Synthesis of actinide chlorides for molten salt preparation

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ABSTRACT

Molten salt reactor (MSR) is a promising advanced reactor system aiming to the transmutation of minor actinides such as americium in order to reduce the inventory of ultimate nuclear waste. The fuel is a molten salt in which actinides are homogeneously dissolved in the liquid phase. A chloride salt may be retained for this concept, as it provides low melting point, high solubility of actinides, harder neutron spectrum. To avoid corrosion and precipitation issues, molten salt composition has to be carefully controlled with impurity content as low as possible. Obtaining pure actinide chlorides without contaminants such as oxide, oxychloride, hydroxide and water is still a challenge. To prepare actinide-bearing salt, the chlorination of actinides oxides was investigated in an unstirred reactor under flowing gas as solid-gas reaction. The carbochlorination of PuO_2 were performed in the temperature range of 600 to 800°C with chlorine gas as a chlorinating agent and the presence of solid carbon. $PuCl_3$ was successfully synthesised by this method and characterised by X-ray diffraction measurements but some impurities such as oxide phase remain inside the formed product. Refinements of anhydrous and hydrated $PuCl_3$ phases by Lebail method were also performed for crystalline materials definition. Conversion mainly depends on the chlorinating temperature and the contact between the oxide and the chlorinating agent. A conversion value of 70-80 % was achieved at 700 °C from PuO_2 with quite high specific surface area. The conversion rate was not improved with increasing the chlorination time. The volatilisation of Pu was observed during the carbochlorination experiments. To avoid a loss of Pu caused by sublimation, the chlorination temperature should be limited to 650 °C despite that the conversion of PuO_2 to $PuCl_3$ was enhanced by increasing temperature. Both carbochlorination and hydrochlorination of AmO_2 were also carried out leading to the formation of $AmCl_3$. These first results suggest that americium oxide was chlorinated more readily than plutonium oxide. The purity of produced $PuCl_3$ and $AmCl_3$ still deserves further investigations.

INTRODUCTION

Molten Salt Reactors (MSR) represent a potential new answer to the question of transmutation of minor actinides in order to reduce the footprint of nuclear waste storage. Producing low-carbon electricity and heat, MSR allow reducing the generated radioactive waste and the closure of the fuel cycle. A fast-neutron reactor used as actinides converter, especially for americium, is currently investigated in France. The fuel is a molten salt in which actinides are homogeneously dissolved in the liquid phase. A chloride salt is selected for this concept, as it provides high solubility of actinides, low melting point, harder neutron spectrum than fluoride salts and is consistent with French nuclear waste management using hydrometallurgical processes. To avoid corrosion and precipitation issues, molten salt composition has to be carefully controlled with oxygen impurity content as low as possible. Obtaining pure actinide chlorides without contaminants such as oxide, oxychloride hydroxide and water is still a challenge and mandatory to produce an actinide bearing salt suitable for its use in a reactor.

Data on the synthesis of plutonium and americium trichloride ($PuCl_3$ and $AmCl_3$) are reported in the literature. Anhydrous $PuCl_3$ was usually prepared using a carbochlorination technique, a solid gas reaction between a metal oxide and a chlorinating gas with the addition of carbon. Different chlorinating agents such as gas mixture of argon and tetrachloride Ar-CCl_4 (Tolley, 1953), of tetrachloride and chlorine CCl_4-Cl_2 (Ferran and Michael, 1993), of carbon monoxide and chlorine CO-Cl_2 (Ferran and Michael, 1993) and phosgene $COCl_2$ (Ferran and Michael, 1993, Rasmussen and Hopkins, 1961, Tolley, 1953) are used for the carbochlorination of plutonium oxide (PuO_2). According to these studies, $COCl_2$ seems to be the most efficient gas at 500 °C and yields 98 % of conversion to the plutonium chloride on a large scale in batch (around 500 g). Due to the use of hazardous $COCl_2$ gas, a mixture of oxide and carbon powder with Cl_2 gas were also performed to produce many other chlorides such as rare-earth elements (Anderson and Mishra, 2015, Esquivel et al., 2003b, Esquivel et al., 2003a, Gaviría and Bohé, 2010, Pomiro et al., 2015, Wang et al., 2019). Chloride salts containing $PuCl_3$ were prepared thanks to bubbling of Cl_2 in the molten salt in which solid PuO_2 and graphite rod were present (Caravaca et al., 2008, Vigier et al., 2018). Few data in the literature are available on the synthesis of americium trichloride by a solid-gas reaction. The carbochloration of americium oxide (AmO_2) with CCl_4 vapor between 800 and 900 °C yielded a

