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# Recovery of actinides from actinide–aluminium alloys by chlorination: Part I

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## A B S T R A C T

Pyrochemical processes in molten LiCl–KCl are being developed in ITU for recovery of actinides from spent nuclear fuel. The fuel is anodically dissolved to the molten salt electrolyte and actinides are electrochemically reduced on solid aluminium cathodes forming solid actinide–aluminium alloys. A chlorination route is being investigated for recovery of actinides from the alloys. This route consists in three steps: Vacuum distillation for removal of the salt adhered on the electrode, chlorination of the actinide–aluminium alloys by chlorine gas and sublimation of the formed AlCl<sub>3</sub>. A thermochemical study showed thermodynamic feasibility of all three steps. On the basis of the conditions identified by the calculations, experiments using pure UAl<sub>3</sub> alloy were carried out to evaluate and optimise the chlorination step. The work was focused on determination of the optimal temperature and Cl<sub>2</sub>/UAl<sub>3</sub> molar ratio, providing complete chlorination of the alloy without formation of volatile UCl<sub>5</sub> and UCl<sub>6</sub>. The results showed high efficient chlorination at a temperature of 150 °C.

## 1. Introduction

In recent years, much attention has been paid to the management of spent nuclear fuel in a safe, economic and proliferation resistant way. “Partitioning & Transmutation” (P&T) strategy [1,2] represents a promising alternative to direct disposal of spent fuel in deep geological repositories. Application of the P&T approach would yield significant reduction of the long-term radioactivity and volume of the disposed spent fuel. P&T is based on recovery of Pu, minor actinides (MA–Np, Am and Cm) and <sup>99</sup>Tc from the fuel and their nuclear incineration. New types of nuclear reactors are under development within different international projects (e.g., Generation IV International Forum [3] and The Sustainable Nuclear Energy Technology Platform [4]). These innovative reactor concepts allow for usage of Pu and MA containing fuels, which will be reprocessed and recycled within closed fuel cycles.

The efficient separation of all actinides (An) from spent fuel is a key point for implementation of closed fuel cycle technology. The fuels will probably be significantly different from today’s commercial fuels. Owing to the fuel type and the high burn-up, hydrometallurgical separation processes might not be the most adequate techniques because of the poor solubility of some fuel materials in acidic aqueous solutions and the limited radiation stability of the organic solvents used in extraction processes. Therefore, pyrochemical separation processes are under development, typically

using electrochemical or reductive extraction techniques in high temperature molten salt solvents [2,5].

The process developed at the Institute for Transuranium Elements (ITU) is based on electrorefining of metallic spent fuel and exhaustive electrolysis in a molten LiCl–KCl bath using reactive solid aluminium cathodes [6–8]. In both methods, actinides are separated from the molten salt electrolyte as solid actinide–aluminium (An–Al) alloys. A chlorination route is proposed for back-extraction of actinides from the alloys formed. The chlorination process is composed of three main steps: (i) vacuum distillation for removal of the residual salt adhering to the electrodes surface, (ii) chlorination of the alloys by pure chlorine gas yielding actinides and aluminium chlorides and (iii) selective removal of aluminium chloride by sublimation. The final step, which may consist of chemical reduction of the An chlorides to metals, is presently not being investigated in ITU. A scheme of the chlorination route is shown in Fig. 1.

The present article consists of two parts. First, a thermodynamic survey of the complete chlorination process is presented. According to the study, all steps are thermodynamically possible and the optimum process parameters are discussed. The results indicate that the most problematic part of the process is the complete chlorination of U–Al alloys without formation of volatile U chlorides. Therefore, the second part of this work is dedicated to the experimental study of the chlorination step using UAl<sub>3</sub>. The influence of the working temperature under the given Cl<sub>2</sub>/UAl<sub>3</sub> molar ratio was investigated in order to determine the optimal process conditions providing complete chlorination without uranium losses by formation of volatile UCl<sub>5</sub> and UCl<sub>6</sub>. The test temperatures were 150, 160 and 170 °C.

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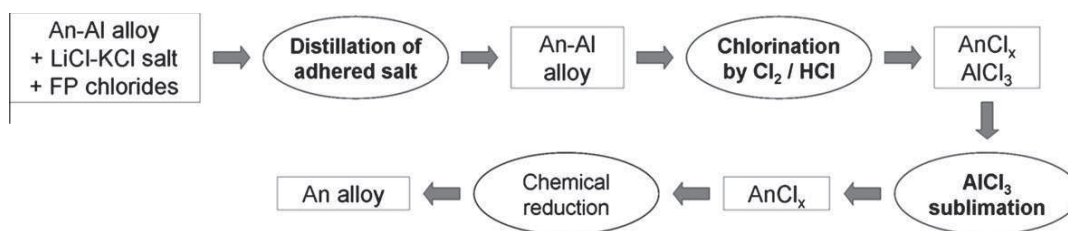


Fig. 1. Principle of the chlorination route for recovery of An from An-Al alloys.

## 2. Thermodynamic survey

For most of the compounds (pure An, Al, fission product chlorides, chlorine gas), the SGPS-SGTE pure substances database of the FactSage 6.0 software was used [9]. A bibliographic study was carried out to collect the available thermochemical data ( $\Delta_f G_{(T)}^\circ$ ,  $\Delta_f H_{298}^\circ$ ,  $S_{298}^\circ$ ,  $C_{p(T)}$ ) and transition temperatures) for An chlorides and An-Al intermetallic compounds. These data were input in the FactSage compound database, and equilibrium calculations were performed for each step of the process. As detailed in Table 1, the thermochemical data of the main An chloride compounds were published [10–12], apart from  $\text{AmCl}_2$  and  $\text{AmCl}_3$  gaseous compounds and all Cm compounds. Therefore, Cm was disregarded in the present study.

