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ADVANCED STUDIES ON PLUTONIUM FOR PU ISOTOPE TRANSMUTATION AND PU SEPARATION

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ABSTRACT

In this paper, I discuss and present the advanced experiments methods for thermochemical properties of plutonium in liquid gallium at 1073 k, application to plutonium cerium separation and the theoretical studies on Pu isotope transmutation. Electrochemical investigations on plutonium diluted in liquid gallium using molten chlorides showed that gallium can be used as solvent metal for pyrochemical processes involving plutonium at 1073 k. In particular, a selective extraction of plutonium from gallium by anodic oxidation is thermodynamically possible. The deposition of plutonium on a liquid gallium cathode is also possible with CaCl₂ as molten salt with a careful control of cathode potential.

KEYWORDS

Thermal spectra, subcritical reactor, isotopic composition, equilibrium cycle, activity coefficient, chloride salts, solvent metal.

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INTRODUCTION

In this paper, I discuss and present the advanced experiments methods for thermochemical properties of plutonium in liquid gallium at 1073 k, application to plutonium cerium separation and the theoretical studies on Pu isotope transmutation. Electrochemical investigations on plutonium diluted in liquid gallium using molten chlorides showed that gallium can be used as solvent metal for pyrochemical processes involving plutonium at 1073 k. In particular, a selective extraction of plutonium from gallium by anodic oxidation is thermodynamically possible. The deposition of plutonium on a liquid gallium cathode is also possible with CaCl₂ as molten salt with a careful control of cathode potential.

A TRANSMUTATION STUDY ON PU ISOTOPE TRANSMUTATION

The most important plutonium isotopes are Pu 239, Pu 240 and Pu 241. The Pu 239 is a very good fissile isotope, especially in fast spectrum. Pu 241 is still better as it presents a very high *sf* and a very low *sc*. If it is transmuted without allowing a long decay span, the amount of Am 241 built-up remains small, and the residual radiotoxicity can be highly decreased by eliminating the aforementioned Pu isotopes. Pu 240 is not a good fissile material, and it is still worse for thermal spectra, but in fast spectrum it can be eliminated either directly or by conversion to Pu 241. In the following, the inherent burnup features of Pu isotopes transmutation are studied. It is presumed that a subcritical reactor provides for a flux *F* and creates a spectrum in which the microscopic cross section for these isotopes are known. We take the following values of table:

Pu 239	sa= 2.21	sf=1.75
Pu 240	sa=0.82	sf=0.35
Pu 241	sa=2.43	sf=2.43

Conversion of Pu 241 into Pu 242 is not taken into account in the model, as it accounts for much less than 1% of the radiotoxicity. It is also assumed that the reactor is loaded with the Pu discharged from LWR, which corresponds to the following inventory (per ton of initial uranium loaded in the LWR) as:

Pu 239 = 5.19 kg	Pu 240 = 2.17 kg	Pu 241 = 1.03 kg
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We use this information as starting point. After each burnup cycle, the total amount of eliminated Pu is computed, and the same mass is reloaded with the isotopic composition given above.

The governing equations are:

$$\begin{aligned}
 d \text{ Pu 239} / dt &= sa_{239} \cdot F \text{ Pu 239}, \\
 d \text{ Pu 240} / dt &= sa_{240} \cdot F \text{ Pu 240} + sc_{239} F \text{ Pu 239}, \text{ and} \\
 d \text{ Pu 241} / dt &= sa_{241} \cdot F \text{ Pu 241} + sc_{240} F \text{ Pu 240}.
 \end{aligned}$$

We can find the following:

$$Pu_{239}(t) = Pu_{239} \cdot e^{-sa_{239} F} ,$$

$$Pu_{240}(t) = Pu_{240} \cdot e^{-sa_{240} F} + Pu_{239} \cdot (sc_{239} / sa_{239} - sa_{240}) \cdot (e^{-sa_{240} F} - e^{-sa_{239} F}) .$$

$$Pu_{241}(t) = Pu_{241} \cdot e^{-sa_{241} F} + Pu_{240} \cdot (sc_{240} / sa_{241} - sa_{240}) \cdot (e^{-sa_{240} F} - e^{-sa_{241} F}) + Pu_{239} \cdot sc_{239} \cdot sc_{240} \cdot (e^{-sa_{239} F} / (sa_{240} - sa_{239}) \cdot (sa_{241} - sa_{239})) + (e^{-sa_{240} F} \cdot (sa_{239} \cdot sa_{240}) \cdot (sa_{241} - sa_{240})) + (e^{-sa_{241} F}) / ((sa_{239} - sa_{241}) \cdot (sa_{240} - sa_{241})) .$$

The evolution of the inventory is given for 24 cycles of $(2.5 \cdot 10^{23} \text{ n/cm}^2)$ fluence every one. It is presumed that the microscopic cross sections do not change along the burnup, which is a hypothesis that can not be admitted for detailed calculations of a given reactor in a given cycle, but is acceptable for an analytical study. It is observed that an equilibrium cycle is achieved after 12 cycles. Then, the material unloaded from the reactor has composition given by the following fraction:

