Uranium (III)-Plutonium (III) co-precipitation in molten chloride

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Graphical abstract
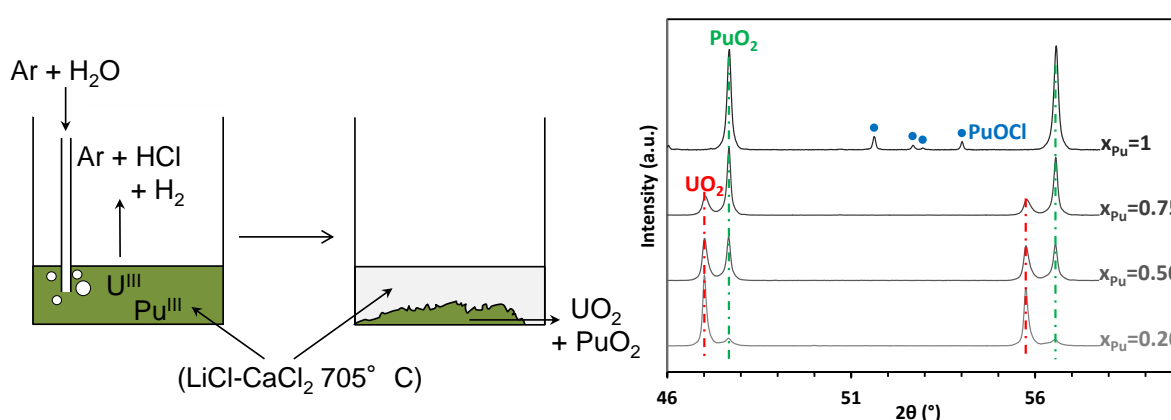
Highlights

- ● Co-precipitation of U(III) and Pu(III) is quantitative in molten salt LiCl-CaCl$_2$ (30-70 mol%).

- ● Pu(III) is prepared *in situ* in the molten salt by carbochlorination of PuO$_2$ and U(III) is then introduced as UCl$_3$.

- ● Precipitation of Pu(III) leads to a mixture of PuO$_2$ and PuOCl.

- ● Co-precipitation of U(III) and Pu(III) leads to consecutive precipitation of UO$_2$ and PuO$_2$.

Abstract

Co-management of the actinides in an integrated closed fuel cycle by a pyrochemical process is studied at the laboratory scale in France in the CEA-ATALANTE facility. In this context the co-precipitation of U(III) and Pu(III) by wet argon sparging in LiCl-CaCl$_2$ (30-70 mol%) molten salt at 705°C is studied. Pu(III) is prepared *in situ* in the molten salt by carbochlorination of PuO$_2$ and U(III) is then introduced as UCl$_3$ after chlorine purge by argon to avoid any oxidation of uranium up to U(VI) by Cl$_2$. The oxide conversion yield through wet argon sparging is quantitative. However, the

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preferential oxidation of U(III) in comparison to Pu(III) is responsible for a successive conversion of the two actinides, giving a mixture of UO_2 and PuO_2 oxides. Surprisingly, the conversion of sole Pu(III) in the same conditions leads to a mixture of PuO_2 and PuOCl, characteristic of a partial oxidation of Pu(III) to Pu(IV). This is in contrast with coconversion of U(III)-Pu(III) mixtures but in agreement with the conversion of Ce(III).

1. Introduction

In the nuclear field, the recycling of valuable actinides from spent nuclear fuel requires dissolution of the fuel, partitioning of the elements, and finally recovering the valuable actinides in a solid form by means of a conversion step. In the framework of the next generation nuclear fuel cycles, co-management of two (or more) actinides was proposed for recycling reusable energy-producing actinides (mainly U and Pu) together, or for transmuting radiotoxic minor actinides within UO_2-based materials [1]. Many researches are still focused on co-conversion processes to obtain mixed actinide oxides to refabricate fresh fuel or dedicated fuels or targets. In France, spent nuclear fuel is currently recycled at industrial scale by the hydrometallurgical PUREX process and co-conversion processes were studied involving a co-precipitation of mixed actinide precursors and then a co-calcination into mixed actinide oxides. Oxalic co-precipitation emerged as a convenient process for actinide co-conversion into oxalate solid solutions, precursors of actinide oxide solid solutions with homogeneous actinide distribution at molecular scale [2-4].

In addition to the PUREX process based on an aqueous solution, pyro reprocessing methods for spent nuclear fuels are being developed. Pyrochemical processes show specific advantages such as high resistivity to radiolysis and a reduced criticality risk [5-6]. Different kinds of process are considered [7], including actinide separation from fission products based on electrorefining methods [8-9] or on molten salt – liquid metal extraction process [10]. The latter one is studied at CEA (French Atomic Energy and Alternative Energies Commission) at the laboratory scale. After the separation step, actinides are back-extracted in the $LiCl$-$CaCl_2$ (30-70 mol%) molten salt at high temperature (705°C) [11]. Solubilized at the oxidation state (III) in the salt, actinide conversion to AnO_2 oxides needs to be considered for the fabrication of new nuclear fuel.

