

## **DEMONSTRATION OF PYROMETALLURGICAL PROCESSING FOR METAL FUEL AND HLW**

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### **Abstract**

CRIEPI and JRC-ITU have started a joint study on pyrometallurgical processing to demonstrate the capability of this type of process for separating actinide elements from spent fuel and HLW. Experiments on pyro-processing of un-irradiated metal alloy fuel (U-Pu-Zr or U-Pu-MA-RE-Zr) by molten salt electrorefining and molten salt/liquid metal extraction will be carried out. The necessary equipment is installed in a new experimental set-up at JRC-ITU. The stainless steel box equipped with telemanipulators is operated under pure Ar atmosphere and prepared for later installation in a hot cell. In first electrorefining tests, U (about 10 g) and Pu (about 5 g) were deposited on a solid and a liquid Cd cathode respectively. Preliminary experiments on molten salt/liquid metal extraction in counter-current batch extraction systems with REs were conducted in CRIEPI. The results showed good separation efficiency in 3 batch extraction stages.

## 1. Introduction

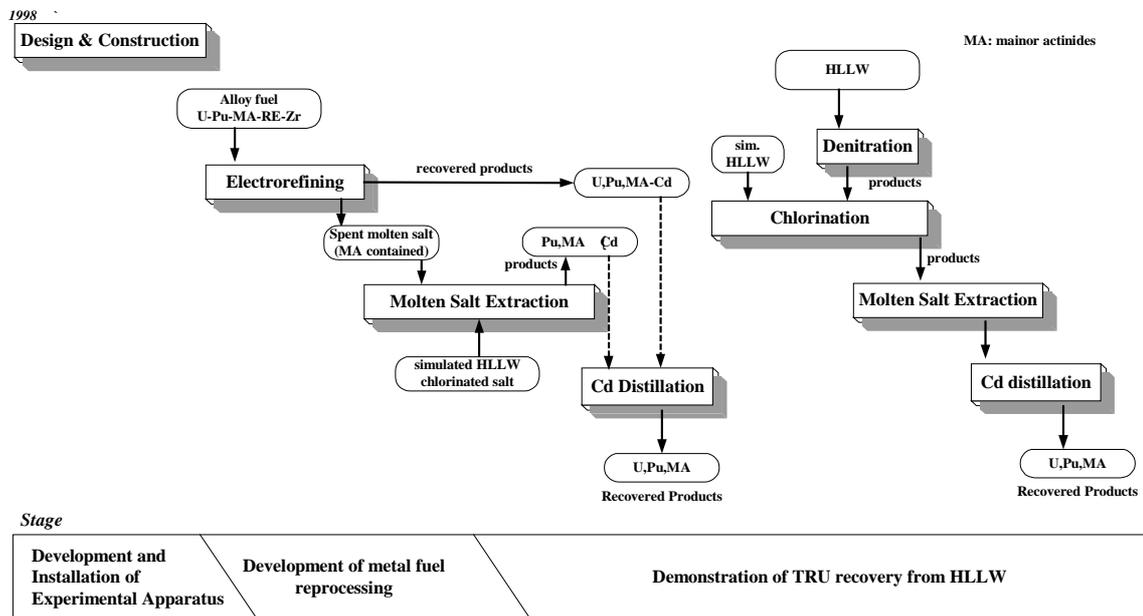
The increasing interest in pyrometallurgy after the selection a few decades ago of oxide fuel and aqueous reprocessing as the fuel cycle reference can be attributed to the drastic change of boundary conditions around the nuclear fuel cycle in the world. The former mission of the fuel cycle was to recover Pu as an important fissile material for the fast breeder reactor, however at present positive credit from recovered Pu can hardly be expected. Today's main emphasis is put on a maximal cost reduction of the fuel cycle. Furthermore recovery of long-lived nuclides becomes a new requirement, since geological disposal of high level waste (or once-through fuel) is facing large difficulties to get public acceptance. Recovery of long-lived nuclides means to use of various reactor systems for transmutation, resulting in new requirements to reprocess different fuel types e.g. MOX, metal fuel, nitride fuel, high burn-up fuel, etc. These new requirements may result in a different choice for future fuel cycle technology. Pyrometallurgical processing is one of the most attractive alternatives to meet these requirements. The requirement for product purity being much less stringent, the recovery of minor actinides (MA: Np, Am, Cm) will take place simultaneously with plutonium due to the thermodynamic properties of molten salt media. The recovery of MA allows the reduction of TRU wastes, and decrease at the same time the risk of nuclear proliferation. The molten salt media also have two important advantageous properties as a solvent material in nuclear processing. The radiation stability of molten salt allows the processing of spent fuels of high radioactivity (e.g. spent fuel with short cooling time) without any increase of solvent waste. Since molten salt is not a neutron moderator such as water is, comparatively large amount of fissile material can be handled in the process equipment, i.e. experimental facilities are compact and economical.

