

**ELECTROCHEMICAL PROPERTIES OF ACTINIDES IN MOLTEN CHLORIDES**

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Abstract

The chemical properties of plutonium and cerium chlorides have been studied in the fused CaCl₂-NaCl equimolar mixture at 550°C using a tungsten working electrode and a pO²⁻ indicator electrode. The standard potential of Pu(III)/Pu was determined using cyclic voltammetry. The solubility product of Pu₂O₃ was calculated by potentiometric titration. The standard potential of Ce(III)/Ce have been determined by a potentiometry method. Potentiometric titrations of Ce(III) have been shown the existence of a soluble cerium oxychloride. All these data allowed us to draw the potentiel-pO²⁻ diagram which summarises the properties of plutonium and cerium compounds in the melt.

Introduction

Pyrochemical techniques, which consist in performing high temperature separations in a molten salt medium, appear as a promising and valuable route compared to aqueous methods in the field of the separation and transmutation strategies for the long life elements (1991 French law) [1]. The available molten salts, suitable for chemical processes, are numerous. A good knowledge of the molten salt actinide chemistry (and in particular for plutonium and americium) is essential to master those separation techniques.

A salt using in plutonium purification [2] have been employed to determine plutonium behavior. Actinide behavior in molten salt depend both on potential and oxoacidity level, and we have to take these two parameters into account. Thus in order to describe actinide behavior in molten chlorides in a summarizing form, potential-oxoacidity diagrams are necessary. In fact, these diagrams give an instantaneous and comprehensive view of the properties of selected elements in a solvent of interest.

Experimental*Apparatus and electrodes*

The equimolar mixture (CaCl₂ and NaCl, ACS Reagents) is melted in a vitreous carbon crucible placed in a quartz cell inside a furnace. The temperature of the furnace is controlled by a Pekly XS 30 programmable device. The mixture is fused under atmospheric pressure using dry argon. No preliminary purification was made. The reference electrode is made of a silver wire (1 mm diameter) dipped into a Pyrex tube containing a solution of silver chloride in CaCl₂-NaCl (0.75 mol/kg). The 1 mm diameter tungsten wires is used as working and counter electrodes. Electrode active surface area is determined measuring the depth of immersion. Cyclic voltammograms are performed using a AUTOLAB PGSTAT30 potentiostat coupled with a PC computer.

Preparation of plutonium chloride

Plutonium chloride is prepared by Pu/Ga metal oxidation. The first step consists of the oxydation of the Pu/Ga metal with Cl_{2(g)}. The Gallium trichloride so obtained is volatile and observed at the top of the cell [3]. After oxydation step, insoluble plutonium is chlorinated by a carbo-chlorination : graphite powder is added in the melt and Cl_{2(g)} is bubbled through the melt using a graphite gas tube. The molten salt takes on a light green tinge indicating PuCl₃ formation. The concentration of PuCl₃ is determined by alpha-analysis of salt dissolved in nitric acid.

Results and discussion

Electrochemistry of plutonium

The electrochemistry of plutonium is studied at a metallic tungsten electrode. Cyclic voltammograms are performed at different sweep rates on tungsten electrode (Fig.1). Many studies have demonstrated the Pu(III)/Pu system in molten chlorides [4-8]. Our study shows that the peak potential is not sweep rate dependent, indicating the reversible character of Pu(III)/Pu redox system. In LiCl-KCl, melt the reversibility of plutonium system was not clearly shown. Burris [9] reported that plutonium system is reversible and controlled by the diffusion mass transfer, whereas Martinot and Duyckaerts [6] described the plutonium system as a irreversible redox system. In the eutectic NaCl-CaCl₂ melt fused at 550°C, plutonium redox system appears as a reversible system controlled by a diffusion step.

The equilibrium potential of Pu(III)/Pu couple, E_{eq} was approximated from the zero current intercepts of the reverse scans of the cyclic voltammetry [10]. By using the following Nernst equation [11]:

$$E_{eq} = E^{\circ} + \frac{RT}{3F} \ln[\text{Pu(III)}] \quad (1)$$

The value of standard potential of Pu(III)/Pu is equal to $E_{\text{Pu(III)/Pu}}^{\circ} = -2.74 \text{ V} / \text{Cl}_2 (1 \text{ atm}), \text{Cl}^- (\text{molal scale})$.