Precipitation in molten chloride can be achieved by adding phosphates [12-13] or by increasing the O^{2-} ion concentration in the salt. This increase is generally performed by adding oxo donor solids like alkaline or alkaline-earth oxides or carbonates [14-15], or by oxobasic gas sparging [16]. The former method isn't convenient because of the increasing quantity and the changing composition of the molten salt. The latter method is generally achieved by sparging oxygen in the media. However, oxygen is a too oxidative for uranium which precipitates in the form of oxides with higher oxidation states than the target UO_2 oxide [17-18]. A technique based on wet argon sparging that is less oxidative than oxygen and which does not change the molten salt composition was patented for pyro reprocessing of actinides from spent nuclear fuel [19]. A similar technique was used in the past for crystal growth of UO_2 and ThO_2 in fluoride molten salt [20]. A first study on the precipitation of non-radioactive elements (cerium (III) and neodymium (III)) by wet argon sparging was reported [21-22]. Several $CeCl_3$/$NdCl_3$ ratios were studied, the lanthanides precipitation rates were determined around 99.9% and the precipitates mainly contained mixed oxychloride $(Ce_{1-x}Nd_x)OCl$ and a small amount of mixed oxide $Ce^{IV}_{1-y}Nd^{III}_yO_{2-0.5y}$. Then, the uranium (III) precipitation using wet argon sparging was

studied [23]. The main part is converted into UO_2 powder but some uranium is lost during the process due to the volatility of uranium chloride. Finally, as a preliminary study of uranium (III) co-precipitation with trivalent actinides (plutonium and/or minor actinides), the co-precipitation of uranium (III) and neodymium (III) by wet argon sparging was investigated [23]. There was a preferential precipitation of Uranium (III) compared to neodymium (III) and the two elements react consecutively during the precipitation avoiding solid solution formation.

The present work deals with the study of the conversion of Pu(III) and the co-conversion of U(III) and Pu(III) dissolved in the LiCl-CaCl$_2$ (30-70 mol%) molten chloride by wet argon sparging. The experiments described were performed in the CEA-ATALANTE facility at Marcoule.

2. Experimental

2.1 General features

The experimental device used for Pu(III) and U(III)-Pu(III) precipitation experiments is shown schematically in Figure 1 and was previously described [23]. This device is used in this study both for initial plutonium solubilisation in the salt through carbochlorination, and for precipitation studies. The gas nature and path is modified depending on the considered step. To prevent plutonium health hazards, the use of this highly radioactive element required the installation of the assembly used in a nuclear glove box. The LiCl-CaCl$_2$ (30-70 mol%) melt was prepared from LiCl (Sigma Aldrich, 99%) and CaCl$_2$ (Alpha Aesar 96%).
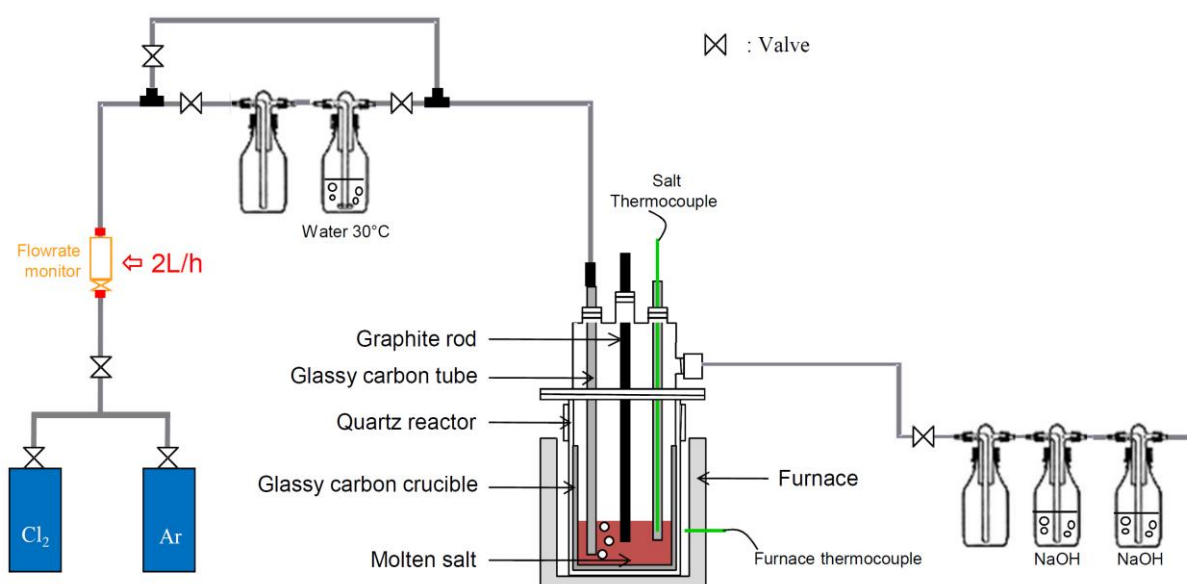

Figure 1: Experimental set-up used both for conversion of PuO_2 into dissolved $PuCl_3$ by carbochlorination (using Cl$_2$ gas and by-passing the water bubbler) and for plutonium or uranium-plutonium precipitations in molten LiCl-CaCl$_2$ by wet argon sparging (using Ar gas and water bubbler). Reference electrode and pO^{2-} electrode are not represented for clarity (§ 2.5).

The precise mass flowmeter used for argon and chlorine gas allows us to accurately determine the amount of gas injected in the salt. The downstream ~1 M NaOH solution neutralizes the hydrochloric acid gas produced by the water reaction in the fused salt.