Phase diagrams were published for U-Al [13,4], Pu-Al [14,15] and Np-Al [14] systems, and several An-Al intermetallic compounds have been identified ( $\text{UAl}_2$ ,  $\text{UAl}_3$ ,  $\text{UAl}_4$ ,  $\text{Pu}_3\text{Al}$ ,  $\text{PuAl}$ ,  $\text{PuAl}_2$ ,  $\text{PuAl}_3$ ,  $\text{PuAl}_4$ ,  $\text{NpAl}_2$ ,  $\text{NpAl}_3$  and  $\text{NpAl}_4$  [13–15]). In all cases, the melting points of the intermetallic compounds increases with An content and  $\text{AnAl}_2$  compounds have the highest melting points (1620 °C, 1540 °C and 1585 °C for  $\text{UAl}_2$ ,  $\text{PuAl}_2$  and  $\text{NpAl}_2$ , respectively). No data were found for the Am-Al system. The available thermochemical data for An-Al compounds are summarised in Table 2.

### 2.1. Distillation step

To ensure a high purity product at the end of the chlorination process, it is necessary to remove the residual salt adhered to the cathode after it is withdrawn from the molten salt electrolyte. The salt is composed of a LiCl-KCl eutectic mixture, containing certain portion of dissolved actinides and fission products (FPs), according to the stage of the electrochemical process. Since chloride compounds are soluble in most aqueous media, it is possible to clean the electrodes with a liquid solvent, e.g., ethanol. However, on an

**Table 1**  
Source thermochemical data for actinide chloride compounds and phase transition temperatures.

Compound	Solid	Liquid	Gas	Ref.
UCl	g	g	g	[10]
UCl <sub>2</sub>	g	g	g	[10]
UCl <sub>3</sub>	$T_{s-1} = 842$ °C	$T_{l-g} = 1837$ °C		[10]
UCl <sub>4</sub>	$T_{s-1} = 590$ °C	$T_{l-g} = 801$ °C		[10]
UCl <sub>5</sub>	$T_{s-1} = 327$ °C	$T_{l-g} = 552$ °C		[10,11]
UCl <sub>6</sub>	g	g	g	[10,11]
PuCl <sub>3</sub>	$T_{s-1} = 768$ °C	$T_{l-g} = 1769$ °C		[10]
PuCl <sub>4</sub>	g	g	g	
NpCl <sub>3</sub>	$T_{s-1} = 802$ °C			[10]
NpCl <sub>4</sub>	$T_{s-1} = 538$ °C	$T_{l-g} = 724$ °C		
AmCl <sub>2</sub>	$T_{s-1} = 948$ °C		x	[12]
AmCl <sub>3</sub>	$T_{s-1} = 638$ °C		x	

x – no data are reported in literature, g – the only stable state of the compound is gas.

industrial scale this would produce a large amount of highly contaminated liquid waste, which would have to be treated.

An alternative, that is being investigated within the proposed pyrochemical route, consists of crushing the electrode, distilling the salt and recycling the distillate for the electrochemical processes. This procedure requires that the vapour pressure of the salt and the An-Al compound is appreciably different. Since there are not enough thermochemical data to evaluate the properties for the specific complex components of the considered system, the vapour pressures of selected compounds were calculated in order to obtain a clue about their order of magnitude. The results for various FP chlorides and An metals are summarised in Fig. 2, where the log of their vapour pressures  $P$  are plotted against  $1/T$ . In order to perform the distillation, the working pressure  $P_{\text{exp}}$  has to be lower than the vapour pressure of the compound at the working temperature  $T_{\text{exp}}$ . The efficiency of the distillation increases proportionally to  $T_{\text{exp}}$  and inversely-proportionally to  $P_{\text{exp}}$ . A trial evaluation of the feasibility of distillation was carried out taking into account the experimentally achievable parameters in the available set-up, i.e., maximum  $T_{\text{exp}} \sim 1000$  °C and minimum  $P_{\text{exp}} \sim 10^{-5}$  bar.

To remove pure LiCl-KCl eutectic salt, a temperature of 800 °C seems to be sufficient at the pressure  $10^{-5}$  bar. A laboratory-scale experiment carried out at  $T_{\text{exp}} = 900$  °C and  $P_{\text{exp}} = 5 \times 10^{-5}$  bar supported this evaluation, since 2 g of pure LiCl-KCl were distilled out. However, other compounds, especially lanthanide (Ln) chlorides, are much less volatile. A temperature of 1000 °C is required to remove all Ln chloride compounds. Even at these conditions, some FP chlorides (e.g.,  $\text{MoCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$ ) might not be fully separated. All An metals except Am have lower vapour pressures than the chloride compounds. Known  $\text{AnAl}_3$  and  $\text{AnAl}_2$  intermetallics have significantly higher melting points than the pure metals, which indicates that the vapour pressures of the alloys are very probably lower than that of the pure metal. Although the Am-Al phase diagram does not exist, it is expected that Am-Al alloys show the same trend as other An-Al alloys and thus they probably have sufficiently low vapour pressure to avoid distillation of Am-Al alloys. However, experimental verification of the Am-Al alloy behaviour is needed.