sublimed product, namely an anhydrous and pure $AmCl_3$ (Fried, 1951). $AmCl_3$ was also synthesised in LiCl-KCl melt by carbochlorination using chlorine gas bubbling and a mixture of carbon and AmO_2 as starting material (Lambertin et al., 2000). Contrary to PuO_2 (West et al., 1988), AmO_2 can react with hydrogen chloride gas (HCl) at 500–600 °C to form anhydrous $AmCl_3$ by hydrochlorination process (Burns and Peterson, 1970, Fuger, 1966).

This study focused on evaluating the conversion of plutonium and americium oxides to their respective chlorides, main compounds of the molten salt fuel used for transmutation purposes. $PuCl_3$ and $AmCl_3$ were synthesized based on a solid gas reaction between an oxide precursor and a chlorinating agent. Chlorination experiments were carried out in a static bed reactor and several reaction parameters were investigated such as the reactivity of solid precursor, the nature of chlorinating gas and temperature.

MATERIAL AND METHODS

All experiments took place in a glove-box under air atmosphere. The chlorination experiments were conducted in a fixed-bed reactor allowing a gas-solid reaction at high temperature between an actinide oxide, PuO_2 or AmO_2 powder, and a chlorinating agent in a flow-through mode. PuO_2 with different specific surface area (0.4, 2.9 and 14.0 m^2g^{-1}) are used. For carbochlorination experiments, actinide oxides and carbon powder were mechanically mixed into a carbon crucible, inserted into the quartz reactor vessel. Carbon used as a reducing agent was introduced in excess (molar ratio Pu/C < 0.5) to ensure a favourable carbochloration reaction based on thermodynamic calculations. The sample (< 0.5 g) was homogeneously heated up to the desired temperature (600–800 °C) inside a furnace in an argon gas flow (2 L/h). The flow of argon was then shut off and chlorine gas was introduced in a large excess (from 1 to 6 L/h) during the chlorination step. The exit gas were bubbled through 4 M NaOH or KOH which completely trapped excess of chlorinating agent. After the chlorination step during 1–4 hours, the furnace was turned off and argon gas was introduced into the system instead of chlorine during the cooling process. The cooled sample was removed from the reactor and analysed (XRD and Pu and Cl content). For hydrochlorination experiments, the same experimental procedure was followed, except that chorine gas was replaced by hydrogen chloride gas without carbon. Reactions that occurred could be written as follows:

- $PuO_{2\,(s)} + \frac{3}{2}\,C_{(s)} + \frac{3}{2}\,Cl_{2\,(g)} \rightarrow PuCl_{3\,(s)} + CO_{(g)} + \frac{1}{2}\,CO_{2\,(g)}$
- $AmO_{2\,(s)} + \frac{3}{2}\,C_{(s)} + \frac{3}{2}\,Cl_{2\,(g)} \rightarrow AmCl_{3\,(s)} + CO_{(g)} + \frac{1}{2}\,CO_{2\,(g)}$
- $AmO_{2\,(s)} + 4\,HCl_{(g)} \rightarrow AmCl_{3\,(s)} + 2\,H_2O_{(g)} + \frac{1}{2}\,Cl_{2\,(g)}$

The conversion was determined using the solubility of the formed product in an aqueous solution, assuming $PuCl_3$ to be 100 % soluble contrary to PuO_2 and to a lesser extent other plausible impurities such as PuOCl. The product was thus dissolved in aqueous solution with nitric acid (0.3 M HNO_3) to give a blue or purple solution, subsequently filtered to remove insoluble impurities and finally the solution was analysed for Pu and Cl content. Plutonium was measured by alpha counting and spectrometry and chloride by ionic chromatography. The conversion rate R was expressed by :

