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RECOVERY OF THE ACTINIDES BY ELECTROCHEMICAL METHODS IN MOLTEN CHLORIDES USING SOLID ALUMINIUM CATHODE

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An electrorefining process in molten chloride salts is being developed at ITU to reprocess the spent nuclear fuel. According to the thermochemical properties of the system, aluminium is the most promising electrode material for the separation of actinides (An) from lanthanides (Ln). The actinides are selectively reduced from the fission products and stabilized by the formation of solid and compact actinide-aluminium alloys with the reactive cathode material. In this work, the maximum loading of aluminium with actinides was investigated by potentiostatic and galvanostatic electrorefining of U-Pu-Zr alloys. A very high aluminium capacity was achieved, as the average loading was 1.6 g of U and Pu into 1 g of aluminium and the maximum achieved loading was 2.3 g. For recovery of the actinides from aluminium, a process based on chlorination and a subsequent sublimation of $AlCl_3$ is proposed.

I. INTRODUCTION

Most innovative reactor systems are conceived to have an integrated waste burning and a homogenous recycling of all actinides [1]. Therefore, the fuels used in these reactors will be significantly different from the commercial fuels of today. Because of the fuel type and the very high burn-ups reached, traditional hydrochemical reprocessing such as used today will probably not be the preferred method. The main reasons are the limited solubility of the fuel materials in acidic aqueous solutions and the poor radiation stability of the organic solvents used in extraction processes. For this reason different pyrochemical separation techniques are under development, liquid metal-molten salt extraction [2, 3] and electrodeposition [4-8] are the two major processes used. Due to the chemical similarity between trivalent Ln and minor actinides (MA), an efficient separation of Am and Cm from Ln, is the most difficult to achieve.

According to the known activity coefficients of Pu, U and Ce in different reactive metals, aluminium has been identified as the electrode material enabling the highest

separation factors of actinides from lanthanides (Ln) [9]. This has led to the development of a process based on the separation of actinides by reductive extraction into a molten Al [2]. In ITU, an electrorefining process in molten chloride salt using solid aluminium cathodes is being developed. [10]. In this process, actinides are recovered from a metallic An-Zr alloy fuel in the form of An-Al alloys. A very high selectivity of the process for recovery of An from Ln has been already shown as well as the capability of solid aluminium electrodes to form stable An-Al alloys using Al rods, foils [9] and a foam [11] as the cathodes. In addition, a large-surface aluminium electrode has been used to study the maximum amount of actinides that can be collected on a single electrode by a constant current electrolysis [12].

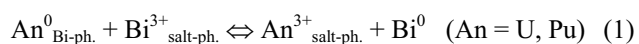
In this work this issue has been further investigated by U and Pu electrodeposition applying potentiostatic and galvanostatic electrolytic techniques using Al plates of different dimensions. The experiments were carried out with U-Pu-Zr alloy and a very high capacity of aluminium to alloy An was demonstrated.

The recovery of actinides from the An-Al alloys formed during the electrorefining is a key point in order to complete the actinide separation process. A process based on chlorination of the An-Al alloy was selected and evaluated. A thermochemical study of each step of the chlorination process was performed: (i) distillation of the residual salt incorporated in the deposit, (ii) chlorination of the alloy and (iii) removal of formed $AlCl_3$ by sublimation. According to the conditions defined by this study, the first experiment was performed showing promising results.

II. EXPERIMENTAL

All experiments, storage and handling of chemicals were carried out in a glovebox under purified Ar atmosphere (<5 ppm of water and oxygen). The detailed description of the technical background is described elsewhere [13]. A bath consisting of U^{3+} , Pu^{3+} and Gd^{3+} ions dissolved in LiCl-KCl eutectic mixture (Aldrich

99.99%) was prepared by oxidising of U-Pu-Zr metallic alloy (ITU stock material, 71-19-10 wt. % respectively) introduced into the melt in a tantalum basket by adding BiCl_3 according to the reaction (1).