### 2.2. Chlorination step

The aim of the chlorination step is to fully chlorinate all metals composing the alloy, in order to evaporate aluminium chloride in the following step. Calculations were carried out to assess stability of the species formed and to evaluate conditions inhibiting formation of volatile actinide chlorides. The thermochemical study of the chlorination of U-Pu-Np-Am-Al alloys is a complex problem, because the reactions are highly dependent on the prevailing conditions and many compounds can be formed. As a first approach, two main parameters were taken into account: (i) the temperature of the reaction, (ii) the  $\text{Cl}_2/\text{metal}$  molar ratio (i.e., the  $\text{Cl}_2$  excess).

**Table 2**  
Source thermochemical data for actinide–aluminium intermetallic compounds [16].

Reaction	Gibbs energy (kJ/mol)	Temperature range (K)
$U(\alpha) + 4 Al(s) = UAl_4(s)$	$\Delta G^\circ = -133.972 + 0.178T - 0.021T \ln T$	298–933
$U(\alpha) + 3 Al(s) = UAl_3(s)$	$\Delta G^\circ = -103.931 - 0.067T - 0.010T \ln T$	298–933
$U(\alpha) + 2 Al(s) = UAl_2(s)$	$\Delta G^\circ = -92.173 + 0.006T$	298–933
$Pu(\epsilon) + 4 Al(s) = PuAl_4(s)$	$\Delta G^\circ = -183.385 + 0.042T$	790–930

The following calculations were performed:

- Gibbs energy of the chlorination reaction of pure An metals, pure aluminium,  $UAl_4$ ,  $UAl_3$  and  $PuAl_4$  at 150 °C.
- Chlorination of  $UAl_3$  in the temperature range 100–1000 °C for given  $Cl_2/UAl_3$  ratios.
- Maximum working temperature ensuring U losses in the gas phase less than 0.1 mol.%, as a function of the  $Cl_2/UAl_3$  molar ratio.

### 2.2.1. Gibbs energy of chlorination reactions

The Gibbs energies of various chlorination reactions at 150 °C ( $\Delta_r G^\circ_{(150\text{ °C})}$ ) are compiled in Table 3. At this temperature, all chloride compounds are stable in the solid phase, with the exception of  $Al_2Cl_6(g)$ ,  $UCl_6(g)$  and  $PuCl_4(g)$ . In order to compare the affinity of each An or An–Al compound to chlorine, the reactions are balanced with one mole of  $Cl_2(g)$ . As noted in Table 2,  $UAl_3$ ,  $UAl_4$  and  $PuAl_4$  compounds are the only An–Al alloys for which a full set of data exists.

As is evident from Table 3, each reaction with metallic An yields chloride compounds at 150 °C, since the respective  $\Delta_r G^\circ_{(150\text{ °C})}$  are negative. The following compounds should be formed in a descending order according to their stability at the given conditions:  $AmCl_2(s)$ ;  $AmCl_3(s)$ ;  $PuCl_3(s)$ ;  $NpCl_3(s)$ ;  $UCl_3(s)$ ;  $UCl_4(s)$ ;  $NpCl_4(s)$ ;  $AlCl_3(s)$ ;  $Al_2Cl_6(g)$ ;  $UCl_5(s)$ ;  $UCl_6(g)$ . The calculation illustrates that precise control of the  $Cl_2$  amount (i.e.,  $Cl_2/An$  ratio) is needed to avoid the volatilisation of U compounds. In contrast, gaseous  $PuCl_4$  is very unlikely to form from the chlorination of  $PuCl_3(s)$  ( $\Delta_r G^\circ = 110.4$  kJ/mol). At higher temperatures up to

**Table 3**  
Gibbs energy of various chlorination reactions at 150 °C.

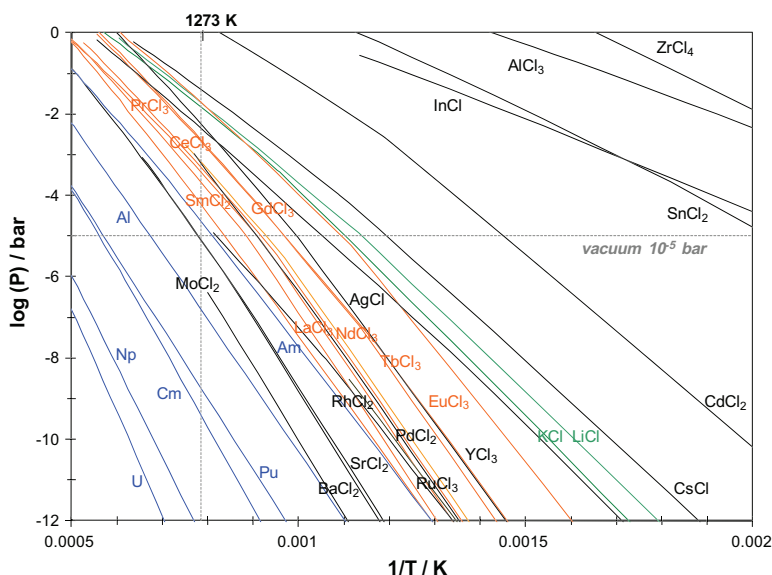
Chlorination reaction	$\Delta_r G^\circ(150\text{ °C})$ kJ/mol
$Am(s) + Cl_2(g) = AmCl_2(s)$	–599.2
$2/3 Am(s) + Cl_2(g) = 2/3 AmCl_3(s)$	–583.8
$2/3 Pu(s) + Cl_2(g) = 2/3 PuCl_3(s)$	–576.0
$2/3 Np(s) + Cl_2(g) = 2/3 NpCl_3(s)$	–532.9
$2/3 U(s) + Cl_2(g) = 2/3 UCl_3(s)$	–514.2
$1/2 U(s) + Cl_2(g) = 1/2 UCl_4(s)$	–446.4
$1/2 Np(s) + Cl_2(g) = 1/2 NpCl_4(s)$	–427.9
$2/3 Al(s) + Cl_2(g) = 2/3 AlCl_3(s)$	–399.7
$2/3 Al(s) + Cl_2(g) = 1/3 Al_2Cl_6(g)$	–396.6
$2/5 U(s) + Cl_2(g) = 2/5 UCl_5(s)$	–354.2
$1/3 U(s) + Cl_2(g) = 1/3 UCl_6(g)$	–288.6
$AmCl_2(s) + 0.5 Cl_2(g) = AmCl_3(s)$	–276.0
$PuCl_3(s) + 0.5 Cl_2(g) = PuCl_4(g)$	110.4
$NpCl_3(s) + 0.5 Cl_2(g) = NpCl_4(s)$	46.2
$UCl_3(s) + 0.5 Cl_2(g) = UCl_4(s)$	–122.1
$UCl_4(s) + 0.5 Cl_2(g) = UCl_5(s)$	7.5
$UCl_5(s) + 0.5 Cl_2(g) = UCl_6(g)$	18.5
$2/15 PuAl_4(s) + Cl_2(g) = 2/15 PuCl_3(s) + 8/15 AlCl_3(s)$	–412.3
$1/6 UAl_3(s) + Cl_2(g) = 1/6 UCl_3(s) + 1/2 AlCl_3(s)$	–410.3
$2/15 UAl_4(s) + Cl_2(g) = 2/15 UCl_3(s) + 8/15 AlCl_3(s)$	–406.7

