SOLUBILIZATION STUDIES OF RARE EARTH OXIDES AND OXOHALIDES. APPLICATION OF ELECTROCHEMICAL TECHNIQUES IN PYROCHEMICAL PROCESSES

C. Caravaca, P. Díaz Arocas, J.A. Serrano, C. González
CIEMAT, Dpto. de Fisión Nuclear, Avda. Complutense, 22, Madrid 28040, Spain
E-mail: c.caravaca@ciemat.es

R. Bermejo, M. Vega, A. Martínez and Y. Castrillejo
Universidad de Valladolid, Dpto Química Analítica, F. de Ciencias,
Prado de la Magdalena s/n, 47005 Valladolid, Spain.
E-mail: ycastril@qa.uva.es

Abstract

Chemical and electrochemical properties of rare earths (La, Ce, Pr and Y) chloride solutions in the eutectic LiCl-KCl and the equimolar $CaCl_2$-NaCl mixture were studied at 450 and 550^0C respectively.

The stability of the oxidation states of rare-earths and the standard potential of the different redox couples have been determined. The solubility product of oxides and oxychlorides were calculated, the differences observed on pKs values between the two molten media demonstrate the different oxoacidic properties of both molten baths. All these data have been summarised in E-pO^{2-} diagrams which displays the stability domains of rare earth compounds on each melt.

Gaseous HCl was used as chlorinating agent during the solubilization tests of the corresponding rare earth oxides and oxychlorides, efficiencies close to 100%.

The electrochemical behaviour of rare earth solutions has been studied at W and Mo electrodes using different electochemical techniques, observing that Me electrodeposition could be complicated by alkaline co-deposition (Li or Na). Mass transport towards the electrode is a simple diffusion process, and the diffusion coefficients of Me(III) were obtained. In LiCl-KCl, nucleation and crystal growth of the rare earth metal seems to be the controlling step in most cases, while in $CaCl_2$-NaCl this phenomenon has not been observed.

1. Introduction

The long-term radiological hazard of spent nuclear fuel is determined by the transuranium elements (TRU: Pu, Am, Cm, Np) and some long-lived fission products (LLFP: Cs, I, Tc). If these elements could be separated efficiently from the spent fuel and be transformed into short-lived or stable ones, a significant positive on the overall performance repository will be achieved [1].

Over the last years, a renewed interest on pyrochemical separation processes in molten salt media has been shown mainly due to the progress in the assessment of new concepts for transmutation and the corresponding fuel cycles [2]. Pyrochemical processes are considered to have potential advantages over aqueous processes to reduce the inventory of actinides and long lived fission products in the nuclear wastes. In order to assess its feasibility, several processes have been developed for the recovery of actinides from spent metallic, nitride, oxide nuclear fuels, and high level radioactive liquid wastes [3].

Some of the main advantages of the pyrometallurgical process are that the purity of the product is less stringent, the recovery of minor actinides takes place simultaneously with plutonium due to the thermodynamic properties in molten salt. The recovery of minor actinides allow the reduction of TRU. On the other hand, the radiation stability of molten salt enables to process spent fuels of high radioactivity without increasing the secondary waste, and since molten salt does not act as neutron moderator comparatively higher amount of fissile material can be handled in the processes equipment than in the aqueous processes [4].

Since the separation behaviour of actinides and rare-earths is essential for designing the pyrochemical processes, much effort has been made to study actinide and rare-earth chemistry in molten salt media in order to have a reliable data base [3]. As a part of a wider UE project that is focused on separation of actinides from LLFP from oxide nuclear fuels, the present work presents a study of the chemical and electrochemical properties of several rare-earths in two different molten chloride baths.

Separation prediction can be made from thermodynamic data by means of the so called generalised Pourbaix type diagrams (GPTD), E-pO^2, for rare earth (i.e. La, Ce, Pr and Y)-O compounds and the chlorinating gaseous mixtures in two molten chloride mixtures of different intrinsic acidities, the LiCl-KCl eutectic melt and the $CaCl_2$-NaCl equimolar mixture, which enables to propose the main lines for the pyrochemical separation process. Thermodynamic data of metal oxides are often available in the literature but unfortunately, in most cases, data for most of the pure metal oxychlorides are not available. Therefore, the stability of these species has to be experimentally determined by using specific tools such as the yttria-stabilized zirconia membrane electrode (*ysze*).