Reduced Bi metal was collected in a Bi pool at the bottom of an Al_2O_3 crucible. GdCl_3 (Aldrich 99.99%) was used as received from the producer without any additional treatment. The initial concentrations in the bath were analysed to be 3.85 wt. % of U, 1.53 wt. % of Pu and 1.61 wt. % of Gd.

Cyclic voltammetry measurements were carried out using a three-electrode setup and a PAR 273 potentiostat with EG&G M270 electrochemical software. The working electrode was prepared using a wire ($d = 1 \text{ mm}$) from the desired material (W, Al) and inserted 5 mm into the bath. A Mo wire bent into the shape of a spiral served as the auxiliary electrode and a reference electrode used was an Ag/LiCl-KCl-AgCl (1 wt %) prepared in a Pyrex glass tube. All potentials stated in this work are related to the corresponding reference potential.

Electrorefining experiments were performed at 450°C and the working electrode was replaced by an aluminium plate. A tantalum basket filled with U-Pu-Zr alloy (71-19-10 wt.%, ITU stock material) was inserted instead of the auxiliary electrode. The experimental set-up is shown in Fig. 1.

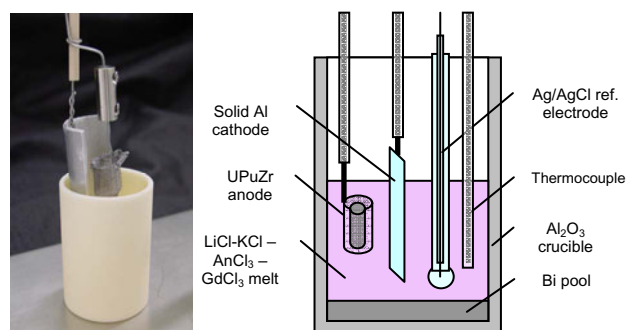
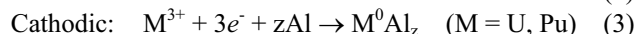
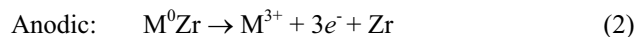


Fig. 1 Picture of anodic Ta basket, Al cathode and Al_2O_3 crucible used in the experiments (left) and the experimental set-up for electrorefining

Both anodic and cathodic potentials were monitored during the electrorefining experiments using a specially prepared combination of two multimeters with a laboratory power supply. The expected electrode reactions were anodic oxidation of actinides from the alloy and their reduction on the cathode forming An-Al surface alloys according to the following reactions (2, 3):



Two techniques were used to examine the maximum possible loading of the solid Al electrodes: Galvanostatic electrorefining limited by cut-off potentials in order to ensure a selective An separation, and potentiostatic electrorefining. In the galvanostatic mode, the maximum current was reached after applying a stepwise current increase to keep both cathodic and anodic potentials within the selected limits. The cathodic cut-off potential was set to a value of -1.25 V which ensures conditions for a selective group separation of An from Ln [11, 12]. A potential of -1.00 V was used as the anodic cut-off potential to avoid oxidation of Zr from the U-Pu-Zr alloy. The electrolysis was terminated either when too low current was reached. For all runs realized under potentiostatic conditions, a cathode potential of -1.25 V was applied.

The purity of the bath was regularly checked by cyclic voltammetry (CV) measurements using inert tungsten electrodes. The chemical composition of the salt was determined by ICP-MS analysis of regularly taken salt samples dissolved in 1 M nitric acid. After the electrorefining, adhered salt on the electrodes was removed by vacuum distillation and/or by washing in ethanol. SEM/EDX was used for surface analysis and the deposit composition was investigated by XRD and gamma spectrometry [14].