- $R = \frac{n_{Pu\,from\,dissolved\,Pu}}{n_{Pu\,from\,starting\,PuO2}}$

Considering the small amount of matter used and the possible loss of matter, R is probably underestimated. To ensure that the synthesised product was primarily $PuCl_3$, the molar ratio Pu/Cl was checked to be close to 3 for all chemical analyses and X-ray diffraction (XRD) analyses were also performed. Before analysing, powder samples were stored in a desiccator. XRD measurements were carried out on powders by a Bruker D8 Advance diffractometer (Bragg-Bretano geometry using the Cu Kα radiation, solid detector Lynexe XE-T) and crystalline phases were identified using the DIFFRAC.EVA software from Bruker company. The data acquisition was performed in the step scan mode (10–140° 2θ, step size 0.01 ° 2θ, total counting 4h or 18h). Gold was introduced into the XRD samples as an internal standard. Lattice parameters were determined by refinement using the Le Bail method (Le Bail, 2012) and the Fullproof software (Carvajal, 1990).

RESULTS AND DISCUSSION

Carbochlorination of PuO$_2$

Carbochlorination experiments from plutonium oxide were performed at several temperatures. The chlorination with Cl$_2$ gas at 600 °C was not really efficient. After synthesis, the C7 sample was a brownish-coloured powder similar to the starting material. Although some low intensity peaks belonging to the anhydrous and probably hydrated phases were detected, the main phases observed in the product by XRD analysis were PuO$_2$ and carbon as shown in FIG 1. Carbochlorination reaction was more effective between 650–700 °C as a green-blue fine powder, feature of PuCl$_3$ compound (Rasmussen et al., 1961), was obtained as shown in FIG 2. The conversion of PuO$_2$ to PuCl$_3$ was confirmed by XRD analysis but chlorination was incomplete since some residual PuO$_2$ was still present in the chlorinated C5 sample (FIG 1).
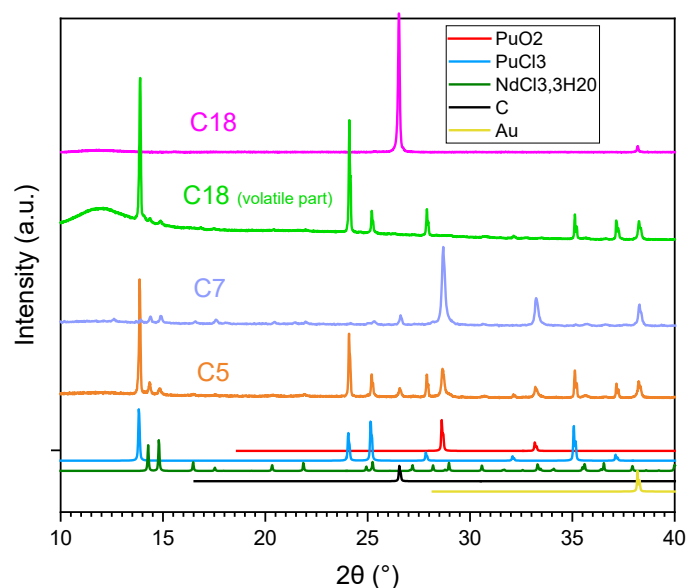

FIG 1 – XRD patterns of C5, C7 and C18 samples synthesised by carbochloration of PuO$_2$ at 700 °C, 600 °C and 800 °C, respectively.


(b)

(a)

FIG 2 – Pictures of (a) C5 sample in the carbon crucible and (b) a part of C23 sample located in the quartz off-gas line the after carbochlorination reaction at 700 °C.

The average conversion values achieved for carbochlorination experiments are given in TABLE 1. The conversion rate for carbochlorination at 700 °C was evaluated at 70–80 %. When the chlorination temperature increased up to 800 °C, above the melting point of $PuCl_3$, the conversion might be almost complete because there was no evidence of PuO_2 in the C18 sample. However, an important volatilisation rate of the product was observed in good agreement with thermodynamics (FIG 2, b). Blue-green needle-shaped crystals corresponding to $PuCl_3$ without PuO_2 contamination as shown in FIG 1 (C18 sample) were collected on the surface of the colder area of the quartz tube in the off-gas line (< 550 °C). The volatilization process is explained by the formation of $PuCl_4$ gas by the following equilibrium (Gruen and DeKock, 1967):

- $PuCl_{3\,(s)} + \frac{1}{2} Cl_{2\,(g)} \leftrightarrow PuCl_{4\,(g)}$
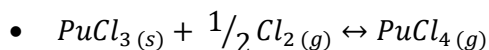
According to the literature, condensed $PuCl_4$ turns into solid $PuCl_3$ and gaseous Cl_2 as Cl_2 gas feed stops. When the chlorination temperature was reduced to 650 °C, the conversion rate remained similar to run at 700°C in the same experimental conditions (C15 and C22 samples) but the volatilization process was limited. To minimize sublimation of plutonium tetrachloride which could be an issue for an industrial process, the chlorination temperature must be limited to 650 °C with chlorine gas without any impact on the conversion rate. However, the sublimation of Pu chloride is a good way of purifying $PuCl_3$ and leads to a complete conversion.