Electrochemical techniques provide an efficient tool to investigate the reaction mechanisms. The establishment of modern electrochemical technologies requires early engineering evaluation of the cell behaviour with reliable procedures. To reach a better view of the feasibility of the process, the kinetic parameters of the reaction steps are measured from transient techniques taking into account the diffusion's contribution of electroactive species, electron transfer, kinetics and additionally adsorption or crystallisation, the last one generally is controlled by the rate of nucleus formation and the diffusion of active species.

2. Experiment details

Cyclic voltammetry and other pulse techniques were performed. The working electrodes (WE) used were tungsten or molybdenum wires of 1mm diameter, as counter electrode tungsten was used. The active surface area of the WE was determined by measuring the depth of immersion.

The reference electrode consisted of a silver wire (1 mm diameter) dipped into a silver chloride solution (0.75 $molKg^{-1}$) in the $CaCl_2$-NaCl or LiCl-KCl molten mixture contained in a quartz tube. Potentials were measured by reference to the AgCl/Ag couple.

The pO^{2-} indicator electrode used is a tube of yttria-stabilised zirconia, filled with molten $CaCl_2$-NaCl or LiCl-KCl and oxide and silver ions (3×10^{-2} and 0.75 $molkg^{-1}$ respectively) in this mixture a silver wire was also immersed (inner reference Ag^+/Ag).

The chloride mixtures $CaCl_2$-NaCl or LiCl-KCl (analytical-grade) were melted under vacuum, next raised to atmospheric pressure using dry argon, and then it was purified by bubbling HCl through the melt for at least 30 minutes, and then kept under argon atmosphere [5-7]. Working temperature was measured by a thermocouple introduced into the melt. Salt handling was carried out in a glove box under argon atmosphere.

Solutions of the electroactive species was prepared by direct addition of $MeCl_3$. In order to remove any traces of oxide ions, the solutions were purified by gaseous HCl bubbling.

2.1 pK_s determinations

pKs determinations were performed using a *ysze* electrode placed into the melt. A known amount of metal ion introduced as chloride was potentiometrically titrated either with Na_2CO_3 or BaO. Continuous stirring with dried argon was required.

3. Results and discussion

3.1 Determination of the stable oxidation states of rare earths

The electrochemical properties of dilute solutions of rare earth ions (Ce(III), La(III), Pr(III) and Y(III)) in the equimolar $CaCl_2$-NaCl and eutectic LiCl-KCl, at 550 and 450^oC respectively, were studied.

Figure 1 shows voltammograms obtained with a solution of $CeCl_3$ in the eutectic LiCl-KCl melt using a tungsten electrode. The process is characterised by one cathodic peak well defined, associated with the corresponding sharp re-oxidation peak, (anodic dissolution), which is characteristic of the formation of a product that remains adhered to the electrode. This fact has been confirmed by examination of the voltammograms, the ratio of the anodic to the cathodic current was higher than unity, the ratio between the total anodic to cathodic charge was close to unity and independent of the scan rate (Figure 2). In the anodic region, there was not observed the electrochemical system Ce(IV)/Ce(III), in none of the melts, which indicate that the standard potential of that system is out the range accessible in these melts, and that Ce(IV) is a powerful oxidizing agent which oxidizes the chloride ions of the melt according to the reaction:

$$Ce(IV) + Cl^- \leftrightarrow Ce(III) + 1/2\ Cl_2\ (g) \qquad (1)$$

The voltammograms obtained for other rare earth trichlorides solutions,in both chloride melts, behaved in a similar way except for a positive or negative shift of the peak potential value compared to that of the $CeCl_3$. Moreover, it has been observed that the peak potential values obtained in the melt $CaCl_2$-NaCl are slightly less cathodic than those obtained in the eutectic LiCl-KCl.