The chlorination experiments were carried out in a glove box under nitrogen atmosphere, specially designed for work with $\text{Cl}_2(\text{g})$. The box is equipped with a chlorine gas line ended by a system of gas wash bottles containing KOH solutions (4 and 8 M), where non reacted chlorine gas is absorbed. A quartz reactor used for the chlorination was placed in a vertical oven. Chlorine gas was introduced by a quartz tube guided through the lid of the reactor by a gastight connection. The lid was also equipped by sealed ports for a thermocouple and the gas outlet connected to the chlorine off gas treatment. After the reactor was filled with chlorine gas, it was isolated and the gas flow was stopped. Boron nitride crucibles were used as containers for the chlorinated material and positioned on the bottom of the reactor. For the chlorination experiments, a well defined UAl_3 alloy was prepared by arc melting at a temperature $>3000^\circ\text{C}$ to represent An-Al alloys from electrorefining experiments. The composition determined by XRD was 98 wt.% of UAl_3 , 1 wt.% of UAl_2 and 1 wt.% of Al.

III. RESULTS AND DISCUSSION

III.A. Electrorefining experiments

Two galvanostatic runs (labelled 1 and 2 in TABLE I below) were carried out using Al electrodes made from plates 0.5 mm thick with active areas 8 and 9 cm^2 . An excess of U-Pu-Zr alloy was introduced as anodic material to avoid Zr co-dissolution during the

electrolyses. The anodic potential varied between -1.30 and -1.00 V, which corresponds to a congruent oxidation of the actinides from U-Pu-Zr alloy. Selective reduction of uranium and plutonium forming a U-Pu-Al surface alloy occurred at the cathode and the potential showed a decreasing trend, starting from -1.05 V and in the end reaching the minimum value of -1.25 V. With the build up of the An-Al surface alloy layer, the cathodic reaction is more and more limited by diffusion of the reduced elements forming the surface alloy layer, i.e. U, Pu and Al. A typical record of potentials and current for the galvanostatic electrolysis is presented in Fig. 2.

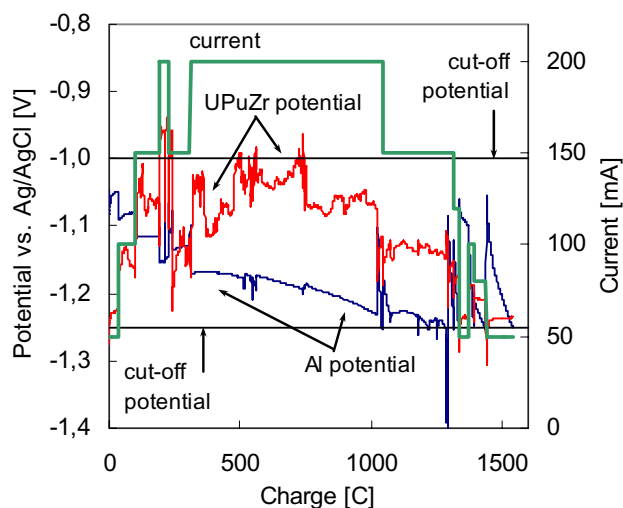


Fig. 2 Evolution of cathodic and anodic potentials during the galvanostatic electrolysis

In addition, two potentiostatic runs (labelled 3 and 4 in TABLE I below) were performed using small area electrodes (1.5 and 3.6 cm²) made from plates of 0.5 and 2.0 mm thickness. The cathodic potential was kept constant at -1.25 V in both runs to ensure a selective deposition of only actinides. In this case, the current gradually decreased with increasing thickness of the formed U-Pu-Al surface alloy and the anodic potential dropped from -1.0 V up to -1.3 V. The record of the anodic potential development and the current for a typical potentiostatic electrolysis is shown in Fig. 3.