2.2 Preparation of LiCl-CaCl$_2$ melt containing Pu(III)

The preparation of the LiCl-CaCl$_2$ (30-70 mol%) molten chloride containing up to 2% plutonium (8.4 x 10^{-2} mol.kg^{-1}) is carried out by *in situ* conversion of plutonium (IV) oxide PuO$_2$ (from CEA) into plutonium (III) chloride PuCl$_3$. This conversion is carried out by carbochlorination at 705°C in the precipitation reactor, consisting of subjecting the molten chloride and the dissolved oxide to bubbling of gaseous chlorine in the presence of graphite carbon according to the reaction (1) [24]:

$$PuO_2 + C_{(gr)} + 2Cl_{2(g)} \rightarrow PuCl_{4(salt)} + CO_{2(g)} \quad (1)$$
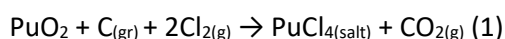
Pu^{4+} in solution in the molten chloride is unstable and spontaneously reduces to plutonium Pu^{3+} [17]:

$$PuCl_{4(salt)} \rightarrow PuCl_{3(salt)} + 1/2Cl_{2(g)} \quad (2)$$
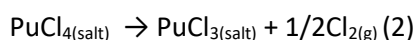
The mixture of 40 g of LiCl-CaCl$_2$ containing the appropriate PuO$_2$ amount was introduced in a vitreous carbon crucible (SGL Carbon, Sigradur type), itself placed into a leak tight quartz reactor heated in a vertical tubular furnace (Figure 1). The salts were dried under vacuum at 250°C before use. The mixture was heated to 705°C (2°C.min^{-1}) under 2 NL.h^{-1} of dry argon (Air Liquide, Ar N60, H$_2$O<0.6ppm, O$_2$<0.1ppm). The bath temperature was measured with an S-type thermocouple (±1°C) sheathed into a glassy carbon closed end tube (Carbone Lorraine, V25 type) immersed into the molten salt. The molten salt containing PuO$_2$ in which graphite rods (Graphitec, ATJ49 type) are immersed is subjected to bubbling of Cl$_2$ at 2 NL.h^{-1} for 1 hour by means of a vitreous carbon tube (SGL Carbon, Sigradur type) and then the salt is maintained under a chlorine atmosphere for 12 hours by closing the reactor upstream and downstream. At the end of this carbochlorination, the chlorine is purged abundantly with argon, graphite rods are removed from the salt, and the effective dissolution of the plutonium is controlled by extracting and dosing a salt sample. These samples had the characteristic blue colour of plutonium (III). The results of the analyses are presented in Table 1.

2.3 Preparation of LiCl-CaCl$_2$ melt containing Pu(III) and U(III)

For the mixed U(III)/Pu(III) precipitation study, uranium cannot be introduced in the mixture at the same time as plutonium because of the oxidation of uranium to U(VI) by Cl$_2$. After carbochlorination of PuO$_2$ and chlorine purge by argon, U(III) is introduced in the molten salt containing Pu(III) as UCl$_3$ powder. Samples of the salt were then extracted for analyses (Table 1). Uranium trichloride was synthesized at the laboratory from uranium oxide U$_3$O$_8$ in two steps: conversion to UCl$_4$ and then to UCl$_3$. The details of the synthesis method were described previously [23] and the product is actually composed of 93 wt.% UCl$_3$ and 7 wt.% UO$_2$ [23]. Three compositions X$_{Pu}$ = n$_{Pu}$/(n$_U$+n$_{Pu}$) = 0.20, 0.50, 0.75 were studied. In each case the precipitation is carried out on 40 g of LiCl-CaCl$_2$ salt containing 2 wt.% of actinides (U + Pu = 8.4 x 10^{-2} mol.kg^{-1}). An additional pure uranium precipitation X$_{Pu}$ = 0 was also performed to use as a reference for potentiometric measurement.

2.4 Plutonium and uranium-plutonium precipitations

Plutonium and uranium-plutonium precipitations were performed by sparging wet argon through the glassy carbon tube (SGL Carbon, Sigradur type) in the molten chloride containing dissolved Pu(III) and/or U(III). Wet argon was obtained by argon sparging (2 NL.h^{-1} through a PTFE frit) in water at 30°C (glovebox temperature), in a dedicated bottle placed upstream of the reactor (Figure 1). The reaction of water in the fused salt produced hydrochloric acid gas (Equation 3) neutralized downstream by a ~1 M NaOH solution.

$$H_2O_{(g)} + 2Cl^-_{(salt)} \rightarrow O^{2-}_{(salt)} + 2HCl_{(g)} \quad (3)$$
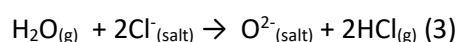
Using the saturation water vapor in these conditions [25] which was previously confirmed [21], the water molar flow is calculated (3.6 x 10^{-3} mol.h^{-1}).

The precipitation experiments were run at 705°C for about 4 hours. After the precipitation, wet argon was replaced by dry argon for about one hour. The bubbling tube was then removed from the salt. The mixture was cooled to room temperature under argon atmosphere, then recovered from the crucible and dissolved in 100mL of water. The precipitate was filtered, washed several times with deionized water and dried at room temperature. The final powder was analysed by XRD.