1000 °C, the relative chloride compound stability is the same, but now liquid and gaseous (for U–Np) chloride compounds also form (see Table 1). The data compiled in Table 3 for An–Al alloys indicate that, despite the strong stabilizing enthalpy of mixing of the intermetallic compounds, the Gibbs energy of chlorination is also largely negative.

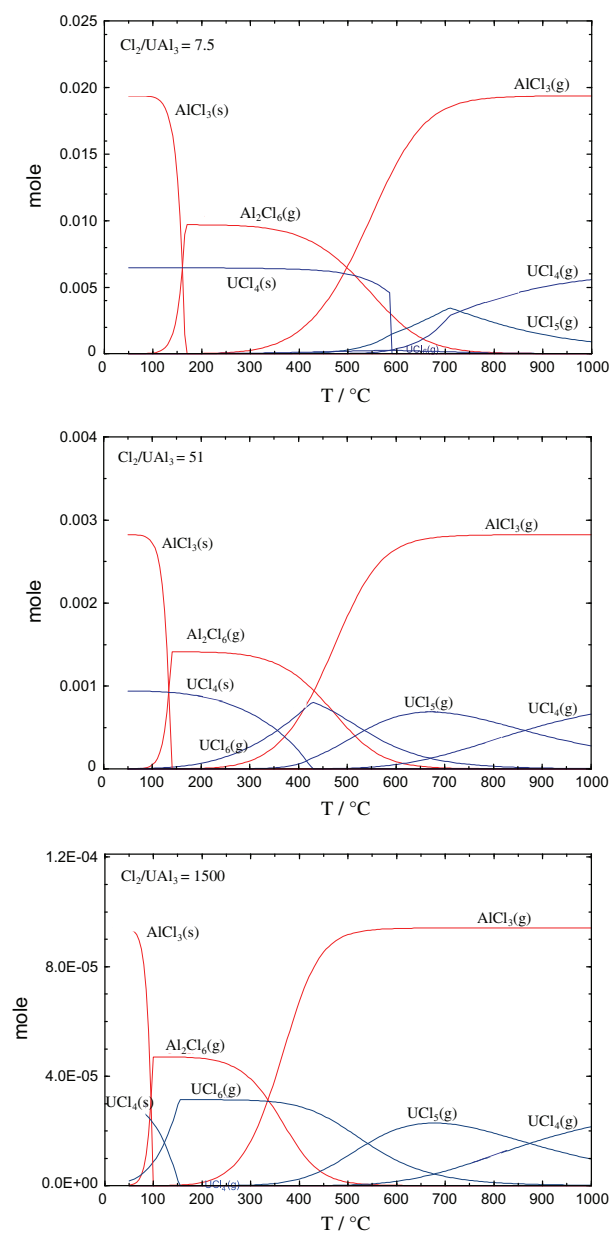
It is expected that these heterogeneous reactions will be inhibited by the kinetic, similarly to the passivation phenomenon observed for oxidation of some metals. Indeed, a solid chloride layer might form at the surface of the alloy preventing further chlorination. Therefore, crushing of the alloy to a very fine powder is recommended to increase the reactive surface area.