$Pu_{239} = 0.2735$	$Pu_{240} = 0.5625$	$Pu_{241} = 0.164$
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The residual fraction of each isotope is given and it is defined as the inventory of an isotope still in the reactor divided by the total amount that has been loaded in the previous cycles. This depicts an integral view of the accumulated inventory that was loaded in the reactor along the successive cycle and the total amount that was transmuted. The information clearly points out an almost asymptotic behaviour in the Pu-isotopes elimination, if the previous scheme is adopted. The reactor fuel becomes more and more Pu-240 dominated, which enables us to reconsider a second pattern of recycling instead of keeping the isotopic composition of the LWR-unloaded Pu, after reaching the equilibrium cycle, the successive cycles must be loaded with the isotopic composition of the Pu discharged from the equilibrium cycle. The isotopic composition was given before. It has shown that the evolution of residual fraction of the Pu-isotopes. A third phase was set up after cycle 24, once the new isotopic composition reached again the equilibrium cycle.

In this case, the isotopic composition of the discharged Pu is :

$Pu_{239} = 0.0962$	$Pu_{240} = 0.7054$	$Pu_{241} = 0.1984$
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The very small amount of Pu-odd isotopes poses a problem about the quality of the fuel in order to get a high-enough Keff. This problem disappears if it is considered that the reactor neutronics is mainly boosted by U-233 (albeit this isotope poses a new problem, related to its own radiotoxicity along a very long time span, as its half-life is $1.6 \cdot 10^5$ years). Also, it has shown that depicts that the residual fraction of Pu-239 reaches very low values, of the order of 0.17, while Pu-240 arrives to 15% and Pu-241 to 13% (this one is mainly created by Pu-240 conversion). In fact, from the

governing equations and from the values, it is seen that it is possible to destroy Pu 239, but it is difficult to get a high level of Pu 240 cleaning and therefore of Pu 241 elimination. It is seen that the residual fraction of Pu 239 follows nearly the law:

$$F_q = 10^{-x}$$

where; $x = F t / 10^{24}$.

However, the residual fraction of Pu 240 and Pu 241 follows the law:

$$F_{0.1} = 10^{-y}$$

where; $y = F t / 3 \cdot 10^{24}$, Hence, for $F t = 6 \cdot 10^{24}$.

Which is a very large value of fluence, the residual fraction of Pu 239 would be 1 ppm, while the fraction of Pu 240 would be 1.1% and that of Pu 241 --- 0.87. Thermochemical properties of plutonium in liquid gallium at 1073

Cyclic voltammograms, recorded in molten CaCl₂ on a liquid gallium working electrode containing or not plutonium, are reported in references, without plutonium, that represents the electrochemical window on gallium metal in CaCl₂ media, exhibits two peaks Ia and IIc that are attributed to the oxidation of gallium metal into gallium chloride (mono or trichloride) and to the reduction of Ca²⁺ into cerium metal in liquid gallium. In presence of plutonium, to the oxidation of Pu (dissolved in liquid gallium) into Pu III and to the reduction of Pu III into PuGa. The deposition a such intermetallic solid compounds have been reported by scientist for the reduction of Pu II on a Ga electrode at 833 k. In those experiments, no plutonium was dissolved in the gallium. These redox systems seem to be irreversible so, we can not deduce any characteristic potential value from cyclic voltammograms. In order to obtain equilibrium potential values, chronoamperograms have been performed and reported as I = Fe curves at various time with CaCl₂ and with the equimolar NaCl -KCl molten salts. The curves present an anodic wave before the anodilimit II a. Those redox systems are, respectively, attributed to the oxidation of Pu (dissolved in the gallium) into Pu III and to the oxidation of Ga into Ga (I) or Ga (III). The equilibrium potential at zero current can be obtained from current-potential curves. This potential is set by the redox system Pu III / PuGa given by the following equation:

$$F_{Pu\ III / PuGa} = F^*_{Pu\ III / Pu} + (2.3 R t / 3 F) \cdot \text{Log} (X_{Pu\ III} / X_{PuGa}) - (2.3 R T / 3 F) \cdot \text{Log} Y_{PuGa}$$

where $F^*_{Pu\ III / Pu}$ is the formal potential of Pu III /Pu in the chloride media ($F^*_{Pu\ III / Pu} = 2.51\text{ V}$ in CaCl₂ and $F^*_{Pu\ III / Pu} = 2.54\text{ V}$ in NaCl -KCl), Y_{PuGa} is the activity coefficient of plutonium and X_{PuGa} the molar fraction of plutonium in liquid gallium. The activity coefficients of plutonium in liquid gallium calculated by using the previous relation. The values obtained with two molten chloride salts are of the same order of magnitude. This is consistent with that the activity coefficient in the metal phase does not depend on the nature of the solvent. We can retain a value of $\text{Log} (Y_{PuGa})$ equal to 7.3 (changing 0.5) at 1073 K for low concentrations of plutonium in liquid gallium (near 0.01 molar fraction). For an exhaustive study of the potentialities of gallium as solvent metal for pyro processes, this data could be completed by values of the activity coefficient of plutonium in gallium near saturation

by using the protocol proposed by references. In this work, values of Log (YPuGa) at saturation between 733 and 833 K are deduced from measurements on liquid Ga in equilibrium with a solid PuGa intermetallic compound.