The Central Research Institute of Electric Power Industry (CRIEPI) investigated these promising features in pyroprocessing according to an information exchange with US-EPRI in 1985. The feasibility of pyrometallurgy to separate/recover actinides from spent nuclear fuel or high level waste (HLW) has been started on 1986 [1,2,3]. As a joint study with US-DOE, CRIEPI had participated in the Integral Fast Reactor (IFR) Program of Argonne National Laboratory (ANL) from 1989 to 1995 in order to study the pyrometallurgical technology development [4,5] and to demonstrate the pyroprocess of spent metal fuel [6]. In parallel, the measurement of thermodynamic properties of actinides as well as pyrometallurgical partitioning of TRUs from simulated HLW had been carried out by CRIEPI in collaboration with the Missouri University and Boeing North American [7,8]. In the course of the study, the feasibility of pyrometallurgical processing to recover/separate actinides from spent metal fuel or HLLW was confirmed by the results of experiments with unirradiated TRU materials and theoretical calculations based on measured thermodynamic properties. The demonstration of TRU recovery from spent metal fuel (or even from unirradiated ternary alloy fuel) could however, not be realised because of a sudden cancellation of the IFR program. The Institute for Transuranium Elements (JRC-ITU) has studied since many years the capacities of aqueous processing as for the separation of TRUs from HLW [10]. The CRIEPI and JRC-ITU collaboration to study metal target fuels for the transmutation of TRU [9] has led to a new joint study on pyrometallurgical processing. This study will demonstrate the feasibility of pyrometallurgical processes for separating actinide elements from real spent fuel and HLW, also in view of a rational evaluation of future fuel cycle technology. Furthermore this study has also been included in a project of the European 5th Framework program, where CRIEPI and ITU are a joint partner in an international network. In this paper, the current status as well as the whole test plan of this project will be reported.

## 2. Experimental plan of the joint study

The first phase of the joint study will be carried out from 1998 to 2004, where three different stages are to be carried out as shown in Figure 1.

Figure 1. Experimental test plan of the joint study



The first stage is *the development and installation of the experimental apparatus*. In this stage, an argon atmosphere hot cell equipped with an electrorefiner dedicated for pyrometallurgical experiments is developed. The second stage is *the development of metal fuel reprocessing*, where recovery of actinides from unirradiated metal alloy fuel such as U-Pu-Zr and U-Pu-MA-RE-Zr are to be carried out. The metal alloy fuel is first submitted to an electrorefining step followed by a reductive extraction process of the molten salt electrolyte to recover residual actinides and to separate them from lanthanides. The recovered TRU-Cd metal will be treated by distillation to separate Cd from TRUs. The third stage is *the demonstration of TRU recovery from HLLW* where pyrometallurgical partitioning is to be demonstrated on actual HLLW. In this stage, reductive extraction, Cd distillation and chlorination are first tested with simulated materials. For the experiments on actual HLLW, the whole system will be moved inside a lead shield. The actual HLLW will be converted into oxide and afterwards into chlorides in a Cl<sub>2</sub> gas flow. The obtained chloride salt mixture will be used for the reductive extraction process described previously. The reprocessing of metal fuel irradiated in the French PHENIX reactor will be carried out in the last phase of the project.

### 3. Development and installation of the Ar-atmosphere hot cell system

The experimental apparatus was newly designed and fabricated for this study and was conceived for later installation in the hot cell system. The apparatus consists of a stainless steel box to be installed in a 15 cm-thick lead shielding. The stainless steel box was first installed in an alpha laboratory Figure 2.

