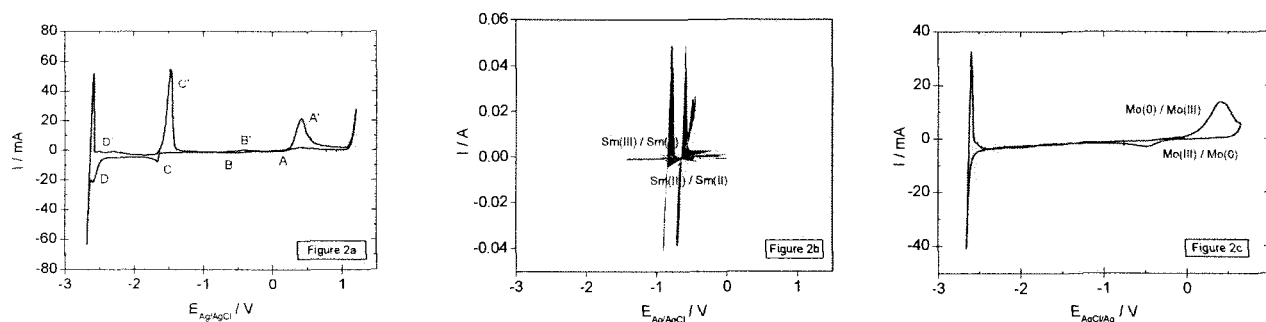
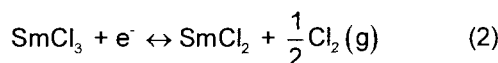
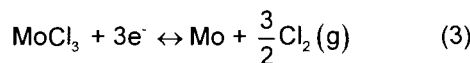


Fig. 2 CV obtained at 450°C from U (2a), Sm (2b) or Mo (2c) solutions in LiCl – KCl. Tungsten working electrode

from a Sm solution in LiCl – KCl where it can be observed a cathodic wave associated with an anodic wave. Its shape is characteristic of a soluble-soluble system corresponding to the Sm(III)/Sm(II) redox system with the exchange of one electron (Cordoba, G. y Caravaca, C., 2004):



The analysis of the cyclic voltammograms registered at different scan rates indicates that the electrode process Sm(III)/Sm(II) is reversible and controlled by the diffusion of the electroactive species. Stable oxidation states for Mo were found to be (III) and (0) in this media. The reduction reaction of Mo(III) ions to Mo(0), involving three electrons, has a quasi – reversible behaviour and can be expressed by:



Cyclic voltammogram in Fig. 2c shows a single cathodic peak associated with an anodic peak whose shape is characteristic of an insoluble product formation system corresponding to the Mo(III)/Mo(0) redox couple. Analysis of the cyclic voltammograms indicates that the reduction reaction of Mo(III) to Mo(0) occurs in a single step with exchange of three electrons, presenting a quasi – reversible behaviour.

Apparent standard potential determination

The experimental determination of the apparent standard potential of the Me(III)/Me(0) redox couples is based on equilibrium potential measurements, which is given by the Nernst equation:

$$E_{\text{eq}} = E_{\text{Me(III)/Me(0)}}^{\circ} + \frac{2.3RT}{3F} \log[\text{Me(III)}] - E_{\text{Ref(Ag/AgCl)}} \quad (4)$$

The apparent standard potential $E_{\text{Me(III)/Me}}^{\circ}$ was determined by measuring the equilibrium potential between a Me electrode and the Ag/AgCl reference electrode in a Me(III) solution. In Table 1 are indicated the apparent standard potential values obtained at 450°C for the U(III)/U(0) and Mo(III)/Mo(0) redox systems.