2.5 Electrodes and potentiometric instrumentation

In order to follow the evolution of the actinides precipitation in the LiCl-CaCl$_2$ molten salt, O^{2-} oxide ion activity in the molten salt was measured by potentiometry (4):

$$pO^{2-} = -\log [O^{2-}] \quad (4)$$

Zero current potentiometric measurements were performed with a two-electrode set-up connected to a potentiostat-galvanostat Autolab PG Stat 30 controlled with the Autolab software package (Metrohm).

The electrodes used consisted of an AgCl/Ag reference electrode and a selective oxide ions electrode made of yttrium stabilized zirconia (YSZ electrode). The details of the electrodes preparation and YSZ electode calibration have already been reported [23]. The O^{2-} concentration was determined by measuring the electromotive force (e.m.f.) between the reference and the YSZ electrodes. The measurement is performed continuously and the plot of the pO^{2-} as a function of the normalized term (n_{H2O}/n_{An}) allows a qualitative monitoring of the precipitation. Indeed, after the precipitation ended, the bubbling of wet argon causes an increase in the concentration of free O^{2-} ions in the salt which results in a fall of the measured potential. This potential drop should theoretically take place for a ratio n_{H2O}/n_{An} equal to 2 for the precipitation of an oxide AnO$_2$, to 1.5 for the precipitation of an oxide An$_2$O$_3$ and to 1 for that of oxychloride AnOCl.

2.6 Analytical techniques

Alpha spectroscopy and thermal ionization mass spectrometry (TIMS)

The precipitation yields and the progress of the precipitation of each of the actinides for the U(III)/Pu(III) precipitations were determined from the concentration of soluble plutonium and uranium remaining in the molten salt at the end or during the precipitations. Samples of about 100 mg were extracted from the hot mixture by suction through a quartz tube at the end or during the

precipitations, were dissolved in 100 mL of water and filtered to remove any precipitate. The filtrate was then acidified with nitric acid to stabilize the solubilized elements. The concentrations of soluble species in the salt were measured by alpha counting for Pu and by thermal ionization mass spectrometry (TIMS) for U. The analyses of the solutions gave the amount of unreacted plutonium and uranium in the molten salt.

X-ray diffraction (XRD)

The powder X-ray diffraction patterns of the precipitates were recorded using a Bruker AXS D8 Advance diffractometer in θ-θ Bragg Brentano configuration, with CuKα radiation (Kα1 = 1.5406 Å, Kα2 = 1.5444 Å) and a LYNXEYE sensitive detector. Measurements were performed over a 2θ range of 10-80°, the scan step was 0.02°. The profile fitting and the cell parameters refinements were performed using the powder option of JANA2006 [26].

3. Results and discussion

3.1 Potentiometric monitoring of precipitation.

The potentiometric monitoring of pO^{2-} in the molten salt was carried out on plutonium (III) alone, the three mixed compositions, and also on sole uranium (III) for comparison ($X_{Pu} = 0$), the latter not being reported in [23] (Figure 2a). Surprisingly, the variation of pO^{2-} as a function of n_{H2O}/n_{Pu} during pure plutonium precipitation (X_{Pu}=1) does not show a sudden drop, at most a slight inflection point for n_{H2O}/n_{Pu} close to 1.5. However, the absence of plutonium revealed by alpha counting analysis in a salt sample taken at a ratio n_{H2O}/n_{Pu} of 2 (resulting in a signal perturbation for this ratio) indicates that the precipitation of the plutonium is complete at this time.
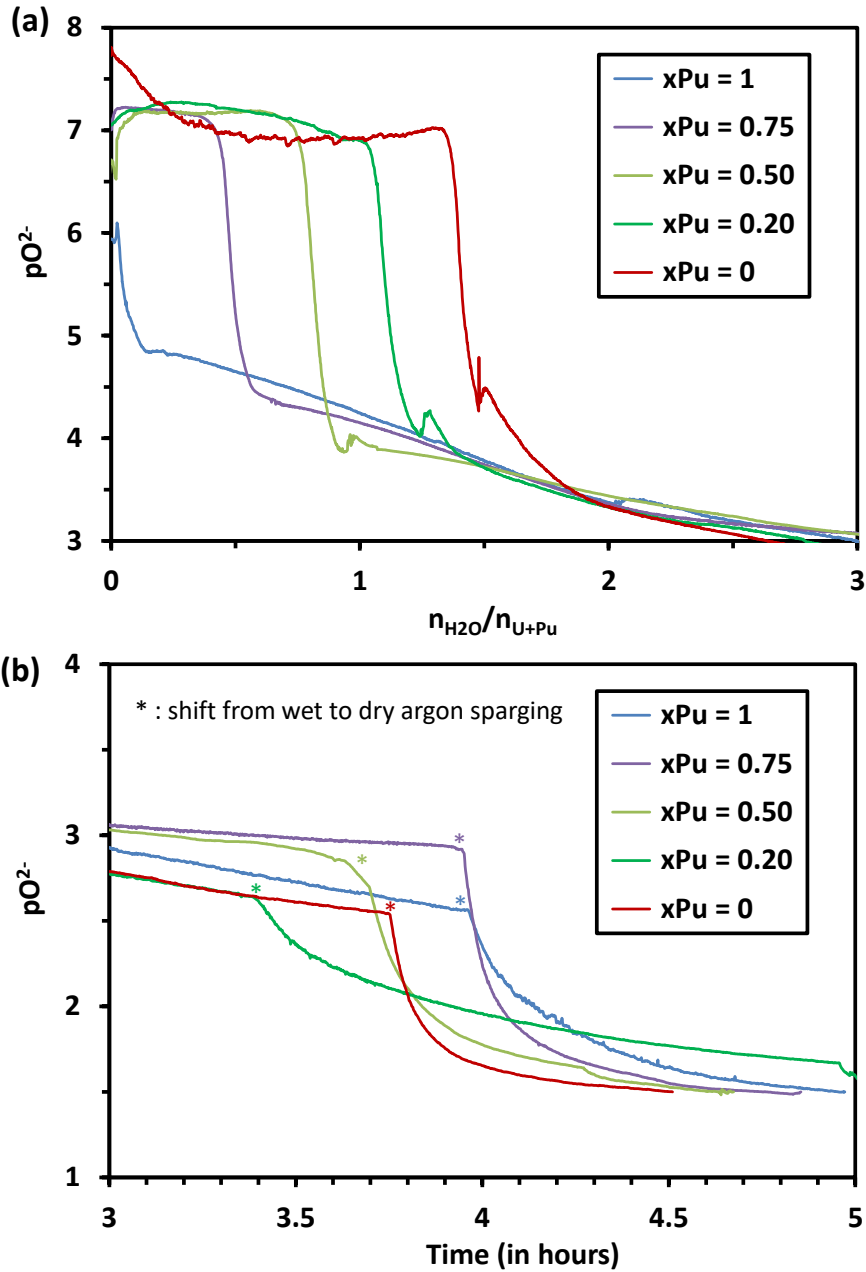
Figure 2: (a) Variation of pO^{2-} during precipitation of U(III)-Pu(III) for X_{Pu} = 0, 0.20, 0.50, 0.75, 1 in molten $LiCl-CaCl_2$ by wet argon sparging. (b) drop of the potential due to the shift from wet argon to dry argon sparging in the salt after the end of precipitation (t=0 refer to the beginning of actinides precipitation by wet argon sparging).

