

Pyrochemical Separation at CEA : Current Results and Future R&D Program

J. Lacquement¹, S. Bourg¹, H. Boussier¹, O. Conocar¹, C. Hamel¹, A. Laplace¹,
C. Maillard², L. Donnet² and J. Duhamet³

CEA/VRH/DEN/DRCP/SCPS/LPP¹
CEA/VRH/DEN/DRCP/SEAA/LEMA²
CEA/VRH/DEN/DTEC/STCF/LGCI³

BP17171, Bagnols-sur-Cèze, France, 30207
jerome.lacquement@cea.fr

Abstract - R&D studies are conducted at CEA/DEN to assess the potentialities of the pyrochemical processes which could be an advantageous alternative to hydrometallurgy for the reprocessing of: (i) targets as well as dedicated fuels for M.A transmutation if multiple recycling is considered, (ii) Generation IV gas cooled reactors. This paper gives an overview of the major experiments performed either in molten fluorides or chlorides.

INTRODUCTION

In France separation processes of radionuclides found in spent nuclear fuel are essentially based on hydrometallurgy. Both the operating experience at La Hague and the separation performances made the aqueous processes been the reference route either for the reprocessing of current spent nuclear fuel (PUREX process) or for the recovery of long-lived radionuclides coming from high-level waste in the future Partitioning & Transmutation scenarios (French legislative act of Dec. 91 on the management of nuclear waste).

For mid and long-term strategies, innovative fuels and the associated recycling technology will have to take up new challenges with very ambitious requirements compared to the current ones. It will be notably required: (i) to have a grouped recycling of all the actinides, (ii) to reprocess fuels having both high burn-up & the shortest cooling time for minimizing the actinide balance outside the reactor, (iii) to re-fabricate the fuel on-site just after reprocessing for avoiding nuclear material transportation, (iv) to treat nuclear objects with highly refractory ceramics used for ensuring a high level confinement of fission products.

Face to these new requirements, hydrometallurgy may not be adequate especially because of the high activity and specific nature of the material. Conversely pyrometallurgical processes – developed in the past in order to achieve rapid &

economic recycle of high burn-up reactor fuels [1]– have known (or presumed) advantages that may make them suitable for such challenges. The more promising ones are: the perspective of processing high TRU content fuels with a short cooling time (criticality constraints less restrictive, no sensitivity to radiolytic degradation), equipment compactness, potential flexibility in relation with different fuel compositions and the ability to treat refractory materials.

At the Nuclear Energy Direction of the French Atomic Energy Commission (hereafter CEA/DEN), research & development studies are conducted for providing a general overview of the potentialities of the pyrochemical processes with regard to various assessment criteria (separation performance, chemical engineering, operating conditions, waste treatment) and covering the largest possible number of applications [2].

Up to 2005 the studies are mainly devoted to lab-scale research and the works are focused to the evaluation of separation performances of the classical non aqueous separation techniques for the above-mentioned requirements, especially the grouped actinide recovery with sufficient fission products removal. Basic investigations on actinides and fission products chemistry in non aqueous media are carried out partly with CNRS laboratories, partly with PARIS and GEDEPEON French research groups. Separation techniques are both assessed and consolidated in CEA laboratories (Marcoule facilities) and

through collaborations with foreign partners or institutes : Europe (PYROREP partners), Russia (RIAR, Dimitrovgrad), USA (ANL) and Japan.

CEA/DEN currently foresees two possible applications of pyrometallurgy: (i) the reprocessing of targets or dedicated fuels coming from minor actinide transmutation if multiple recycling is necessary, (ii) the reprocessing of Generation IV gas cooled reactors. By 2006, a more comprehensive development program could be launched if the preliminary results obtained at lab-scale on separation efficiencies are promising. This paper gives an overview of the major experiments performed in the frame of this R&D program, either in molten fluorides and chlorides.

FRONT-HEAD INVESTIGATIONS

In Gen IV gas cooled reactor there will be no secondary cooling loop in order to gain in overall energy yield. Thus the fuel will have to exhibit very high level of radionuclides confinement and highly refractory ceramics are proposed to ensure that confinement. The choice of these latter depends on the nature of the future fuel (carbide or nitride); but some candidates have been already proposed : SiC, ZrC, TiN and ZrN.

The front-head operations of the future reprocessing scheme will also depend on the fuel design. Maybe it will be necessary to remove the ceramic coating in order to reach the fuel core. Investigations are carried out at lab-scale in that frame either by chemical or electrochemical methods; the goal is to convert the ceramic into volatile and/or gaseous products. Experiments are performed in gas phase o/w in molten chlorides (see Figure 1).