Figure 1. **Cyclic voltammograms of LiCl-KCl with $CeCl_3$ ($1.57.10^{-4}$ mol/cm^3), W_E: tungsten 0.28 cm^2**

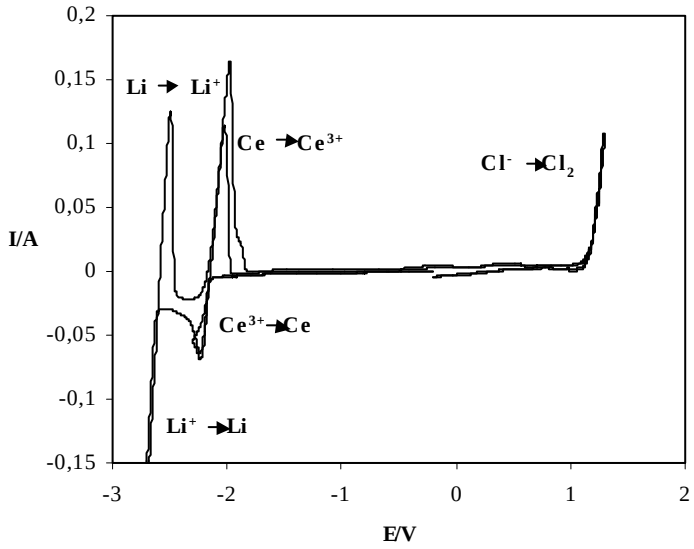


Figure 2 (a). **Voltammogram that proves the formation of a solid product at the tungsten surface. Reduction step Me(III)+3e ⇔Me and the subsequent anodic dissolution of the deposit**

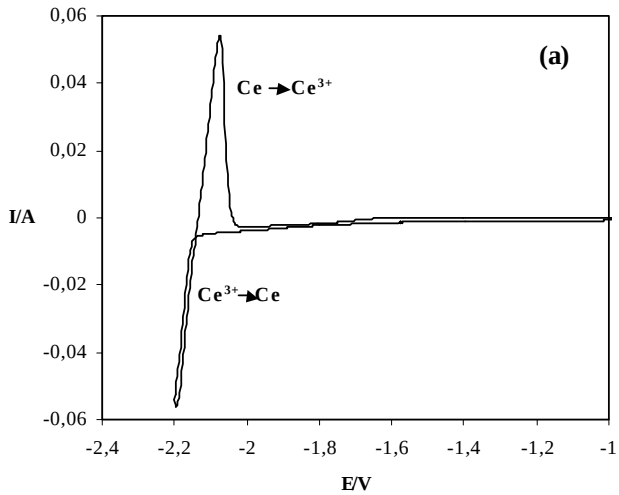
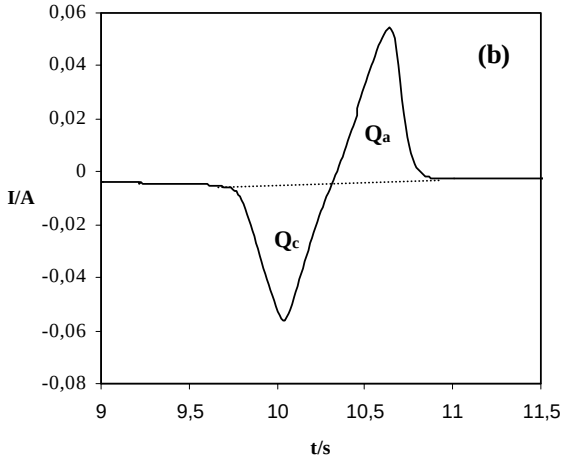


Figure 2 (b). **Comparison between the cathodic and anodic charge for the deposition and subsequent reoxidation of solid cerium**