Unlike the case of plutonium, the potentiometric tracking curve for uranium conversion (X_{Pu} = 0) shows a sudden drop in potential at the end of precipitation. During the conversion, it was previously shown that U(III) is totally oxidized to U(IV) and precipitates as UO_2 oxide [23]. Then the drop should occur for n_{H2O}/n_U = 2 (equation 5), but it is experimentally observed for $n_{H2O}/n_U \approx 1.5$.

$$UCl_{3(salt)} + 2H_2O_{(g)} = UO_{2(solid)} + 3HCl_{(g)} + \frac{1}{2}H_{2(g)} \quad (5)$$
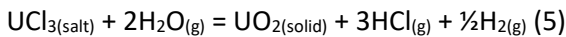
However, analysis of a salt sample taken immediately after this fall (resulting in a signal perturbation on the curve) indicates that all the uranium is precipitated at this time. Several

explanations can justify this result (i) approximately 7% of the uranium is already present in the form of UO_2 in the UCl_3 used to prepare the molten salt [23], (ii) some of the uranium is lost through volatilization [23], (iii) in spite of precautions (UCl_3 is preserved in a sealed micro-tube under argon), a moisture intake of UCl_3 cannot be excluded, chlorides being highly hygroscopic.

Concerning the U(III)-Pu(III) co-precipitation, the sudden potential drop, characteristic from the end of uranium precipitation, presents a progressive shift proportional to the initial U(III) quantity in the molten salt. This seems to indicate that there is successive precipitation of uranium and plutonium. Furthermore, pO^{2-} values measured during plutonium precipitation are 2 to 3 units lower than those measured during uranium precipitation. This difference means that the conversion of uranium takes place in a salt 100 to 1000 times less concentrated in O^{2-} ions than for plutonium, indicating a significantly more sensitive character of the uranium to precipitation.

The potential drop during the passage of dry argon is observed whatever the mixture of U(III)/Pu(III) (Figure 2b). It should be noted that this potential drop is unexpected since it reflects an increase of the free O^{2-} ions, though there is no more addition of water. This phenomenon could result from the presence of hydroxide ions in the salt when it is subjected to the bubbling of wet argon, the passage in dry argon would be accompanied by a decomposition of these hydroxides according to the reaction 6, responsible for an increase in the O^{2-} ions concentration.

$$2OH^-_{(salt)} \rightarrow O^{2-}_{(salt)} + H_2O_{(g)} \quad (6)$$
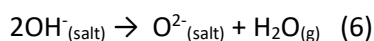
The presence of hydroxide ions in the molten salt is in agreement with the detection of hydroxychlorides formed as intermediates during the lanthanides precipitation in molten $LiCl$-$CaCl_2$ by wet argon sparging [21]. It might be that the absence of sudden pO^{2-} drop at the end of plutonium precipitation described above is caused by these hydroxide ions in the salt, that keep artificially the pO^{2-} high after Pu(III) precipitation and hide the drop of potential.

3.2 *U and Pu concentration during precipitation.*

In order to confirm the successive precipitation of the two actinides during the co-conversion, salt samples were extracted for analysis after the sudden drop of pO^{2-} for each experiment. Salt samples were also taken at the beginning of the precipitation in order to control the preparation of the initial bath and at the end of the reaction in order to evaluate the final conversion rate (Table 1).