Potential-oxoacidity stability ranges of plutonium compounds in the molten salt CaCl₂-NaCl can be defined and expressed in equilibrium diagrams potential-pO²⁻ [10, 12]. The nature of plutonium oxides as well as their solubility products can be determined by potentiometric titration of an oxoacid (Lux-Flood oxoacidity [13, 14]) by an oxide ion. The titration is based on the pO²⁻ (= -log [O²⁻]) measurement using an yttria-stabilised zirconia membrane electrode (YZME) which presents a Nernstian behaviour in this melt [15]. In order to evidence and to determine the stability of plutonium oxide compounds, the titration of Pu³⁺ by O²⁻ ions was realized adding small amounts of sodium carbonate in the molten salt containing an initial concentration of PuCl₃ equal to 2,48.10⁻³ mol/kg. The titration curve given Fig.2. shows only one equivalent point for α equal to 1.5 (defined as the ratio of added O²⁻ ion over the initial Pu(III) concentration, C₀). The principle of solubility product determination has been previously described [16] for plutonium compounds. Value of pK_{s(Pu₂O₃)} obtained from potentiometric titration is equal to 17.6 (molal scale). All these results allowed us to draw the potential-oxoacidity equilibrium diagram (Fig.3).

Several electrochemical studies on cerium have been done in LiCl-KCl at 500°C [17-19]. An electrochemical study on cerium has been done in NaCl-CaCl₂ at 550°C. Cerium can be considered as an americium simulator[20]. The standard potential has been determined by a potentiometric method, and its equal to $E_{\text{Ce(III)/Ce}}^{\circ} = -3.05 \text{ V} / \text{Cl}_2 (1 \text{ atm}), \text{Cl}^- (\text{molal scale})$. In order to evidence and to determine the stability of cerium oxide compounds, the titration of Ce³⁺ by O²⁻ ions was performed by adding small amounts of barium oxide in the molten salt containing an initial concentration of cerium(III) The titration curve given in Fig.4 shows only one equivalent point for α equal to 1 (defined as the ratio of added O²⁻ ion over the initial cerium(III) concentration, C₀). By comparing our titration curve and those of observed for cerium in NaCl-KCl at 727°C [21], the beginning of the titration curve indicates that a soluble species is produced.

The titration can be written as follow:



The equilibrium constant of reaction (2) is given by :

$$K_1 = \frac{[\text{Ce}^{3+}] * [\text{O}^{2-}]}{\text{CeO}^+} \quad (3)$$

By using the theoretical titration curve for soluble species [21, 22], the constant value K₁ has been obtained (best fitting of the experimental titration curve), and is equal to pK₁ = 4.7 ± 0.05. The difference between the experimental points and the theoretical curve, observed at the beginning of the titration, can be ascribed to the original presence of a low fraction of Ce(III) in the form of CeO⁺.

Conclusions

This study confirms the stability of two oxidation states of plutonium and cerium: (0 and III) in the equimolar mixture $\text{CaCl}_2\text{-NaCl}$ fused at 550°C . The oxidation states (II) and (IV) were not evidenced. The electrochemical study indicated a reversible behavior of the redox system Pu(III)/Pu . The standard potential obtained are $E^\circ_{\text{Pu(III)/Pu}} = -2.74 \pm 0.02 \text{ V}$ and $E^\circ_{\text{Ce(III)/Ce}} = -3.05 \text{ V/Cl}_2(1\text{atm}), \text{Cl}^-$ versus the Cl_2/Cl^- electrode system (molal scale).

The stability of Pu-O and Ce-O compounds were investigated. The solubility product of Pu_2O_3 was determined by potentiometric titration of Pu(III) ions by sodium carbonate and the potentiometric titration of Ce(III) ions by BaO has been demonstrated the existence of a soluble oxychloride CeO^+ .

All these data allowed us to draw the potential- pO^{2-} diagram which summarizes the properties of plutonium and cerium compounds in the melt and can be used to predict the separation conditions.