The conversion rate was not affected by increasing the chlorination time up to 300 min (C22 and C23 samples). This result suggested that the carbochlorination reaction was kinetically limited, a $PuCl_3$ layer might prevent the chlorinating gas getting to the unreacted oxide. In addition, the conversion rate was enhanced by using PuO_2 with high specific surface area (C19, C21, C22 samples). This leads to the conclusion that the conversion of PuO_2 to $PuCl_3$ was strongly impacted by the contact between the solid oxide, carbon powder and the gaseous chlorinating agent. Conversion might be improved by adding an agitation system for carbochlorination reaction (Soine, 1965).

TABLE 1 – Synthesis parameters, conversion and volatilization values for carbochlorination and hydrochlorination of actinide oxides (Pu and Am). SSA means surface specific area and L,M and H represent respectively, low, medium and high surface specific area used for PuO_2. (*) denotes conversion and volatilization values were probably under-evaluated because the whole volatile fraction might be not totally trapped and collected.

Name	Oxide	Oxide Mass	SSA	Gas	Temperature	Cl_2 : Pu or Am (molar ratio)	Time	Conversion R	Volatilisation
C5	PuO_2	302 mg	M	Cl_2	700 °C	30	45 min	Not complete	Weak
C7	PuO_2	303 mg	M	Cl_2	600 °C	60	75 min	Low	None
C15	PuO_2	151 mg	M	Cl_2	650 °C	100	75 min	72 %	5 %
C18	PuO_2	154 mg	M	Cl_2	800 °C	100	75 min	62 % (*)	62 % (*)
C19	PuO_2	151 mg	L	Cl_2	700 °C	100	75 min	41 %	15 %
C21	PuO_2	156 mg	H	Cl_2	700 °C	100	75 min	80 %	18 %
C22	PuO_2	154 mg	M	Cl_2	700 °C	100	75 min	73 %	14 %
C23	PuO_2	151 mg	M	Cl_2	700 °C	393	300 min	70 %	34 %
A1	AmO_2	34 mg	/	Cl_2	500 °C 680 °C	236	360 min	/	None
A2	AmO_2	31 mg	/	HCl	600 °C	173	240 min	/	None

The refinement by Le Bail method of the anhydrous and hydrated $PuCl_3$ phases obtained by carbochlorination reaction were successfully performed allowing to confirm the crystalline phase identification previously done. The cell parameters, extracted from the refinement, were summarized in TABLE 2. The $PuCl_3$ phase structure was in good agreement with data reported in literature (Zachariasen, 1948). Since the $PuCl_3,3H_2O$ phase were not referenced in the database, the structure of hydrated $PuCl_3$ were determined by X-ray diffraction and refined by the Le Bail method. The $PuCl_3,3H_2O$ phase is isotructural with $NdCl_3,3H_2O$ phase (Reuter et al., 1994). The obtained cell parameters of $PuCl_3,3H_2O$ were consistent with the cell parameters of $NdCl_3,3H_2O$ given in the literature. $PuCl_3$ is hydroscopic (Rasmussen et al., 1961) and can be readily hydrated by moisture from the atmosphere. To avoid hydratation, $PuCl_3$ must be kept in a controlled and dehumidified atmosphere.

TABLE 2 – Cell parameters and angles obtained after refinement by Le Bail method for synthesised anhydrous and hydrated $PuCl_3$ phases compared to data from literature.