Table 1: Percentage of uranium and plutonium solubilized in the salt with respect to the amount of each actinide initially introduced into the molten $LiCl$-$CaCl_2$ mixture

X_{Pu}	Initial conditions		After pO^{2-} step down		After the end of wet argon sparging[*]	
	U	Pu	U	Pu	U	Pu
0.20	55%	94%	< 1%	61%	< 0.1%	< 0.1%
0.50	85%	92%	< 1%	76%	< 0.1%	< 0.1%
0.75	26%	93%	< 1%	70%	< 0.1%	< 0.1%
1		89%				< 0.1%

[*] detection limit is lower for sample after the end of precipitation due to preparation of solutions with higher salt concentration

Samples analyses after carbochlorination indicate a plutonium content relative to the plutonium amount initially introduced in the salt under PuO_2 form between 89 and 94%. This difference reflects losses of plutonium by volatilization during the carbochlorination. During this stage, the salt is maintained for 12 hours under chlorine, implying the formation of volatile $PuCl_4$ which spontaneously reduces to $PuCl_3$ on the cold walls of the reactor. Some of the initial uranium contents measured (X_{Pu} = 0.2, 0.75) are unrealistically low and are inconsistent with the potentiometric measurements. Indeed, the end of uranium precipitation is marked by pO^{2-} drop in the salt, which is clearly proportional to initial uranium quantity introduced. Therefore, all the salts studied obviously contain comparable proportion of the UCl_3 powder introduced in the initial conditions. These deviations from expected values are probably the result of problems happening during sample preparation for analysis, maybe due to the uranium chloride partial hydrolysis during the dilution in water, which would be retained during the filtration.

The analyses of the samples taken after the potential drop show the presence in the molten salt of a significant quantity of plutonium while uranium is no longer detected. This uranium absence confirms the observations made during the potentiometric monitoring, indicating a successive precipitation of uranium and plutonium.

The analyses of the salt samples withdrawn at the precipitation end do not detect any uranium and plutonium left. This confirms the quantitative precipitation of both actinides.

3.3 Characterization of precipitated phases.

After the precipitation was completed, the salt was cooled to room temperature (Figure 3), then dissolved in water and filtered. The plutonium precipitate forms a dark green glossy powder, and U-Pu coprecipitates lead to red-brown powders (Figure 4).
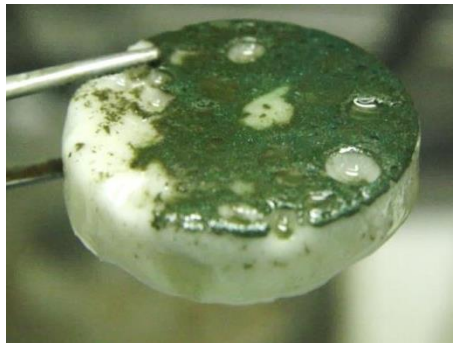

Figure 3: Block of salt at the end of Pu (III) precipitation (X_{Pu} = 1) and return to ambient temperature, being dissolved in water.
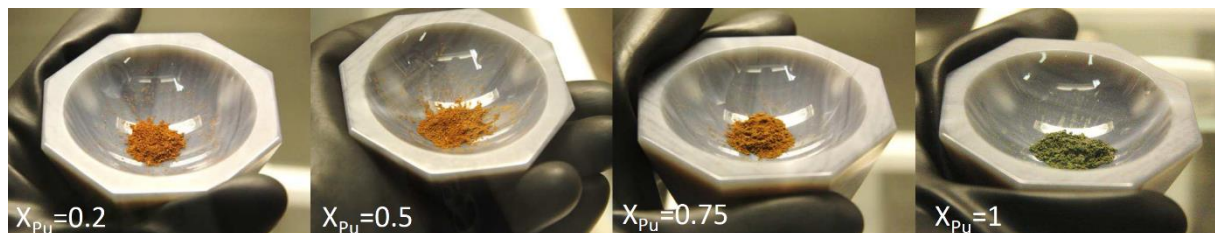

Figure 4: Photos of uranium and plutonium precipitates for an initial ratio in the molten salt X_{Pu} = 0.20, 0.50, 0.75, 1.

Plutonium precipitate (X_{Pu} = 1) is clearly identified as a mixture of crystalline PuO_2 and PuOCl by XRD analysis (Figure 5). The lattice parameters obtained after refinement are presented in Table 2. They are in good agreement with the published values a=5.398(1)Å for PuO_2 [27] and a=4.012(2)Å, c=6.792(10)Å for PuOCl [28] and indicate precipitation of stoichiometric compounds. The precipitation reactions can be described as followed:
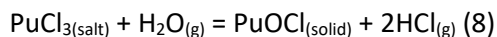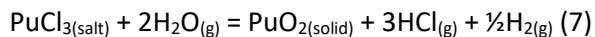
$PuCl_{3(salt)}$ + $2H_2O_{(g)}$ = $PuO_{2(solid)}$ + $3HCl_{(g)}$ + $\frac{1}{2}H_{2(g)}$ (7)

$PuCl_{3(salt)}$ + $H_2O_{(g)}$ = $PuOCl_{(solid)}$ + $2HCl_{(g)}$ (8)