### 2.2.2. Chlorination of $UAl_3$ in the 100–1000 °C temperature range for selected $Cl_2/UAl_3$ ratios

As shown in Table 3, the chlorination of U leads to the formation of  $UCl_4(s)$  at 150 °C, when the  $Cl_2/U$  ratio is equal to the stoichiometric value. Further chlorination of  $UCl_4(s)$ , leading to  $UCl_5(s)$  and



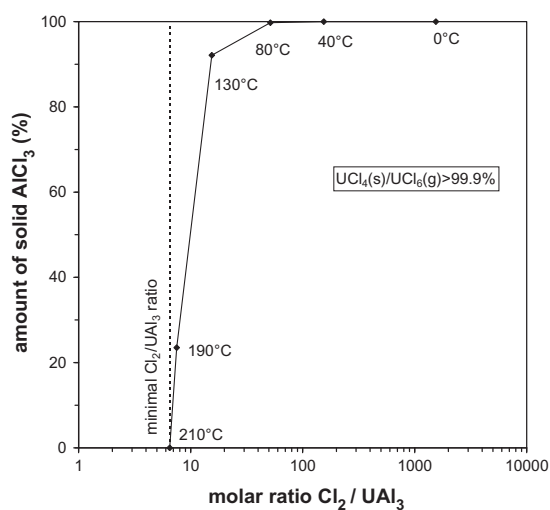
**Fig. 2.** Calculated vapour pressure as a function of temperature for various metals and chloride compounds.



**Fig. 3.** Calculation of the change of the amount of different chloride compounds formed with increase in temperature at different  $\text{Cl}_2/\text{UAl}_3$  molar ratio. Initial conditions:  $1 \text{ dm}^3$  containing 2000–300 – 10 mg of solid  $\text{UAl}_3$  alloy and  $4.843 \times 10^{-2}$  mole of  $\text{Cl}_2(\text{g})$ .

$\text{UCl}_6(\text{g})$  compounds, is forecast with an excess of chlorine gas, since the Gibbs energy of the chlorination reactions are only slightly positive. Furthermore, an increase of temperature, which would enhance the reaction kinetics, would also result in the formation of the gaseous species ( $\text{UCl}_6(\text{g})$ ,  $\text{UCl}_5(\text{g})$  and  $\text{UCl}_4(\text{g})$ ). Therefore, U compounds are the most problematic regarding the actinide losses by volatilisation and other An compounds, which are much less likely to form gaseous compounds, were disregarded for the following calculations.

The equilibrium composition of the chlorination products was calculated using the *Equilibrium module* of the FactSage software. The initial conditions were set according to the available equipment used for the future experiments (see Section 3). A constant



$\text{UAl}_3$ initial mass (mg)	10	100	300	1000	2060	2375
$\text{Cl}_2(\text{g})$ initial volume ( $\text{dm}^3$ )	1	1	1	1	1	1
$\text{Cl}_2/\text{UAl}_3$ molar ratio	1545	154.5	51.5	15.4	7.5	6.5

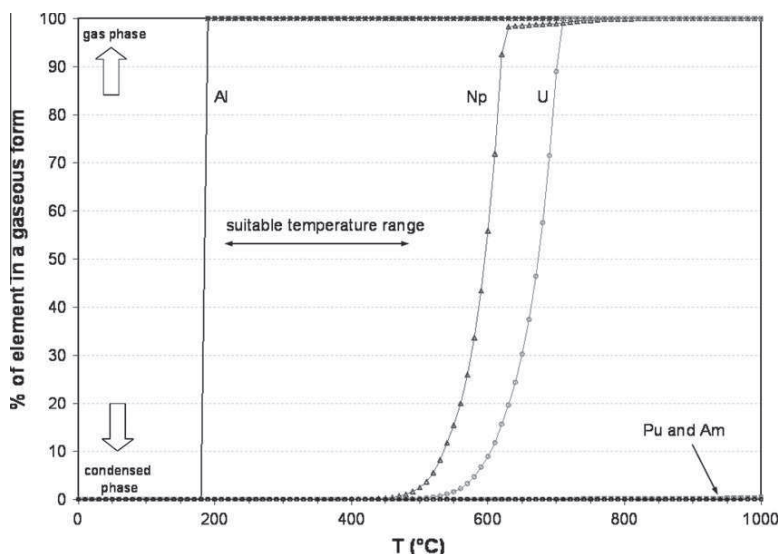
**Fig. 4.** Maximal reaction temperature to ensure a recovery of 99.9% of U in solid phase and residual amount of  $\text{AlCl}_3$  in the solid phase as a function of the initial  $\text{Cl}_2/\text{UAl}_3$  molar ratio. Initial conditions:  $1 \text{ dm}^3$  containing solid  $\text{UAl}_3$  and  $4.843 \times 10^{-2}$  mol of  $\text{Cl}_2(\text{g})$ .

volume of  $1 \text{ dm}^3$  of  $\text{Cl}_2(\text{g})$  was considered, corresponding to the volume of the experimental reactor, and the  $\text{Cl}_2/\text{metal}$  molar ratio was fixed by the amount of actinide alloy introduced into the reactor. The results are plotted in Fig. 3 for three different initial  $\text{Cl}_2/\text{UAl}_3$  ratios. It is shown that the formation of gaseous uranium chloride compounds increases both with temperature and  $\text{Cl}_2$  excess. For example, at a very high  $\text{Cl}_2/\text{UAl}_3$  molar ratio of 1500,  $\text{UCl}_6(\text{g})$  is stable at temperatures below  $100 \text{ }^\circ\text{C}$ . In addition, solid  $\text{AlCl}_3$  undergoes sublimation to  $\text{Al}_2\text{Cl}_6(\text{g})$  at relatively low temperatures.