After the electrodeposition, the electrodes were left for some time just above the bath at 450°C in order to let the adhered salt drop down. For the galvanostatic runs, a vacuum distillation was used to remove the salt remaining on the electrode surface. A quantitative Pu assay of the electrodes with the deposits was performed by γ -spectrometry in far-field counting geometry. Separate γ measurements with close sample-to-detector distances were carried out for the determination of the Pu/U ratio using gamma rays from ²³⁹Pu and ²³⁵U, knowing the isotopic composition of Pu and U in the used alloy. The

results are summarised in TABLE I together with an evaluation of the loading of the electrodes with actinides.

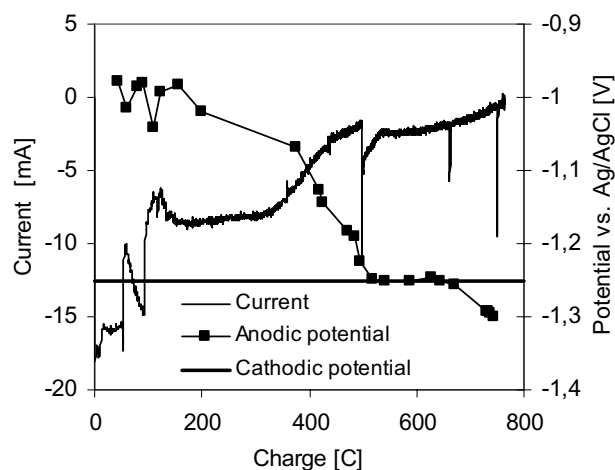


Fig. 3 Evolution of anodic potential and current during the potentiostatic electrolysis (run 5)

TABLE I Evaluation of results for U-Pu-Zr electrorefining experiments

run	Charge [C]	Mass Al [g]	Deposit analysis		An wt. %	Al/An weight ratio
			Pu content [mg]	U/Pu weight ratio		
1	1423	0.61	69.9	10.1	59.9	1:1.49
2	1527	0.54	47.1	18.1	62.5	1:1.67
3	773	0.27	51.0	11.4	70.0	1:2.33
4	766	0.23	67.7	6.4	68.5	1:2.17

The weight percent ratio of An in the Al cathode was calculated according to equation (4):

$$An \text{ wt. \% in Al} = \frac{m_{An}}{m_{An} + m_{Al}} \quad (4)$$

The mass of actinides m_{An} resulting from γ -spectroscopy measurements was used for the calculation and the relevant aluminium mass was derived from the alloy thickness and the measured immersion depths of the electrodes.

III.B. Characterization of the formed alloys

The electrode from galvanostatic run 1 was characterized by SEM-EDX analysis and XRD. SEM micrographs and results of EDX analysis are shown in Fig. 4 and Fig. 5. A thick and homogeneous surface deposit is well visible on the micrograph shown in Fig. 4 and at some places, almost all aluminium has reacted. The

maximum thickness of the electrode with deposit was measured to be 1.2 mm, compared to the 0.5 mm thick Al plate used as the cathode starting material.

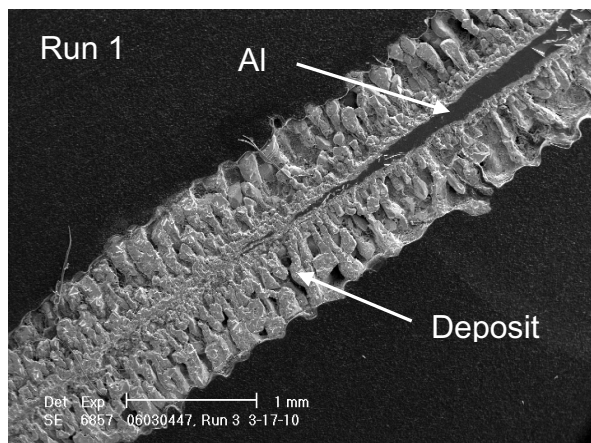


Fig. 4 SEM micrograph of the cross-section of the electrode from run 1 (loading 59.9 wt.% of An in Al)