Table 2: Lattice parameters of PuO_2 and PuOCl in the X_{Pu}=1 precipitate

Phase	Space group	Lattice parameter
PuO_2	*Fm-3m*	a=5.397(3)Å
PuOCl	*P4/nmm*	a=4.020(3)Å c=6.792(3)Å

Pu (III) to Pu (IV) oxidation is therefore not complete under the experimental conditions applied, contrary to the case of uranium where pure oxide UO_2 was obtained [23]. On the other hand, plutonium behaves like cerium for which a mixture of CeO_2 and CeOCl was obtained [21]. To determine the respective PuO_2 and PuOCl proportions in the precipitated mixture, part of the precipitate was dissolved in 1 M hydrochloric acid. The solution takes on a blue-violet colour characteristic of a solution containing Pu(III) cations due to the solubilisation of PuOCl (Figure 6a). PuO_2 oxide is insoluble under these conditions. After filtration and drying of the residue (Figure 6b), the remaining PuO_2 weight gives the initial proportion of the two phases: the PuO_2 oxide represents 75 wt% of the powder and the PuOCl oxychloride 25 wt%.

For the three studied coprecitates, the XRD patterns show the presence of UO_2 and PuO_2 in agreement with the successive precipitation of uranium and plutonium (Figure 5). The refined unit cell parameters are in agreement with the UO_2 and PuO_2 parameters and do not indicate any solid solution formation. However, even for the plutonium-rich composition (X_{Pu} = 0.75), there is no PuOCl formation, in contrast to the plutonium precipitation alone. This difference of plutonium chemical form depending on the presence of uranium in the salt is surprising. Indeed, the process ends up with precipitation of plutonium only in all the cases due to the consecutive precipitation of the two elements. The presence of UO_2 in the molten salt seems therefore involved in Pu (III) precipitation, acting as a precursor or catalyst, promoting Pu (III) to Pu (IV) oxidation and causing this element to precipitate in the form of PuO_2.

The preferential precipitation of uranium has already been observed in the case of co-precipitation with neodymium (III) [23], and is attributed to the higher reactivity of tetravalent than trivalent elements in molten salt. Indeed, Gorbunov et al. [29] shows the preferential uranium precipitation in a molten fluoride salt containing U(IV) and Pu(III), whereas the precipitation of U(IV) and Pu(IV) lead to simultaneous precipitation of the two elements in a solid solution. In our study, uranium and plutonium are both present at the oxidation state III in the molten salt, but they are oxidised to the oxidation state IV during precipitation. For this reason, the consecutive precipitation of uranium and plutonium is probably driven by a higher sensitivity of uranium to oxidation [17]. The Gibbs free energy of the following reaction at 705°C was calculated using HSC 7.1 software [30-32]:

UCl_3 + PuO_2 = UO_2 + $PuCl_3$ ΔrG^0 = -137 kJ.mol^{-1} (9)

10
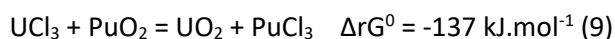
This reaction is particularly relevant in our case since it compares uranium and plutonium both on the change of oxidation state and on the conversion from chloride to oxide. It has to be notice that this calculated value considers only pure compounds and doesn't take into account the solubilisation effect of the salt. The energy calculated confirms that the conversion into dioxide is energetically more favourable for uranium than plutonium, and shows that the preferential precipitation of uranium is not only due to kinetic phenomenon.
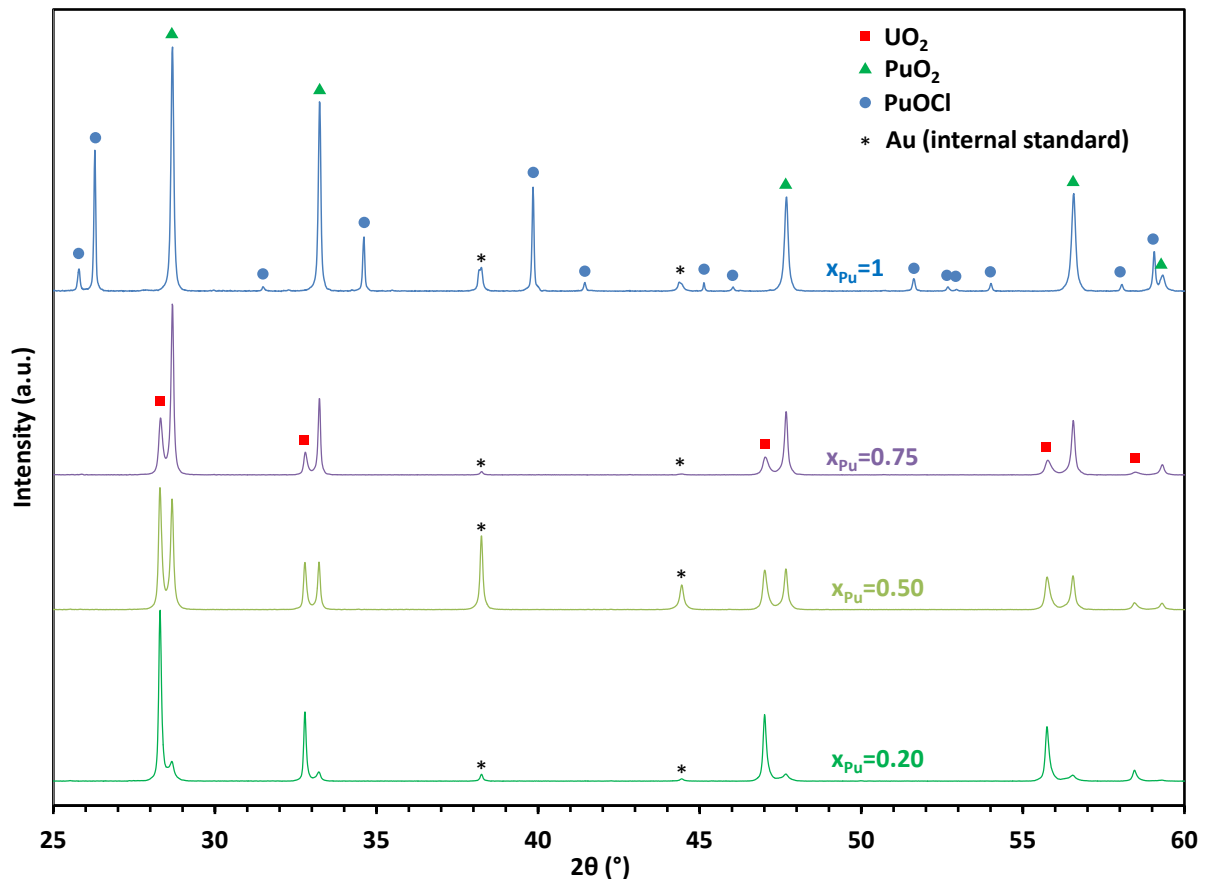