Square wave voltammetry (SWV) to study the stable oxidation states of rare earths in both melts was used. According to Baker *et al.* [8] and Osteryoung *et al*. [9] the width of the half-peak, $W_{1/2}$, depends on the number of electrons exchanged and on the temperature as follows:

$$W_{1/2} = 3.52 \frac{RT}{nF} \tag{2}$$

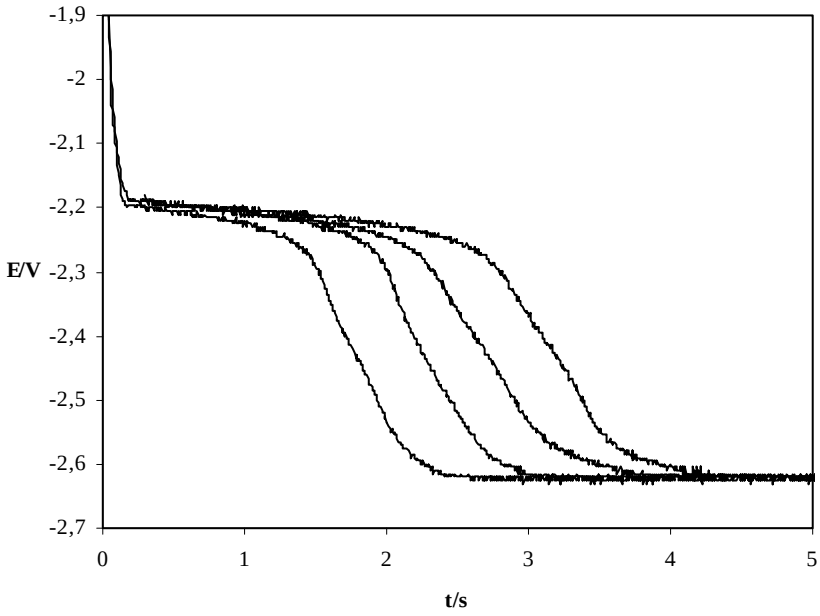
The n-values obtained with all the $MeCl_3$ solutions were close to 3.

Similar results were obtained by chronopotentiometry. This type of transients show the existence of a potential plateau in the range –2,20 V (v.s. Ag^+/Ag). After this plateau a rapid decrease was observed, and then, the electrode potential reaches a limiting value corresponding to the deposition of alkaline metals (Figure 3).

The reduction of rare earth trichlorides (La(III), Ce(III), Pr(III) and Y(III)) to metal takes place in a single step, according to the reaction:

$$Me(III) + 3e \leftrightarrow Me(s) \tag{3}$$

Figure 3. **Chronopotentiograms for the reaction Pr^{3+} + 3e↔ Pr in LiCl-KCl**



3.2 Standard potential of Me(III)/Me(0), and activity coefficient $\gamma(MeCl_3)$ determination

The standard potential of the redox couples Me(III)/Me was determined by measuring the equilibrium potential of a tungsten wire covered with an electrodeposit of Me(0), obtained by coulometry at a constant potential value, avoiding any alkaline deposition.

For each rare earth the e.m.f values were measured for several metal chloride concentrations. Based on these measurements the variations of the e.m.f. is given by the Nernst equation. The plots of the e.m.f. versus the logarithm of the Me(III) concentration were linear with slopes in agreement with the theoretical values for a three-electron process. The standard potentials were deduced from linear extrapolation of the plots at a $MeCl_3$ concentration equal to 1 mol/kg, (see Table 1). The apparent standard potentials are very close, and in the order:

- Eutectic LiCl-KCl: La > Ce > Y, Pr.
- Equimolar $CaCl_2$-NaCl: La > Ce > Pr.

According to Equation (4) the standard potentials can also be deduced from the peak potential values of the voltammetric reduction of Me(III) [10].

$$E_p = E^o + 2.3\frac{RT}{nF}\log C_o - 0.849\frac{RT}{nF} \qquad (4)$$

This equation is valid for conditions where the electrochemical reaction is diffusion controlled. The E^0 values derived, (see Table 1, c.v. values), were several mV more negative than those obtained by e.m.f. measurements. This is probably due to the quasi-reversible behaviour of the electrochemical system, and/or to the influence of nucleation and crystal growth phenomena, since Equation (4) does not take into account any of those phenomena.