Compound	Crystal system	Space group	a(Å)	b(Å)	c (Å)	α, β (°)	γ (°)	Reference
$PuCl_3$	Hexagonal	$P6_3/M$ (n°176)	7.3978 (4)	7.3978 (4)	4.2458 (4)	90	120	This Study
$PuCl_3$	Hexagonal	$P6_3/M$ (n°176)	7.3800 (1)	7.3800 (1)	4.2380 (4)	90	120	(Zachariasen, 1948)
$PuCl_3$, 3 H_2O	Orthothombic	Pnma (n°62)	12.3663 (1)	8.7381 (2)	6.8566 (3)	90	90	This Study
$NdCl_3$, 3 H_2O	Orthothombic	Pnma (n°62)	12.408	8.735	6.832	90	90	(Reuter et al., 1994)

Carbochlorination and hydrochlorination of AmO_2

Carbochlorination and hydrochlorination experiments of americium oxide were performed with chlorine and hydrogen chloride gas (TABLE 1). The carbochlorination of AmO_2 at 680 °C yielded a black powder. XRD analysis revealed the presence of $AmCl_3$ phase and an hydrated $AmCl_3$ phase, being very likely $AmCl_3,3H_2O$, and carbon (FIG 3). No americium oxide was really found in the product. The hydrochlorination of AmO_2 at 600 °C produced a pale green-yellow powder. Some authors (Burns and Peterson, 1970) found that the color of $AmCl_3$ was pale yellow-pink. The main phase present in the product was $AmCl_3,6H_2O$. Some small unidentified peaks at 2θ 31.7° and 52.9° were detected by XRD indicating that some impurities may be present inside the synthesised product. For both syntheses, the conversion of AmO_2 to $AmCl_3$ seemed to be complete and no volatilisation of americium chloride was observed. The strong hydration of $AmCl_3$ might be explained by the XRD measurements were not performed under an inert atmosphere with a low water content. These results suggest that Am was chlorinated more readily than Pu. The chlorination parameters were not optimized for $AmCl_3$ synthesis and the evaluation of actinide chloride purity is the subject of ongoing studies.
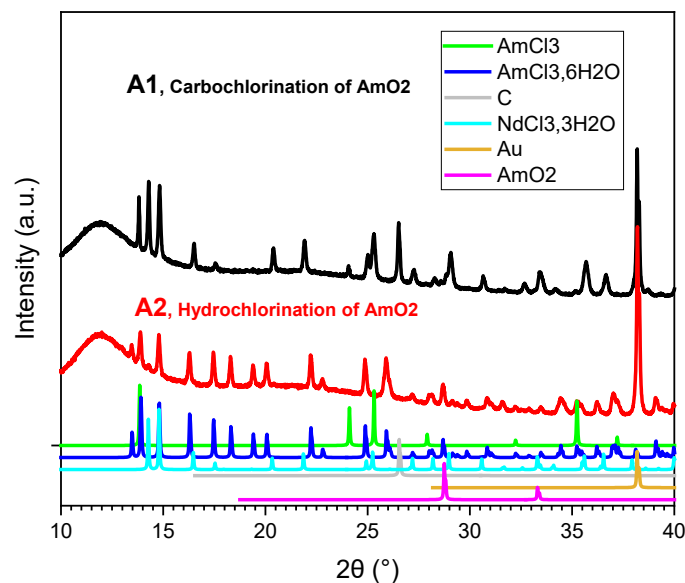
FIG 3 – XRD patterns of A1 and A2 samples synthesised by carbochloration and hydrochlorination of AmO_2, respectively.

CONCLUSION

The main results obtained on the synthesis of $PuCl_3$ and $AmCl_3$ from actinide oxides by carbochlorination or hydrochlorination technique may be summarized as follow:

- $PuCl_3$ and $AmCl_3$ were successfully synthesised by a solid-gas reaction using chlorine or hydrogen chloride gas.

- The conversion by carbochlorination reaction mainly depends on the chlorinating temperature and the contact between the oxide and the chlorinating agent. The conversion rate was not improved with increasing the chlorination time.

- The conversion rate of PuO_2 to $PuCl_3$ was improved by increasing the temperature. However, volatilization of Pu was observed beyond 700 °C. To minimize it, the optimal temperature was adjusted around 650 °C for carbochlorination reaction with Cl_2 gas and carbon powder.

- The sublimation of Pu chloride is a good way of obtaining pure $PuCl_3$.

- Am was chlorinated more readily than Pu, since AmO_2 could directly react with HCl at 600 °C to form $AmCl_3$.

ACKNOWLEDGEMENTS

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