Figure 5: XRD patterns of plutonium precipitate and uranium-plutonium coprecipitates obtained by precipitation of 2 wt% of actinides in LiCl-CaCl$_2$ (30-70 mol%) at 705°C using wet argon sparging. X$_{Pu}$ = 0.20, 0.50, 0.75, 1. K$_{\alpha2}$ contribution has been subtracted for clarity.
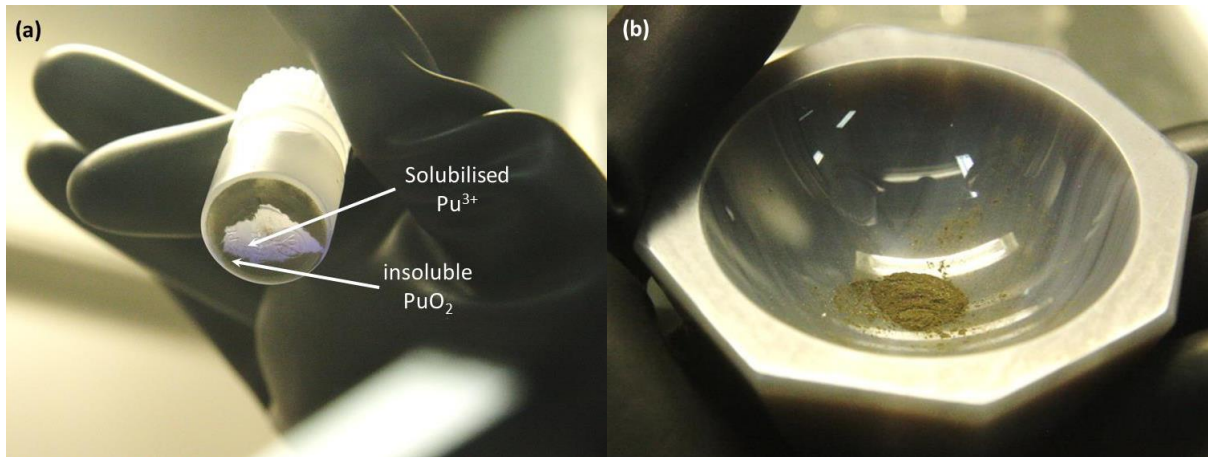
Figure 6: a) Introduction of the plutonium precipitate (X_{Pu} = 1) in 1M HCl and selective dissolution of PuOCl, b) PuO$_2$ powder after selective dissolution of PuOCl.

4 – Conclusion

The precipitation of plutonium (III) alone in the LiCl-CaCl$_2$ (30-70 mol%) salt at 705°C by wet argon sparging leads to an incomplete oxidation of plutonium (III) to plutonium (IV) and to the precipitation of a mixture of PuOCl and PuO$_2$. In the case of U (III)-Pu (III) co-precipitations, uranium first precipitates as UO$_2$. The preferential precipitation of uranium is attributed to the higher sensitivity of this element to oxidation. The presence of UO$_2$ appears to promote the complete oxidation and precipitation of plutonium in the PuO$_2$ form, leading thus to a UO$_2$ and PuO$_2$ mixture which is particularly favourable for the manufacture of MOX fuel. In any case, the uranium and plutonium remaining solubilised in the salt after wet argon sparging is below the detection limit, showing that the conversion method is quantitative (>99.9%).

The conversion method developed here is particularly interesting from an industrial process point of view. Indeed, beyond the fact that it converts uranium and plutonium in a suitable form to produce new fuel, it doesn't introduce any by-product into the molten salt, which can be recycled back to the previous stage of the process, i.e. back-extraction of actinides from liquid aluminium. Industrialisation would require further development based on the separation between the oxide powder and the salt after precipitation, which could be done by salt distillation under vacuum for example.

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