To determine the most appropriate experimental conditions, the maximum reaction temperature allowing the recovery of 99.9 mol.% of U chloride species in the solid phase was calculated as a function of the  $\text{Cl}_2/\text{UAl}_3$  molar ratio. The smallest ratio was set to 6.5, which corresponds to the amount of chlorine gas required to fully convert 1 mol of  $\text{UAl}_3$  to  $\text{UCl}_4$  and  $\text{AlCl}_3$ . Fig. 4 shows the maximum temperature of chlorination for a given  $\text{Cl}_2/\text{UAl}_3$  ratio and the residual amount of  $\text{AlCl}_3$  in the solid phase. The maximum working temperature is about  $200 \text{ }^\circ\text{C}$ , at minimal  $\text{Cl}_2/\text{UAl}_3$  ratios, assuming consumption of all chlorine gas in the reactor. For  $\text{Cl}_2/\text{UAl}_3$  ratio lower than 50, volatilisation of certain portion of  $\text{AlCl}_3$  is expected. For  $\text{Cl}_2/\text{UAl}_3$  ratio higher than 50, an operating temperature lower than  $100 \text{ }^\circ\text{C}$  is required, which is not favourable from the point of view of the reaction rate.

### 2.3. Sublimation step

A successful chlorination leads to a mixture of solid chlorides composed of  $\text{AlCl}_3$ ,  $\text{UCl}_4$ ,  $\text{PuCl}_3$ ,  $\text{NpCl}_4$  and  $\text{AmCl}_3$ . The aim of the next step is to separate  $\text{AlCl}_3$  by sublimation, maintaining all An chlorides in a solid phase. The simulated heating of a mixture containing 1 mol of An chlorides and 2 mol of  $\text{AlCl}_3$  up to a temperature of  $1000 \text{ }^\circ\text{C}$  under argon gas atmosphere was carried out. The sublimation of  $\text{AlCl}_3$  starts at a temperature of  $180 \text{ }^\circ\text{C}$  and no An chloride compounds exist in the gaseous phase at temperatures below  $450 \text{ }^\circ\text{C}$ . At higher temperature,  $\text{NpCl}_4$  melts and volatilises



**Fig. 5.** Sublimation of aluminium chloride from the chloride mixture – Increase in the amount of gaseous compounds with increase in temperature. Initial conditions: reactor containing a mixture of 1 mol of An chlorides and 2 mol of  $\text{AlCl}_3$ . Atmosphere Ar (1 bar).

due to the high vapour pressure of the liquid phase.  $\text{UCl}_4$  exhibits the same behaviour at higher temperature ( $\sim 600^\circ\text{C}$ ). As shown in Fig. 5, a temperature range of more than  $200^\circ\text{C}$  allows selective sublimation of  $\text{AlCl}_3$ .

### 3. Chlorination of $\text{UAl}_3$ alloy

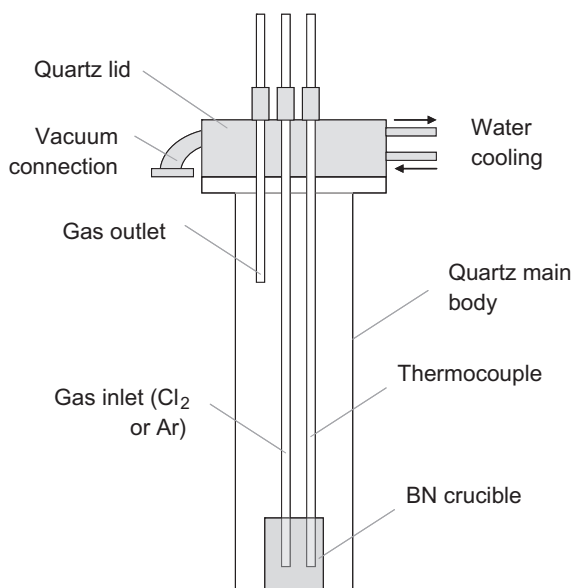
An experimental study was carried out on the chlorination step in order to quantify the efficiency of the process and to estimate actinide losses by volatilisation under the experimental conditions evaluated from the thermodynamic study. Pure  $\text{UAl}_3$  alloy was used, since the thermodynamic study indicated that the process would be feasible under conditions suitable for chlorination of uranium. The working temperatures  $150$ ,  $160$  and  $170^\circ\text{C}$  and  $\text{Cl}_2/\text{UAl}_3$  molar ratios of 36 and 18 were investigated to determine the optimal process conditions providing complete chlorination without uranium loss by formation of gaseous  $\text{UCl}_5$  and  $\text{UCl}_6$ .

#### 3.1. Experimental set-up

The experiments were carried out in a glove box designed for work with  $\text{Cl}_2(\text{g})$ . The box was kept under nitrogen atmosphere and equipped with a chlorine gas line supplied by a system of gas wash bottles containing 4 and 8 M KOH solutions, where unreacted chlorine gas is absorbed. The chlorine content inside the glove box is continuously controlled using a Dräger Polytron 7000 chlorine detector. The experimental set-up used for chlorination experiments is shown in Fig. 6. A quartz reactor placed inside a vertical oven was used for the chlorination. Chlorine gas was introduced by a quartz tube guided through a quartz lid of the reactor by a gastight connection. The lid was also equipped with sealed ports for a thermocouple and a gas outlet connected to a chlorine off-gas treatment. Boron nitride (BN) crucibles with inner diameters 15 and 35 mm were used as containers for the solid reactants.

#### 3.2. Input material

The starting material,  $\text{UAl}_3$ , was prepared by arc melting of pure metals in 1:3 M ratio in an atmosphere of purified Ar on a water cooled copper hearth, using melted Zr as an oxygen/nitrogen get-



**Fig. 6.** Reactor vessel for the chlorination experiments.

ter. Composition of the alloy was determined by X-ray Diffraction (XRD) as 98 wt.%  $\text{UAl}_3$ , 1 wt.%  $\text{UAl}_2$  and 1 wt.% residual Al. In order to increase the reactive surface area, the alloy, very brittle, was crushed into a very fine powder using a manual mortar.