In the case of samarium the standard redox potential of the soluble – soluble system Sm(III)/Sm(II) was determined from the data of the anodic and cathodic peaks potential measured in the cyclic voltammograms at different potential scan rates by applying the equation:

$$E_{Sm(III)/Sm(II)}^{\circ} = \frac{E_p^a + E_p^c}{2} \quad (5)$$

The average values obtained this way are also summarised in Table 1

From the apparent standard potential the activity coefficient of Me(III) ions has also been determined by comparing the value of Gibbs free energy of formation of MeCl₃ obtained from the electrochemical measurements with the Gibbs energy of formation of the corresponding chloride from the pure compounds at the liquid state, obtained from the literature (Barin, I. y O'Knacke, 1973). Activity coefficient gives information about the complexation of metal ions by the solvent, therefore about their stability in the melt (Trémillon, B., 1993). The experimental values obtained for the activity coefficient at 450°C are shown in Table 1

Table 1 Apparent standard redox potential, Gibbs energy of formation and activity coefficient in LiCl – KCl at 450°C

Redox system	E° vs Cl/Cl ₂ / V	$\Delta G_{MeCl_3}^{\circ}$ / kJ·mol ⁻¹	$\gamma_{Me(III)}$
U(III) / U(0)	-2.563	741.99	$2.83 \cdot 10^{-3}$
Sm(III) / Sm(II)	-2.040	196.69	$2.41 \cdot 10^{-4}$
Mo(III) / Mo(0)	-1.050	298.19	$1.64 \cdot 10^{-3}$

The plot of the $\Delta G_{MeCl_3}^{\circ}$ as a function of temperature shows a linear dependence that can be expressed by means of the following equation:

$$\Delta G_{MeCl_3}^{\circ} = \Delta H_{MeCl_3}^{\circ} - T \Delta S_{MeCl_3}^{\circ} \quad (6)$$

from which the values of enthalpy and entropy of formation were obtained:

$$\Delta G_{UCl_3}^{\circ} = -913.75 - 0.241 T / \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta G_{SmCl_3}^{\circ} = -251.18 - 0.074 T / \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta G_{MoCl_3}^{\circ} = -381.27 - 0.107 T / \text{kJ} \cdot \text{mol}^{-1}$$

Diffusion coefficient determination

Diffusion coefficient of the Me(III) ions in the eutectic LiCl – KCl has been determined by convolution analysis applying the following equation (Grenness, M. y Oldham, K. B., 1972):

$$m^* = -nFSCD^{1/2} \quad (7)$$

where n is the number of electrons exchanged, F is the Faraday constant (C·mol⁻¹), S is the electrode surface area (cm²), C the electroactive species concentration (mol·cm⁻³), D the diffusion coefficient (cm²·s⁻¹) and m* the limiting current value of the semi – integral curve (A). The average experimental values of the diffusion coefficient obtained by this technique at 450°C are given in Table 2.

Table 2 Diffusion coefficient in LiCl – KCl at 450°C at a tungsten electrode

Species	D·10 ⁵ / cm ² ·s ⁻¹
UCl ₃	0.76
SmCl ₃	0.95
MoCl ₃	2.00

Diffusion coefficient variation with temperature in the range of 450 – 600°C was also studied. Values obtained at different temperatures follow the Arrhenius law (Bard, A. J. y Faulkner, L. R., 1980), from which it is possible to determine the activation energy of the diffusion process in LiCl - KCl, being $\Delta H_{U(III)} = -48.52 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H_{Sm(III)} = -40.27 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta H_{Mo(III)} = -38.84 \text{ kJ}\cdot\text{mol}^{-1}$

Conclusions

The electrochemical behaviour of U, Sm and Mo has been studied using tungsten as working electrode in the eutectic melt LiCl – KCl in the temperature range of 450 – 600°C. It has been observed that the reduction reactions U(III)/U(0) and Mo(III)/Mo(0) proceed through a quasi – reversible soluble – insoluble reaction with the exchange of three electrons. Sm(III) is reduced to Sm(II) by a single step with the exchange of one electron, being a reversible process controlled by diffusion.

The diffusion coefficients of Me(III) ions were obtained by convolution technique and showed a temperature dependence according to the Arrhenius law.

Apparent standard potential has been determined at 450°C by e.m.f. measurements in the case of the redox systems U(III)/U(0) and Mo(III)/Mo(0) and by cyclic voltammetry when Sm(III)/Sm(II) redox couple was studied. Also activity coefficients of solvation of the Me(III) ions by the melt were determined.

From the experimental results obtained in this study it can be concluded that it is possible to separate these three elements in the eutectic melt LiCl – KCl at 450°C. Molybdenum could be separated by volatilisation at the beginning of the process and could be recovered under vacuum. Uranium can be recovered as metal into a solid cathode while, under this experimental conditions, samarium remains in the electrolyte salt as Sm(II) species.

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