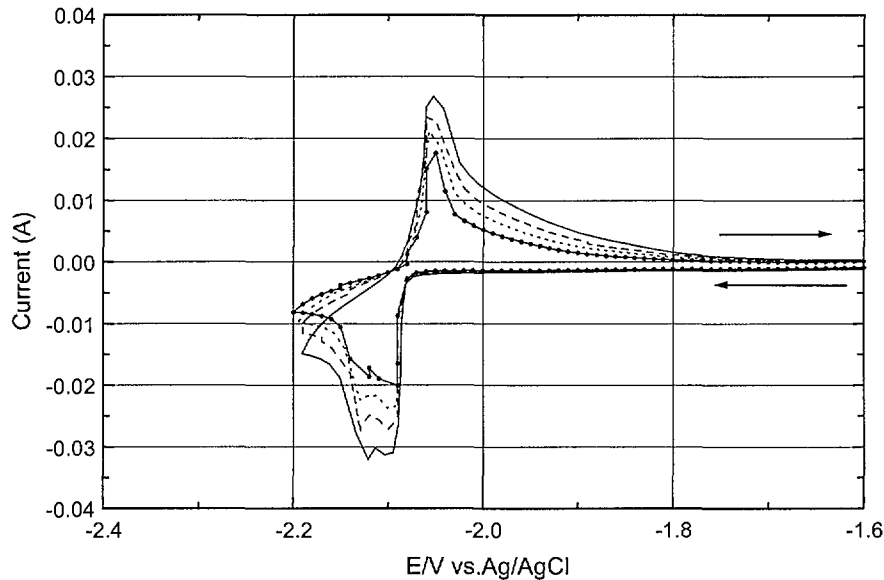


Figure 1: Cyclic voltammograms of PuCl_3 in the molten salt NaCl-CaCl_2 at 550°C . $[\text{PuCl}_3] = 2.48 \cdot 10^{-3} \text{ mol/kg}$. Working electrode: tungsten, electrode area: 0.604 cm^2 , scan rate: 0.2 V/s , 0.25 V/s , 0.3 V/s , 0.4 V/s

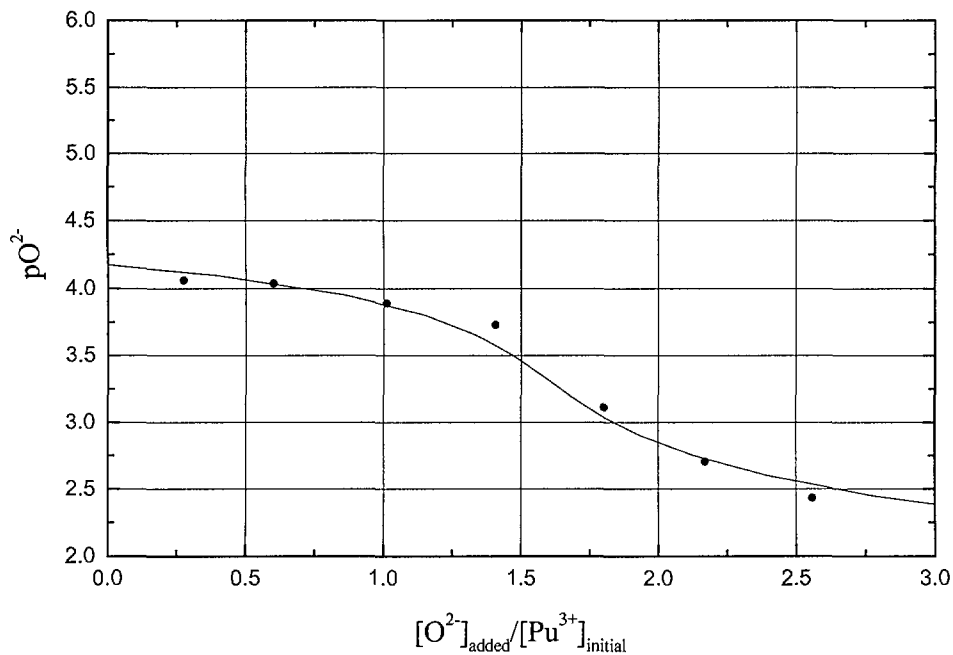


Figure 2: Potentiometric titration curve of 0.00278 mol/kg Pu^{3+} solution by O^{2-} ions added as solid Na_2CO_3 . Experimental points and theoretical curve.