#### 3.3. Analyses

Most of the analyses were made using the XRD technique according to the following procedure. Initially, the samples were homogenised, ground and embedded in an epoxy resin. The analyses were performed on a Siemens D8 advanced diffractometer (Bragg Bentano configuration) equipped with a Ge (1 1 1) incident beam monochromator and a VANTEC position sensitive detector, covering  $6^\circ$  in incident angle  $2\theta$ . For structure refinement and the quantitative phase analysis of the reaction products by the Rietveld

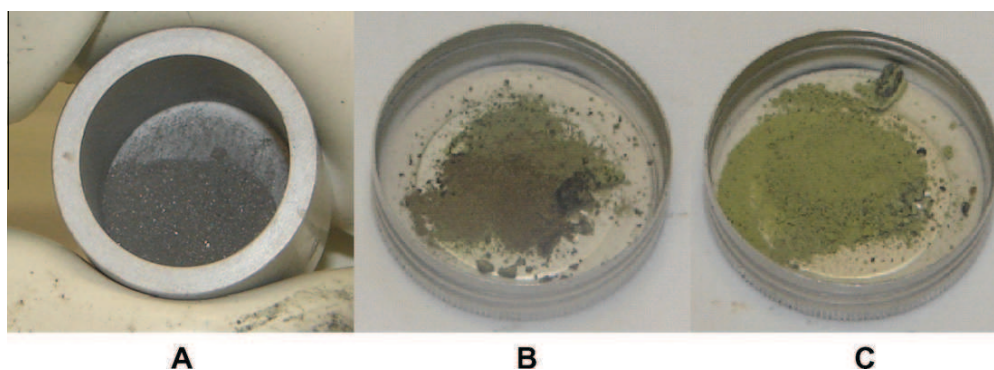


Fig. 7. Pictures of the original powdered  $UAl_3$  alloy (A) and products after the first (B) and second (C) steps of chlorination at 150 °C.

**Table 4**

Composition of the solid reaction products for the chlorination of  $UAl_3$  in wt.%.

Run/compound	$UCl_3$	$UCl_4$	$UAl_3 + UAl_2$	$AlCl_3$
150 (1 p.)	26.8	48.5	1.4	23.3
150 (2 p.)	11.6	82.5	<dl	5.6
150 (2 agg.)	47.5	28.4	14.1	10.0
150 (2)	<b>18.0</b>	<b>72.9</b>	<b>2.7</b>	<b>6.4</b>
160 (1 p.)	22.1	8.3	43.3	26.4
160 (2 p.)	4.5	82.9	1.5	11.1
160 (2 agg.)	46.7	27.9	10.9	14.5
160 (2)	<b>19.0</b>	<b>64.0</b>	<b>4.7</b>	<b>12.2</b>
170	<b>84.5</b>	<b>&lt;dl</b>	<b>&lt;dl</b>	<b>14.9</b>
18	<b>12.2</b>	<b>71.6</b>	<b>&lt;dl</b>	<b>16.0</b>

(1 p.), (2 p.) = composition of powder after the first (second) chlorination.

(2 agg.) = composition of agglomerate after the second chlorination.

(2) = composition of the final product (bold values show the overall efficiencies of the runs).

<dl = below detection limit of XRD-Rietveld method (1 wt.%).

method, the XRD patterns were typically collected in the  $2\theta$  range of 10–110° (step interval 0.0085°), with an exposure time of 5 s per step, and the samples were rotated during data collection to improve the statistics and reduce the effects of any preferred orientation. The fitting and refinement were performed using the Fullprof and/ or Topas software. In one case, the chlorination product was dissolved in 1 M nitric acid and analysed by the inductively coupled plasma mass spectrometry (ICP-MS).

### 3.4. Chlorination experiments

The first experiments were devoted to evaluation of the dependency of the chlorination efficiency and composition of the formed products on the working temperature. Therefore, the molar ratio  $Cl_2$ /alloy was kept constant in these experiments. The volume of  $Cl_2$ (g) was fixed by the volume of the reactor (1 dm<sup>3</sup>) and the amount of chlorinated material was set to be 300 mg yielding a  $Cl_2$ /alloy molar ratio 36. BN crucibles with inner diameter 15 mm were used during this series. Three experiments were carried out at temperatures of 150, 160 and 170 °C, referred to as 'run 150, 160 and 170'. In run 150 and 160, two successive chlorinations were carried out, each of 20 h, whereas run 170 consisted of a single 20 h chlorination. In addition, one experiment was carried out at a temperature of 150 °C with 600 mg of the alloy yielding a lower  $Cl_2$ /alloy molar ratio 18 (referred to as 'run 18'). The chlorination was carried out as a single 40 h run and a larger BN crucible was used (inner diameter 35 mm) to increase the reactive surface area.

All experiments were conducted in the same way – the reactor was heated, filled with chlorine gas and isolated for the desired time. After completion of each run, samples of the powder reaction

product were taken for XRD. If a condensate had formed on the reactor walls, it was scraped off and analysed by ICP-MS. The masses of both the initial material and products were precisely weighted to estimate a process mass balance.