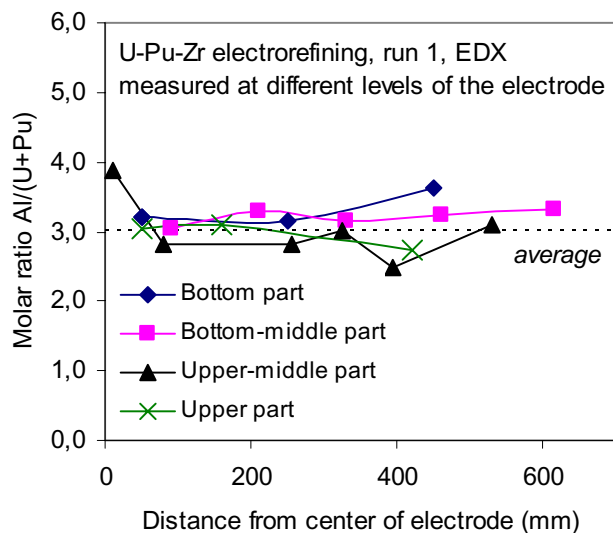


Fig. 5 SEM-EDX determination of the Al/(U+Pu) molar ratio vs. the distance from the electrode surface for the electrode from run 1

An analysis of the deposit was performed using EDX at 21 spots selected at different thickness of the electrode. Composition profiles from the middle towards the surface of the electrode were compiled for U, Pu, Al, Cl and Gd. The molar ratio Al/(U+Pu) is plotted in Fig. 5 versus the distance from the centre of the electrode. The average Al/(U+Pu) ratio was determined to be 3.01. Thus the deposit is most probably composed of a (U,Pu)Al₃ alloy. The values for the U/Pu molar ratio are scattered, with a U/Pu ratio comprised between 4 and 10. The

average value for 21 analyses is U/Pu = 7.0, which is somewhat lower than the ratio determined by gamma spectroscopy (U/Pu = 10.1). The XRD analysis of the deposit was indexed on the base of a cubic (a = 4.2652(1) Å) unit cells corresponding to (U,Pu)Al₃ alloy. This result is in a very good agreement with the EDX determination of the deposit composition.

III.C. Salt concentration profiles

The concentration profile in dependency on the total passed charge is plotted in Fig. 6. The effectiveness in the application of cut-off potentials was verified, as the concentration of gadolinium remained at its initial level and zirconium concentration was below the detection limit. The concentration increase of both actinides at 1500 C was caused by an intentional chemical oxidation of the alloy in order to increase the concentration of the actinides in the bath.

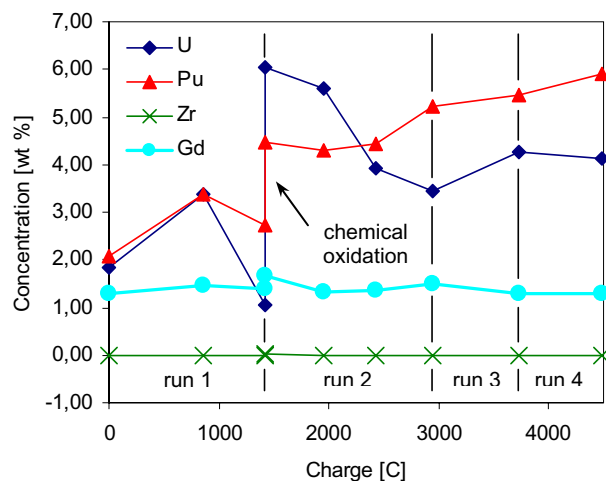


Fig. 6 Concentration profile of U, Pu, Zr and Gd in the bath during the electrorefining

The uranium concentration showed a decreasing trend during the complete run. This is explained by the congruent actinides dissolution from the U-Pu-Zr alloy on the anodic side and the predominant deposition of U compared to Pu (U/Pu mass ratio in the deposit is ~ 10). In addition a chemical reaction, i.e. reductive extraction of U³⁺ by Al from the electrode, can also occur, which would also lead to a slight U³⁺ concentration decrease [15]. The plutonium concentration gradually increased during the experiment, which supports the above mentioned explanation of the uranium concentration decrease.