Figure 2. Stainless steel box with Ar purification unit



The box is operated in a pure Ar gas atmosphere, continuously purified. The airlock system for the introduction or extraction of material is separately flushed by Ar. A so called “La Calhène” container is used for the transport. The box is equipped with a vertical heating well (150 mm in diameter, 600 mm in depth) consisting of an inconel liner and a stainless steel tube. The well sited on the bottom of the box is heated from outside by a cylindrical resistance heater which can be heated up to 1 273 K. Double sleeves with intermediate Ar flushing were employed for the telemanipulators in order to reduce diffusion of oxygen. After many modifications, the stainless steel box is now in an operational condition, with an oxygen and moisture concentration less than 10 ppm.

#### 4. Electrorefining process

##### 4.1 Development of electrorefiner

The electrorefiner is a key part of pyrometallurgical reprocessing, since the fuel dissolution as well as the actinide refining is to be done in this step. An electrorefiner was newly designed and fabricated in CRIEPI based on experience gained in various types of experiments. It should be noted that the design concept of this electrorefiner is to demonstrate the separation yield and recovery yield of metal fuel reprocessing. The electrorefiner consists of three electrodes and a liquid Cd pool covered by a molten LiCl-KCl eutectic mixture. It was shipped to JRC-ITU, and installed in the stainless steel box as shown in Figure 3.

Figure 3. Electrorefiner installed in a stainless steel box (lift-up position)



The electrorefiner cell of 100 mm × 130 mm is hung on a metal flange equipped with cathode, anode, stirrer, reference electrode, sampling etc. Metal alloy fuel previously fabricated at ITU in a joint study with CRIEPI on transmutation of TRU targets is charged into a metal basket working as an anode. The pool of liquid Cd below the molten salt works as an anode, or just as a receiver for the noble elements. The cathode assembly of the electrorefiner uses either a solid iron cathode for U recovery or a liquid metal cathode for TRU recovery. The solid iron cathode ( $\varnothing 18\text{mm}$ ) with a spiral groove can be rotated during electrodeposition to achieve a better recovery [2]. The liquid metal itself will be stirred by means of a ceramic stirrer submerged in the liquid metal cathode (surface area = 8 cm<sup>2</sup>) in order to avoid formation of U dendrites that will hamper the deposition of Pu [2]. The electrode potentials are monitored by a Ag/AgCl reference electrode known for its reliability. The concentration of relevant elements in each phase will be measured by the chemical analyses.

#### 4.2 Electrorefining experiments with U and Pu

The electrorefiner was loaded with approximately 1 000 g of LiCl-KCl eutectic salt and 500 g of cadmium. The whole system was heated up to the operation temperature of 773 K to melt both phases. Depleted U metal was then charged in the anode basket followed by addition of CdCl<sub>2</sub> to oxidise some U metal to UCl<sub>3</sub>, necessary to facilitate the electrotransportation in the molten salt electrolyte. At the concentration of U<sup>3+</sup> of about 1 wt% in the LiCl-KCl salt, notable polarisation was not observed at a current of 1A. Hence electrodeposition of uranium on the solid iron cathode as carried out at a constant current of 500 mA and 1A, respectively. Figure 4 shows the dendritic uranium deposit obtained at 500 mA.

Figure 4. **U deposit on solid cathode (12g)**



The expected amount of uranium metal calculated from the coulomb passed was 12 g. The amount of U deposited will be determined from the chemical analyses of the metal deposit. The electrodeposition of uranium on the liquid Cd cathode was also carried out at a constant current of 200 mA for 1.5 hours resulting in the deposition of about 1 g U in 80 g Cd. After these experiments, the residual U in the molten salt was recovered by the “drow-down electrorefining” where  $U^{3+}$  is reduced to metal form at the cathode while metal Ce is oxidised at the anode. The chemical analysis of the treated salt is still under way, but the colour of molten salt turned from purple ( $U^{3+}$  ions) to white after drow-down electrorefining indicating a high efficiency of the reaction.

About 45g of plutonium metal was then charged with new 1 000g LiCl-KCl eutectic salt in the crucible. About 1 mol% of  $PuCl_3$  was formed in the salt by adding the equivalent amount of  $CdCl_2$ . Then electrodeposition of Pu in liquid Cd cathode was carried out at a constant current of 500 mA for 4 hours. About 5 g of Pu was recovered in the liquid Cd cathode of 85 g. Figure 5 shows the liquid Cd cathode just after the electrodeposition.