Activity coefficients of $MeCl_3$ in the melts, γ_{MeCl3} which take into account the free enthalpy of formation of $MeCl_3$(s) and of solvated $MeCl_3$(dissolved) were calculated by the ΔE corresponding to the reaction:

$$Me + 3/2\ Cl_2 \leftrightarrow MeCl_3\ (dissolved) \quad (5)$$

and related with the ΔE* of the same reaction between pure compounds, by means of the equation:

$$\log \gamma_{MeCl3} = (\Delta E^* - \Delta E)3F/2.3RT \quad (6)$$

ΔE* was derived from the literature [11] and ΔE from previously recorded experimental data. The values obtained are given in Table 1.

Table 1. **Standard potential values and activity coefficient of some rare-earths chlorides in LiCl-KCl and $CaCl_2$-NaCl**

	LiCl-KCl			**$CaCl_2$-NaCl**		
Redox couple	Standard Potential/V Molality scale	ΔE*/V	log γ_{MCl3}	Standard Potential/V Molality sacale	ΔE*/V	log γ_{MCl3}
Ce(III)/Ce	*e.m.f.*-3.155 *c.v.* .-3.201	3.034	-2.53	*e.m.f.*-3.034 *c.v.* .-3.074	2.949	-1.56
La(III)/La	*e.m.f.*-3.160 *c.v.* -3.254	3.100	-1.26	*e.m.f.*-3.138 *c.v.*-3.174	3.023	-2.11
Pr(III)/Pr	*e.m.f.*-3.150* *c.v.* -2.985*	3.032	-2.47*	*e.m.f.*-3.020* *c.v.* –3.007*	2.952	-1.25*
Y(III)/Y	*e.m.f.*-3.152* *c.v.* –3.305	2.774	-7.91*	– *c.v.* –3.023*	2.698	–

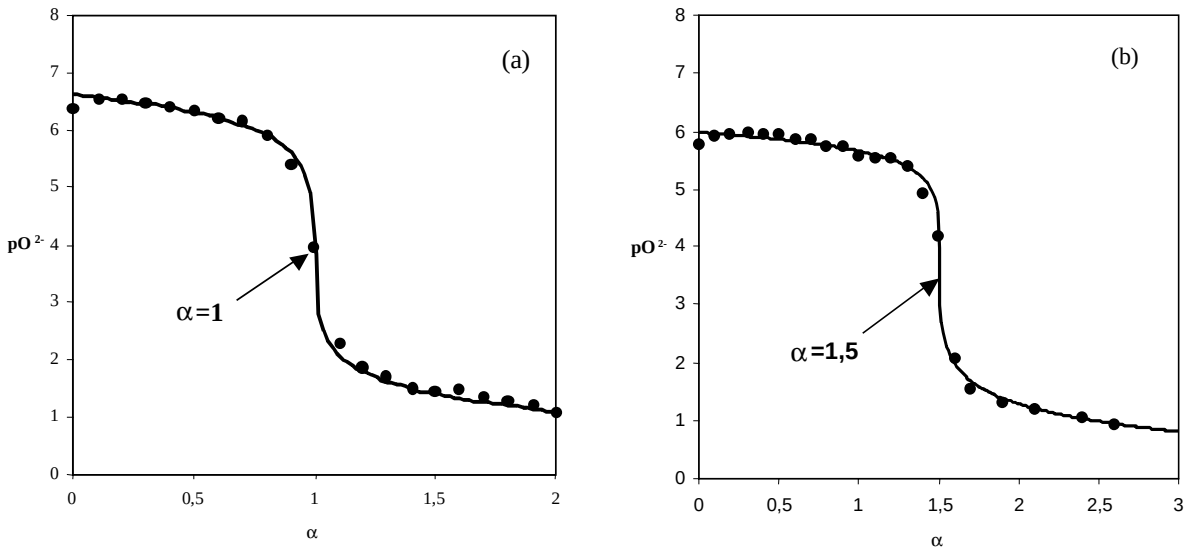
* Preliminary results.