III.D. Recovery of An from AnAl alloys

The chlorination route proposed for the recovery of An from AnAl alloys consists in a three step procedure as presented in Fig. 7. Initially, the salt adhered on the electrode after the electrorefining process is removed by distillation. This salt is composed mainly of LiCl-KCl and some fission products (FP) chlorides. The second step is a chlorination of the An-Al alloy in order to convert the entire alloy to chlorides. The last step consists in the sublimation of AlCl_3 , leaving pure An chlorides, which can be further chemically processed to obtain the desired output product, e.g. An alloy.

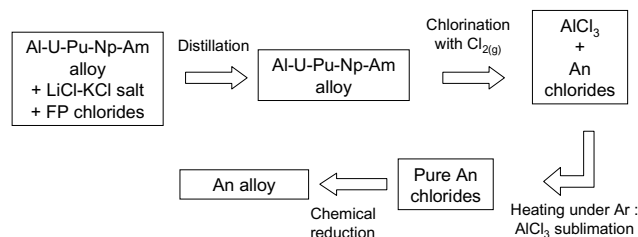


Fig. 7 Principle of the chlorination route (*An=actinides, FP=fission products*)

In order to assess the thermodynamic possibility of the proposed route a theoretical study of each step was performed using the FACTSAGE software. The main results can be summarized as follows:

- A vacuum distillation ($P=10^{-5}$ bar, $T = 1000^\circ\text{C}$) is efficient to completely remove the LiCl-KCl salt and most FP. However, under these conditions, a complete distillation of some chloride compounds (MoCl_2 , SrCl_2 , BaCl_2) will be probably impossible.
- According to the existing thermochemical data of the studied compounds, it is possible to perform a full chlorination of the An-Al alloys at suitable working temperatures, i.e. avoiding volatilisation of An chlorides.
- The molar ratio between chlorine gas and the alloy has a significant influence on the composition of the final products. With increasing Cl_2/alloy molar ratio, the temperature for formation of volatile An chlorides decreases. A temperature of 150°C and minimum Cl_2/alloy molar ratio is recommended for this step in order to avoid the formation of gaseous U chlorides.
- Heating of the resulting mixture under inert Ar atmosphere at $350\text{--}400^\circ\text{C}$ is expected to facilitate the selective evaporation of AlCl_3 , leaving pure An chlorides in the reactor.

Although, from a thermodynamical point of view, all steps were proven possible, the applicability of this

method depends on the reactions kinetics under working conditions suitable for the An recovery. Therefore, an experimental study is necessary to determine the realistic conditions for the process and to quantify the chlorination efficiency and actinides volatilization under these conditions.

The first experiments were focused mainly on the chlorination step. UAl_3 alloy was selected as input material, as volatile U chlorides are formed at the lowest temperature in comparison with other actinides. Accordingly it is expected that the conditions suitable for recovery of U from U-Al alloy can be applied for a process including all actinides. A fine crushed UAl_3 alloy (300 mg) was chlorinated at a temperature of 150°C using a Cl_2/alloy molar ratio of 36 which was set by the fixed volume of the reactor. After 21 hours the reactor was refilled and the chlorination continued at the same temperature for another 20 hours. Both the initial material and obtained products after the chlorination were weighted and analysed by XRD to calculate a mass balance and evaluate the process efficiency.

After the chlorination, a pure green powder was obtained, which indicates the presence of UCl_3 and/or UCl_4 as the major constituents of the product. XRD analysis indicated a high efficiency of the chlorination, as only 2.7 % of the initial alloy remained non-chlorinated. The XRD pattern obtained after the chlorination is presented in Fig. 8.