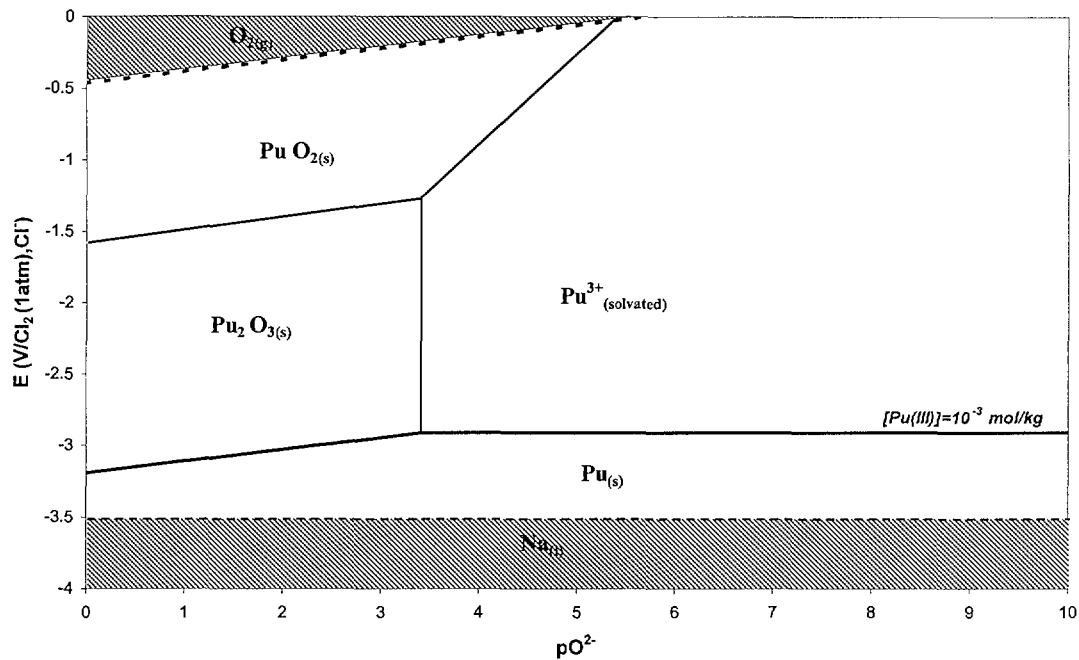


Figure 3: Potential- pO^{2-} diagram for plutonium in the equimolar CaCl_2 - NaCl mixture at 550°C , $[\text{Pu(III)}]=10^{-3}$ mol/kg.