### 3.5. Results and discussion

In all cases, green-grey powder was obtained after the first 20 h of chlorination, indicating the presence of some non-chlorinated alloy. In two samples from run 150 and 160, part of the powder turned into agglomerate that remained stuck to the bottom of the crucible. The reason for the agglomerate formation might be that the BN crucible was too small, combined with the relatively fine grain size of the powder. However, after the second chlorinations, the agglomerate became brittle which allowed its removal and separate analysis. The further chlorinations yielded pure green powder, indicating that mainly  $UCl_3$  and/or  $UCl_4$  was present. An increase of the mass was observed after both chlorination steps. Comparison of the appearance of the initial  $UAl_3$  alloy with that of the chlorination products is shown in Fig. 7.

During all the experiments, a part of the  $AlCl_3$  formed sublimated and deposited on the cold surface at the top of the reactor. While the deposits in runs 150, 160 and 18 were only very thin white layers, run 170 produced a dark brown deposit after 20 h of chlorination. Since this indicated the formation of volatile U chlorides, further chlorination was not carried out with this sample.

The composition of the products and efficiency of chlorination was evaluated from the XRD results. The agglomerates formed in runs 150 and 160 after the first chlorinations could not be removed from the crucible and examined (11.0 and 34.4 wt.% of the product, respectively). Therefore, the evaluation was divided into three parts: Powder after the first chlorination, powder and agglomerate after the second chlorination and overall composition after the complete run. As expected, the XRD of the agglomerate revealed a lower efficiency of chlorination, caused by the slow diffusion of  $Cl_2$  within the solid phase. In run 18, no agglomerate was formed and a very high efficiency was reached, showing the critical importance of the active surface area of the chlorinated material.

Owing to its high reactivity with the used epoxy-resin,  $AlCl_3$  was not detectable by XRD. The concentrations of  $AlCl_3$  in the products were estimated separately using the real and theoretical mass balances and the experimentally determined concentrations of the other compounds present. The results are summarised in Table 4 and an example of a XRD diffractogram is shown in Fig. 8.

ICP-MS of the condensate from run 170 showed the presence of uranium, which was not the case for the other runs. Exact quantification was impossible, because the sample was recovered by

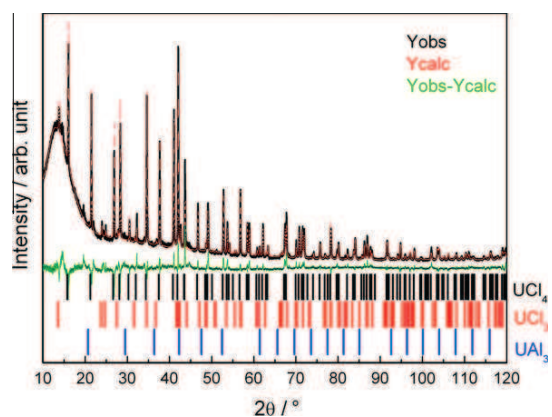


Fig. 8. XRD diffractogram of the powder part of the reaction products from run 150 after 40 h of chlorination at 150 °C.

washing the reactor wall with ethanol and the dilution factor was unknown. Formation of volatile uranium compounds was also confirmed by XRD of the powder products, since traces of  $UCl_5$  were detected in the sample.

#### 4. Summary

Recovery of actinides from actinide–aluminium alloys is a final step of the proposed pyrochemical process for the reprocessing of spent nuclear fuel, based on electrorefining in molten chloride salts using solid Al cathodes. The efficient back-extraction of the actinides from the An–Al alloys formed is one of the crucial points for the overall feasibility of the process. From several options, the chlorination route has been selected and investigated in this work. The process is based on full chlorination of the alloy and removal of the  $AlCl_3$  formed by sublimation, while keeping all actinides in solid phases. The thermochemical study has covered all three main steps of the chlorination route and the following main points have been evaluated based on the available thermodynamic data:

- Distillation of the salt adhering to the alloys needs to be efficient to remove the main salt constituents and most fission products. The proposed conditions (vacuum  $P = 10^{-5}$  bar, temperature  $T = 1000$  °C) have been optimised with regard to the experimental possibilities. Under these conditions, only a few chloride compounds such as  $MoCl_2$ ,  $SrCl_2$  and  $BaCl_2$  might be difficult to remove.
- Full chlorination of the alloy is thermodynamically possible at any temperature.
- The temperature around 150 °C is recommended for the chlorination step in order to avoid formation of gaseous actinide compounds.
- Selective sublimation of  $AlCl_3$  should be possible by heating of the chlorination products under Ar at 350–400 °C.

The calculations have indicated that the chlorination reaction should be carried out at relatively low temperature, using the lowest amount of  $Cl_2$  possible. However, a high amount of  $Cl_2$  is

preferable from the point of view of the reaction rate. The latter is enhanced by the heterogeneous, solid–gas type of the reaction. Therefore, an experimental study has been carried out to verify and optimise the proposed conditions for the chlorination step.

The results are very promising, showing that very efficient chlorination of U–Al alloys with no volatilisation of uranium can be accomplished at a low temperature of 150 °C, if sufficient reacting surface area is provided. The molar ratio  $Cl_2/alloy = 18$  has yielded 99.8% conversion of  $UAl_3$  to chlorides at this temperature. A temperature of 170 °C has been determined as the maximum for the reaction since gaseous uranium products have been detected at this value. A major part of  $AlCl_3$  has been already removed during the chlorination step and the sublimation efficiency has been estimated from the mass balance to be between 85% and 94%.

The next step of this work will be reported in Part II. Demonstration experiments on the complete chlorination route have been carried out using U–Pu–Al alloys, which have been prepared by electrochemical deposition of U and Pu onto solid aluminium plates in molten LiCl–KCl.

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