Figure 5. **Pu deposit in liquid Cd cathode (~5 g)**



The deposit was easily removed from LCC crucible as shown in Figure 6.

Figure 6. Recovered Cd-Pu ingot and AlN crucible



In the next step, unirradiated U-Pu-Zr metal alloy fuels will be charged in the anode basket. Plutonium recovery into liquid Cd cathode will be performed after several fuel treatments to recover only U onto solid iron cathodes. FP simulating elements such as lanthanides will next be added to the system, and electrorefining of U-Pu-MAs-REs-Zr will be performed to simulate the processing of irradiated metal alloy fuel. The TRU recovery into the liquid Cd cathode will then be carried out after U recovery on the solid cathode. The cathode products will be analysed to determine the recovery yields and the decontamination factors. The results will provide data on the up to now unknown behaviour of TRUs during electrorefining as well as the operation sequence to maximise the TRU recovery, that will be crucial for the experiments with real irradiated fuel.

## 5. Reductive-extraction process

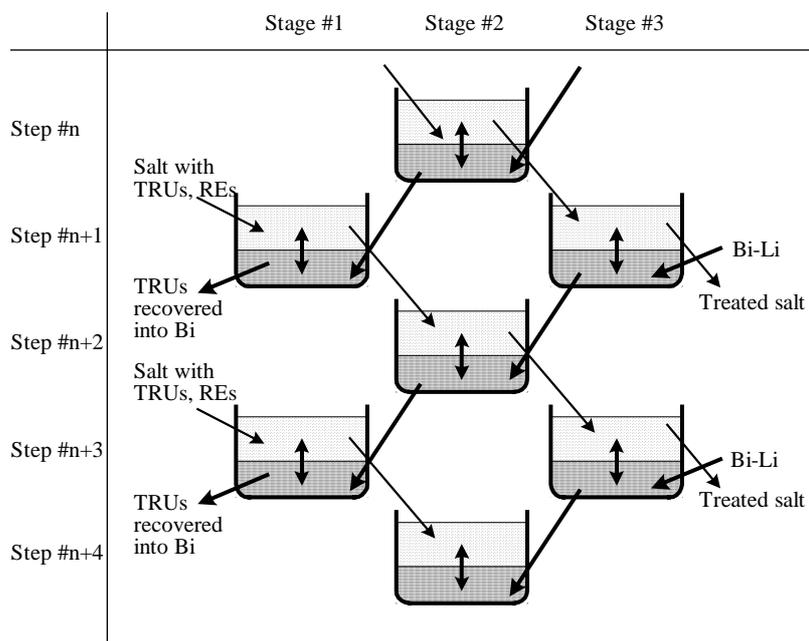
### 5.1 Process description

In the pyro-partitioning process a reductive-extraction technique in LiCl-KCl/Bi or LiCl-KCl/Cd system is the key step for the recovery and separation of actinides. As explained in the former report [8], a multiple batch extraction experiment was successfully carried out with a high recovery yield of TRUs and high separation efficiency between TRUs and FPs. On the other hand, the separation efficiency by means of the countercurrent extraction will be much higher than that by means of the multiple batch extraction. Hence reductive extraction by means of a counter-current batch method should be tested with TRUs. In this joint research, the reductive-extraction experiments will be carried out after the electrorefining experiments.

### 5.2 Preliminary experiments with lanthanides

Before starting experiments using TRUs, the experiment of three stages counter-current extraction was carried out by batch system using REs. Ce, Gd and Y were used as substitution elements for U, Am (TRUs) and Nd (REs), because the relationship of distribution coefficients among these three RE in LiCl-KCl/Bi system were roughly similar to that of U, Am and Nd. Figure 7 shows the schematic flow of the counter-current batch extraction method.