The activity coefficient of rare earth chlorides gives information about the complexation of the cations by the melt. The complexation power depends both on the nature of the cations of the molten salts and on the working temperature. In the melt $CaCl_2$-NaCl at 550°C, which is a more oxoacidic than the eutectic LiCl-KCl, the activity coefficients values obtained are higher than in LiCl-KCl, except for lanthanum. This corresponds to a lower complexation of the $MeCl_3$ by the chloride ions of the melt, which indicates more stable complex ions formation.

3.3 Stability of Me(III)-O compounds. pk_s determination

Identification of the rare earth oxides and oxohalides that are stable in both melts, can be accomplished by the theoretical analysis of the curves obtained by potentiometric titration [12,13]. The solubility of the oxides and oxyhalides can be determined theoretically from the analysis of the experimental titration curves.

Figure 4. **Potentiometric titrations of (a) 0.0797 mol kg^{-1} Pr(III) and (b) 0.1040 Y(III) solutions by O^{2-} ions added as solid Na_2CO_3.in the eutectic LiCl-KCl at 450°C.**



The rare-earth ions were precipitated with oxide (added as Na_2CO_3 or BaO), this reaction was monitored with an *ysze* [7,14-16]. A e.m.f. jump occurrs at the point corresponding to the stoichiometric precipitation of the corresponding oxide or oxohalide. Except for the YCl_3 all the experimental curves obtained with lanthanide ions exhibited similar habits to the one of Figure 4.a. The pO^{2-} values measured by the *ysze* (after calibration), show only one equivalent point for a stoichiometric ratio:

$$\alpha = \frac{\left[O^{2-}\right]_{added}}{\left[LnCl_3\right]_{initial}} = 1.0 \qquad (7)$$

This indicates that the reaction is:

$$Ln^{3+} + O^{2-} + Cl^{-} \leftrightarrow LnOCl(s) \qquad (8)$$

For the YCl_3 solutions titrated in the eutectic LiCl-KCl by O^{2-} (Figure 4 (b)), only one equivalence point was observed for a stoichiometric ratio of α=1.5.

This value indicates that the reaction is in this case:

$$2Y^{3+} + 3O^{2-} \Leftrightarrow Y_2O_3\,(s) \qquad (9)$$

and it can be deduced that no oxychloride species were stable under the present experimental conditions. The LnOCl and Y_2O_3 formation was confirmed by XRD spectrometry analysis.

The theoretical equation corresponding to the titration curve can be elucidate from the mass balance and the solubility product of the reactions, according to the procedure previously described [7,14,15]. The solubility products of LnOCl and Y_2O_3, k_s, were determined by applying the Gauss-Newton non-linear least-squares method to the equation of the corresponding titration curves. The values obtained are shown in Table 2.

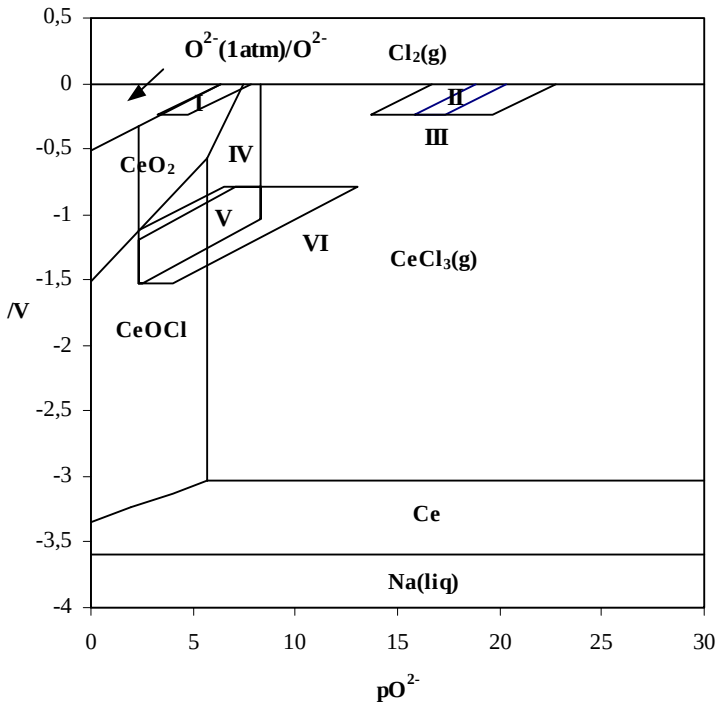
Table 2. **Solubility products, pk_s of the different oxychlorides and oxides**