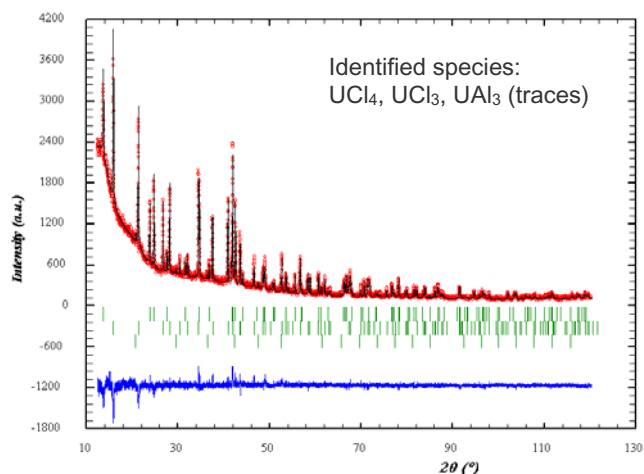


Fig. 8 XRD pattern of the chlorination product (Symbols = observed points, solid line above = calculated profile, solid line below = difference between observed and calculated profiles, ticks below the peaks = $2\theta_{hkl}$ Bragg positions for UCl_4 , UCl_3 and UCl_3 , in descending order)

It was impossible to make a quantitative evaluation of AlCl_3 content by XRD due to its high solubility in the epoxy-resin used for the preparation of the sample.

Accordingly, the concentration of AlCl_3 has to be calculated from the real mass of the chlorination product weighted after the experiment, which was deduced from the calculated theoretical mass of U chlorides and non-reacted residual alloy. The mass balance and an evaluated composition of the chlorination product are shown in TABLE II. The results indicate that a major part of AlCl_3 was evaporated already during the chlorination process. According to the calculations, a mass increase up to 686 – 719 mg was expected after chlorination of the initial 300 mg of the alloy, if all AlCl_3 has remained in the product.

TABLE II Concentrations of the input material and the product obtained after the chlorination

Specie	Concentration [wt.%]	
	Input material	Product
UCl_3	0.0	17.8
UCl_4	0.0	72.6
UAl_3	98.0	2.2
UAl_2	1.0	0.5
AlCl_3	0.0	7.0
Al	1.0	0.0
mass [mg]	300.0	389.1

IV. CONCLUSIONS

The use of solid aluminium electrodes for reprocessing of spent nuclear fuel by electrorefining in molten chlorides seems to be very advantageous. Reduced actinides form solid and dense alloys with aluminium and a very high capacity of aluminium to retain actinides has been proven in this work. If AnAl_3 alloy is formed in the deposit, the maximum possible loading would be 2.94 g of An in 1 g of Al, which corresponds to 74.7 wt. % An in Al. The highest An content in Al during the experiment was achieved for potentiostatic electrolysis, with 2.33 g of An loaded into 1 g of Al (94 % of the maximum Al capacity).

The diffusion of An and Al in the formed An-Al alloy layer seems to be the most important factor for this process. Obviously, the diffusion rate increases with a temperature and therefore a formation of more actinide-rich alloys could be expected at higher temperatures. More detailed studies are necessary to optimise the conditions for a maximum An loading.

Theoretical studies showed the thermodynamical possibility of An recovery from the obtained An-Al alloys using a chlorination procedure consisting of the three main steps: Distillation of the salt adhered on the electrodes, chlorination using chlorine gas and sublimation of formed AlCl_3 . However, the applicability of this method depends on the kinetics of the reactions

under working conditions suitable for the selective An recovery. The first verification chlorination experiment was carried out using UAl_3 alloy, which is the most critical material in the sense of actinide losses during the process by U volatilization. The results indicated that the process can be carried out with a satisfactory chlorination efficiency and without actinides losses caused by volatilization of formed chlorides

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