Molten Chlorides	XPuGa	Log (YPuGa)
CaCl ₂	0,0129 (changing 0.0005)	- 7.5 (changing 0.3)
NaCl-KCl	0.0137 (changing 0.0005)	- 7.2 (changing 0.3)

APPLICATION TO PLUTONIUM CERIUM SEPARATION

The thermo-chemical properties of cerium in gallium were considered previously to plutonium in the frame of this work. The value of the logarithm of the activity coefficient of Ce in liquid Ga at 1073 has been determined to $\text{Log} (Y_{\text{CeGa}}) = - 8.27$ (changing 0.15) , which is consistent with references results: $\text{Log} (Y_{\text{CeGa}}) = - 7.9$, as activity coefficient of Pu in liquid Ga was not available in literature , gallium has been compared to other liquid metals such as aluminum , bismuth and cadmium for the separation of an actinide , i.e. plutonium from a lanthanide , i.e. cerium . To point out the influence of metal solvent on thermodynamic selectivity, we have calculated the difference of potential (i.e. electrochemical selectivity) between plutonium and cerium, by using the present results on liquid gallium and the published values for aluminum, bismuth and cadmium. The activity coefficients of Pu and Ce in these liquid metals are reported. This difference of potential (electrochemical selectivity) between plutonium and cerium with a metallic solvent MS can be calculated as:

$$F_{\text{Pu}} - F_{\text{Ce}} = D F^*_{\text{Pu-Ce}} + (2.3 RT / 3 F) \cdot ((X_{\text{Pu III SALT}} \cdot X_{\text{Ce MS}}) / (X_{\text{Ce III SALT}} \cdot X_{\text{Pu MS}})) + (2.3 RT / 3 F) \cdot \text{Log} (Y_{\text{Ce MS}} / Y_{\text{Pu MS}})$$

where $D F^*_{\text{Pu-Ce}}$ is the difference of the formal standard potential of Pu III / Pu on Ce III /Ce in the molten salt , $D F^*_{\text{Pu-Ce}} = + 0.47 \text{ V}$ in equimolar NaCl - KCl , and $Y_{\text{Pu MS}}$ and $Y_{\text{Ce MS}}$ are the activity coefficients of plutonium and cerium in metal solvent . The selectivity of the separation between plutonium and cerium is:

$$S (\text{Pu} / \text{Ce}) = ((X_{\text{Ce III SALT}} \cdot X_{\text{Pu MS}}) / (X_{\text{Pu III SALT}} \cdot X_{\text{Ce MS}}))$$

At equilibrium, the selectivity between plutonium and cerium becomes:

$$(2.3 RT / 3 F) \text{Log} S (\text{Pu/Ce}) = D F^*_{\text{Pu-Ce}} + (2.3 RT / 3 F) \cdot \text{Log} (Y_{\text{Ce MS}} / Y_{\text{Pu MS}})$$

The influence of the solvent metal on the selectivity between plutonium and cerium in a molten chloride is described by the following equation:

$$D F^*_{\text{Pu-Ce}} \text{'MS} = (2.3 RT / 3 F) \cdot \text{Log} (Y_{\text{Ce MS}} / Y_{\text{Pu MS}})$$

The values of $D F^*_{\text{Pu-Ce}} \text{'MS}$ as function of temperature obtained from published values and from the results. If $(D F^*_{\text{Pu-Ce}} \text{'MS})$ is high absolute value , the selectivity decreases . At 1073 K , the use of liquid gallium is better than bismuth and cadmium . It is more difficult to conclude about the comparison of gallium and aluminum as the gap between their $D F^*_{\text{Pu-Ce}} \text{'MS}$ is small and the uncertainties

should be taken into account .At lower temperatures (873 K), for which, the plutonium and cerium concentrations approach or exceed the solubility limits in the solvent metal, the selectivity between plutonium and cerium decreases in cadmium and is nearly constant in bismuth. For aluminum which solidify at 933 K, the selectivity increases.

CONCLUSION

we discuss the theoretical study on Pu transmutation, thermochemical properties of plutonium in liquid gallium at 1073 K that include the records in molten CaCl₂ on liquid gallium working electrode containing plutonium or not and the application to plutonium cerium separation for the thermochemical properties of cerium in gallium to plutonium .electrochemical investigations on plutonium diluted in liquid gallium using molten chlorides.

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