Compounds	LiCl-KCl (450°C)	$CaCl_2$-NaCl (550°C)
CeOCl	7.45 ± 0.05	5.62 ± 0.07
LaOCl	7.00 ± 0.09	5.19 ± 0.05
PrOCl	7.45 ± 0.25	5.27
Y_2O_3	19.90 ± 0.22	–

3.4 Solubilization studies

With the solubility products of the Ln-O compounds and the equilibrium potentials of the different red-ox couples involved, it is possible to establish the potential-acidity diagram for the Ln-O species in both melts (Figure 5).

Figure 5. **Comparison of the potential-acidity diagram for the Ce-O compounds with the E-pO^{2-} diagram of the gaseous mixtures in the equimolar $CaCl_2$-NaCl mixture at 550ºC. MIXTURES: I: $Cl_2 + O_2$, II: Cl_2 + C, III: Cl_2 + CO, IV: HCl + H_2O, V: HCl + H_2O + H_2, VI: HCl + H_2 + CO**



This type of diagrams gives the oxo-acidity and red-ox properties of the elements in the molten salt mixtures, being possible to predict electrochemical properties and some chemical reactions. The comparison of these diagrams to the those obtained for some gaseous mixtures in the same melt and temperature [6,14,15], allows to predict optimal chlorinating conditions for rare earth oxides and oxychlorides. It is observed in the Figure that all the LnOCl, CeO_2 and Y_2O_3 can be chlorinated by HCl.

Experimental solubilization tests were carried out: i) with samples of LnOCl generated *in situ*, and ii) samples of commercial La_2O_3, CeO_2, Pr_6O_{11} and Y_2O_3. As chlorinating agent HCl was used, and the reaction progress was followed by potentiometry with an *ysze*. After the dissolution an electrochemical spectra was recorded.

During the chlorination, the oxide ions are transformed into water by HCl, according with the following reactions:

$$2HCl + LnOCl \leftrightarrow LnCl_3(disolved) + H_2O \quad (10)$$
$$6HCl + Y_2O_3 \leftrightarrow 2YCl_3(disolved) + 3\ H_2O \quad (11)$$

For CeO_2 and Pr_6O_{11}, the chlorination could occur in two stages, in the first one it is formed the oxidizing Ce(IV) which reacts with the melt evolving Cl_2(g) and dissolving $CeCl_3$, and the insoluble PrOCl respectively.

The concentration of the dissolved rare earths was determined *in situ* by titration of the final solution with sodium carbonate, showing efficiency values close to 100%.

3.5 Metal electrodeposition studies

The mechanism of electroreduction of rare-earth ions in the equimolar $CaCl_2$-NaCl and eutectic LiCl-KCl has been studied by electrochemical techniques. Previous experiments showed that refractory metals such as tungsten or molybdenum are suitable materials to use as electrodes in both melts. It is not possible to use glassy carbon due to the formation of Na-C or Li-C compounds [14].

The diffusion coefficient of the Me(III) ions could be calculated from the data obtained in the rare earth electrodeposition studies (Table 3).

Table 3. **Me(III) diffusion coefficients**

	LiCl-KCl (450ºC)		**$CaCl_2$-NaCl (550ºC)**	
	W	Mo	W	Mo
Ce(III)	1.0×10^{-5}	1.1×10^{-5}	9.2×10^{-6}	8.8×10^{-6}
La(III)	8.9×10^{-6}	8.4×10^{-6}	7.7×10^{-6}	7.8×10^{-6}
Pr(III)	9.4×10^{-6}	–	9.8×10^{-6}	–
Y(III)	1.5×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	–

The diffusion coefficient values obtained in both media were similar. These results can be explained considering the opposite effect of the temperature and viscosity of the melt: The higher temperature in the case of the molten $CaCl_2$-NaCl mixture should produce an increase in the diffusion coefficient values, however, its higher viscosity leads to lower D values.