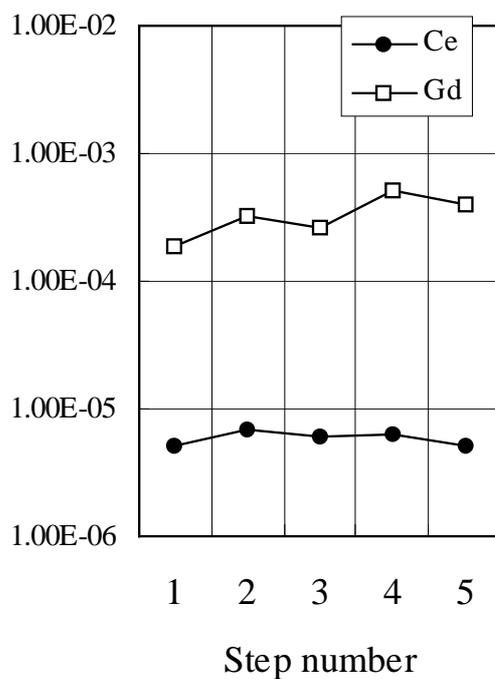
Figure 7. Schematic flow of the countercurrent bath extraction method



An initial salt phase is introduced into stage #1 and recovered as waste from stage #3. The Bi phase with Li is introduced into stage #3 and recovered as product from stage #1.

Figure 8 shows the separation factors of Ce and Gd against Y obtained during three stages at 773K.

Figure 8. Separation factors of Ce and Gd vs. Y



The separation factor (SF(M)) of metal M (Ce or Gd), is defined by:

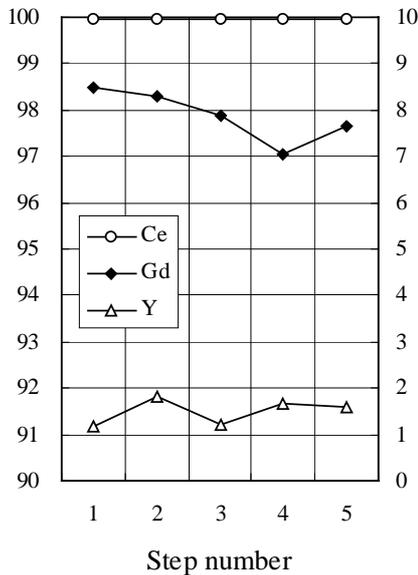
$$SF(M) = \{X(M)/Y(M)\} / \{X(Y)/Y(Y)\}$$

where X(M), X(Y) are the concentrations of  $MCl_3$  and  $YCl_3$  in the salt at stage #3, respectively, and Y(M), Y(Y) are the concentrations of M and Y in Bi at stage #1, respectively.

The separation factors of Ce and Gd vs. Y in the single stage extraction previously measured are  $1.4 \times 10^{-3}$  and  $1.7 \times 10^{-2}$ , respectively [12], while those in the counter-current stages obtained here were given as  $5.9 \times 10^{-6}$  and  $3.4 \times 10^{-4}$ , showing far better separation between TRUs and REs.

Figure 9 shows the recovery yield of each RE.

Figure 9. Recovery yields of Ce, Gd and Y



The recovery yield (RCM) of metal M (Ce, Gd or Y), is defined by:

$$R(M) = W_{1,Bi}(M) / \{W_{1,Bi}(M) + W_{3,Salt}(M)\}$$

where  $W_{1,Bi}(M)$  is the amount of M recovered in Bi at stage #1 and  $W_{3,Salt}(M)$  is the amount of M recovered in salt at stage #3.

The obtained recovery yields R for Ce, Gd and Y were >99.9%, 98% and <2%, respectively. These values agreed well with the target values (>99.9%, >99% and <10%, respectively) [8], suggesting the applicability of a counter-current batch method. The recovery yield of Gd can easily be increased to more than 99% by adding a surplus amount of the reductant, because the obtained separation factor for Gd/Y is much higher than the criterion of partitioning.

## 6. Conclusions

A new joint study on pyrometallurgical processing between CRIEPI and JRC-ITU has successfully started. This study will demonstrate the capability of this type of process to separate

actinide elements from spent (metallic) fuel and HLW and should provide important data in view of a rational selection of future nuclear options.

A successful installation of the equipment in a new experimental set-up was achieved at JRC-ITU. Electrorefining tests on U and Pu using solid cathodes and a liquid Cd cathode prove the operational capabilities of the facility. The next experiments will be on electrorefining of unirradiated metallic U, Pu, Zr fuels containing MA and REs.

Furthermore reductive extraction of TRUs from molten salt will be demonstrated in counter-current batch extraction systems developed in CRIEPI. The preliminary experiments using Ce, Gd and Y as stand-in elements for U and Am showed good separation efficiency from REs (Nd) in 3 batch extraction stages.

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