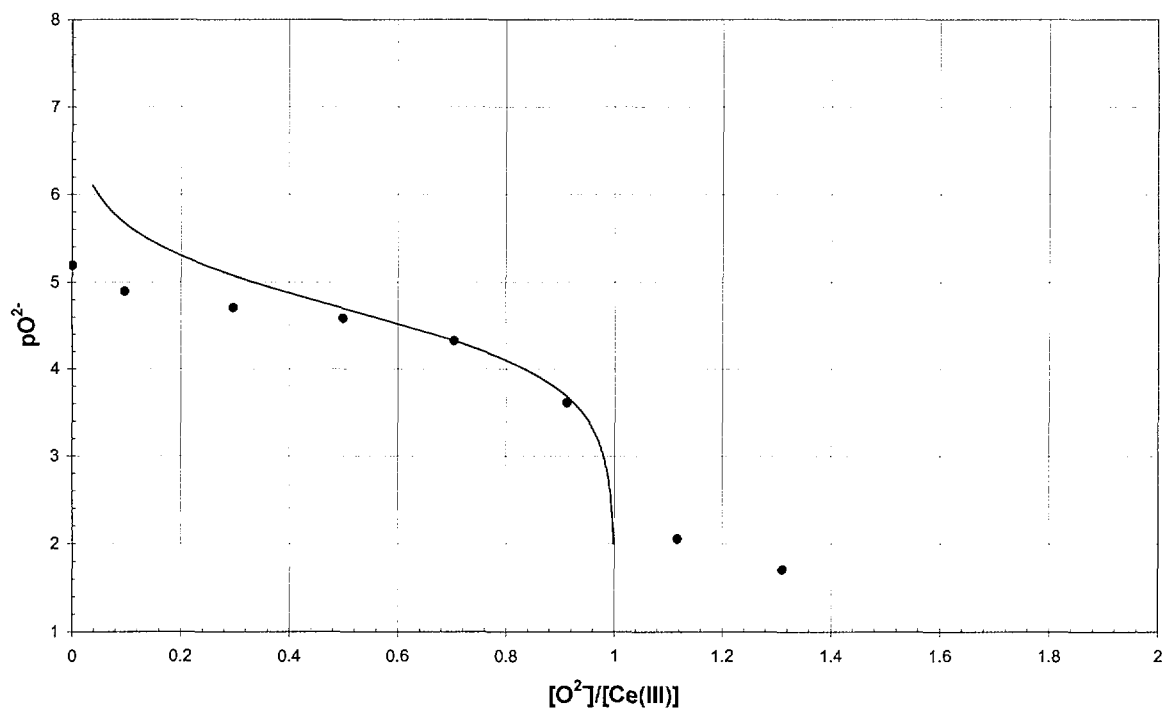


Figure 4: Potentiometric titration curve of Ce^{3+} solution by O^{2-} ions added as solid BaO . Experimental points and theoretical curve.

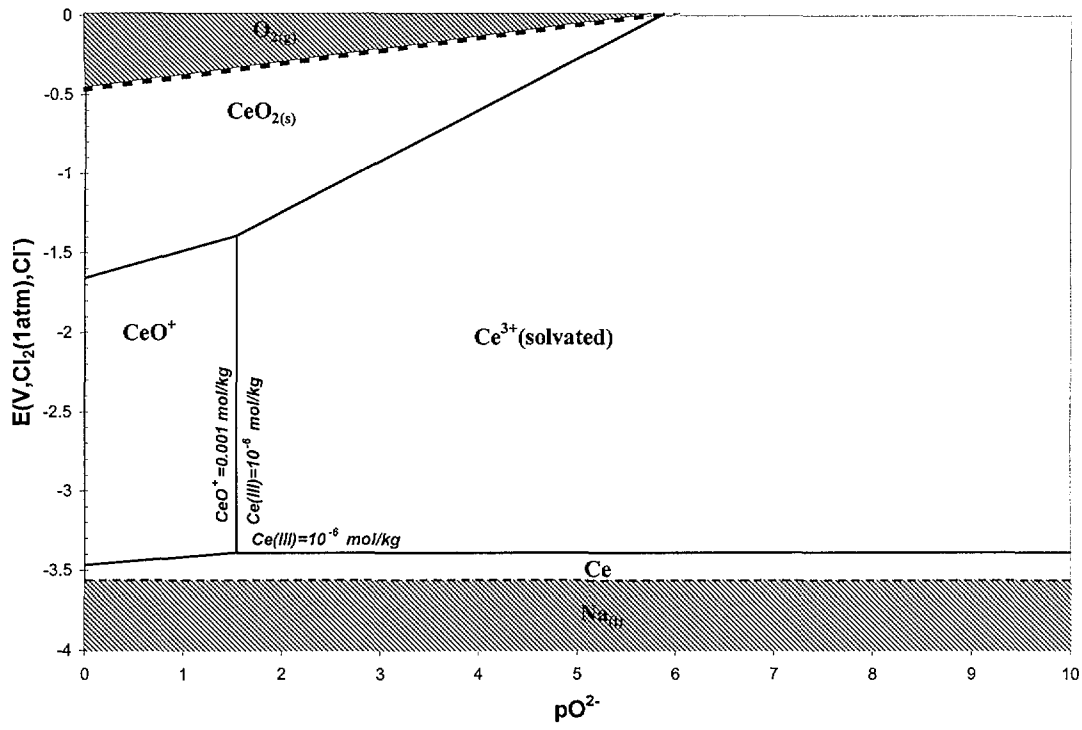


Figure 5: Potential- pO_2^- diagram for cerium in the equimolar $CaCl_2$ - $NaCl$ mixture at $550^\circ C$, $[Ce(III)] = 10^{-6} \text{ mol/kg}$, $[CeO^+] = 10^{-3} \text{ mol/kg}$.

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