Chonoamperometric studies did not show evidence of nucleation phenomena in the equimolar $CaCl_2$-NaCl mixture under the experimental conditions tested. However, the I-t transients obtained in the eutectic LiCl-KCl have proved that nucleation of metallic lanthanum and yttrium plays a significant role in the overall electrodeposition process. Differences between the results obtained in both molten chlorides could be related to the differences on surface tension of the melts, which affect

the interactions Me-substrate and Me-substrate-melt. Information about nucleation kinetics was obtained applying a dimensionless method.

The efficiencies in the rare earth electrodeposition processes were calculated from double potential step measurements, for several potential impossed. The results show that alkaline metal co-deposition can interfere with the metal electrodeposition, complicating thus the process.

Acknowledgements

The authors would like to thank Francisco de la Rosa (Universidad de Valladolid) and Luis Gutierrez (CIEMAT) for the technical assistance and ENRESA (Spain) for the financial support (CIEMAT-ENRESA and CIEMAT-Universidad de Valladolid agreements).

REFERENCES

[1] H. Gruppelaar, J.L. Kloosterman and R.J.M. Konings, *Advanced Technologies for the Reduction on Nuclear Waste*, ECN report, 1998.

[2] OECD Nuclear Energy Agency, *Actinide and Fission Product Partitioning and Transmutation. Status and Assessment Report*, Paris, France, 1999.

[3] Y. Sakamura, T. Inoue, O. Shirai, T. Iwai, Y. Arai and Y. Suzuki, *Proceedings of Global'99*, Jackson Hole, Wyoming, USA, 1999.

[4] T. Koyama, K. Kinoshita, T. Inoue, M. Ougier, J.P. Glatz and L. Koch, *Workshop on Pyrochemical Separation OECD/NEA*, Work 3b-4, Avignon, France, March 2000.

[5] D. Ferry, Y. Castrillejo, G. Picard, *Acidity and Purification of the Molten Zinc Chloride (33.4 mol%)-sodium Chloride (66.6 mol%) Mixture*, Electrochim. Acta, 1989, 34(3), 313-316.

[6] F. Seón, *Tesis Doctoral de Estado*, París, 1981

[7] Y. Castrillejo, A.M. Martínez,, G.M. Haarberg, B. B•rresen, K.S. Osen and R. Tunold, *Oxoacidity Reactions in Equimolar Molten $CaCl_2$-NaCl Mixture at 550°C*, Electrochim. Acta, 1997, 42, 1489-1494.

[8] G.C. Baker, Anal. Chim. Acta, 1958, 18, 118.

[9] J. Osteryoung, J.J. O'Dea, *Determining Kinetic Parameters from Pulse Voltammetric Data*, Electroanal. Chem., 1986, 14, 209.

[10] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, J. Wiley New York, USA, 1980.

[11] J. Barin, O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer, Berlin, Germany, 1973.

[12] H. Lux, Z. Elektrochemi., (1948), 52, 220, (1949), 53, 41.

[13] H. Flood T. Förland and K. Motzfeld, *The Acidic and Basic Properties of Oxides,* Acta Chemica. Scandinavica., 1952, 6, 257.

[14] A.M. Martínez, Y. Castrillejo, E. Barrado, G.M. Haarberg and G Picard, *A Chemical and Electrochemical Study of Titanium Ions in the Molten Equimolar $CaCl_2$-NaCl Mixtures at 550°C,* J. Electroanal. Chem., 1998, 449, 67-80.

[15] Y. Castrillejo, M.R. Bermejo, A.M. Martínez, C. Abejón, S. Sánchez and G.S. Picard, *Study of the Electrochemical Behaviour of Indium Ions in the Molten Equimolar $Cacl_2$-NaCl Mixture at 550°C,* J. of Applied Electrochemistry, 29(1), 65-73, 1999.