Gas Phase Conversion

SiC powder is effectively attacked by chlorine gas at 950°C producing volatile SiCl_4 and residual carbon. A complementary step using pure oxygen converts that amorphous black powder into gaseous carbon oxide. Very promising results have been reached by treating small particles (ZrO_2 surrounded by inner graphite and outer silicon carbide layers) in this manner: the two successive layers have been entirely converted into gaseous products and the zirconium oxide core uncovered. Such a

treatment could be applied to VHTR particle fuel pre-treatment.



Figure 1: Lab-scale chlorinator in molten chloride bath.

Comparable attacks have been tested in molten KCl but are not conclusive yet for the carbon management. Further parametric investigations are in progress in order to overcome this phenomena.

As for nitrides (TiN, ZrN), they are converted into volatile tetrachloride and nitrogen gas by using chlorine both in gas phase and in molten chloride. The conversion is faster in the former case than in the latter.

Electrochemical Dissolution in Molten Salts

First attempts of electrochemical dissolution of SiC samples in molten chlorides have been unsuccessful due to the very low electrical conductivity of the tested samples. Even if the electrical conductivity is increasing with respect to temperature it remains ten to one hundred thousand times as less conductive than a conductor even at 800°C. On the other hand, TiN electrochemical dissolution is effective and can be enhanced by chlorine sparging.

SEPARATION INVESTIGATIONS

Bibliographical surveys of the many pyroprocesses studied in the past or at present thorough the world show that no demonstration has been done of their ability to quantitatively recover all the actinides even at a level of 99%. The major uncertainties always concern the recovery yield and the separation performances related to all the fission products. CEA/DEN has decided to assess his own innovative concept (reductive extraction in molten fluoride/liquid aluminum alloy system) and to go on the evaluation of the other concepts proposed and developed abroad; these latter evaluations are made through international collaborations.

Reductive Extraction in Molten Fluorides

The principle of Liquid-liquid extraction between molten chlorides and lithium-based alloys proposed for actinides/lanthanides separation could be advantageously transposed to fluoride medium in terms of separation efficiency (An/Ln separation factors) and of waste treatment (e.g. spent fluoride salts could be directly introduced in glass matrix). Based on thermodynamic considerations on An and Ln activity coefficients in liquid metals as well as tests on U/La separation, aluminum was identified as both the most promising reducing agent and solvent for the assigned objectives [3-4].

Thus the distribution coefficients for Pu, Am and Ce between LiF-AlF₃ (85-15 mol%) and Al-Cu (78-22 mol%) at 830°C have been determined with respect to the saline melt fluoroacidity ([2],[5]). They have been recently confirmed from a molten AnF₃-LnF₃-LiF-AlF₃ mixture where {AnF₃+LnF₃} loading was 15wt%. Using the above-mentioned Al-Cu alloy (initial melt/alloy weight ratio ~1, Pu/Ln ~3), the results are:

- the distribution coefficients for Pu and Am are 197+/-30 and 144+/-20 respectively,
- the recovery yields for both Pu and Am are about 98.5 wt% in one contact,
- separation factors : $S_{Pu/Ce} = 1307+/-308$, $S_{Pu/Sm} = 3177+/-760$, $S_{Pu/Eu} > 15,000$ and $S_{Pu/La} > 3,000$,

The test is very promising for it shows that the extractive and separative efficiencies are not affected even when the initial {AnF₃+LnF₃} loading in melt is high (15 wt%). As for lanthanides whose oxidation state (II) is stable in fluorides (here Sm and Eu), they are reduced from Ln(III) to Ln(II) but little extracted. Figure 2 presents salt before & after equilibrium. At final state (right), the salt shows a brownish purple colour being distinctive of SmF₂ and EuF₂ species.

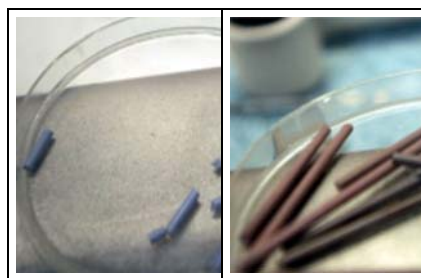


Figure 2. Saline samples before (left) and after (right) salt/metal extraction.

Complementary investigations on Cm behaviour are needed and new experiments are planned for determining if (Pu+Am+Cm) can be co-extracted with sufficient lanthanide decontamination. A high temperature liquid-liquid contactor is under construction and should be implemented in shielded cell (Atalante facility) next year. The back extraction of the actinides from Al-Cu alloy is also investigated, firstly by oxidative extraction (e.g. to molten chlorides by using CuCl₂ as oxidant) but alternative methods such as chlorination for aluminum removal by volatilization of its trichloride are also in the scope of the investigations.

Electrolytic Separation

Numerous works have been done on U and Pu electro-recovery on both inert solid cathode and liquid cadmium cathode [6]. For future applications it is necessary to assess electrolytic techniques again in taking into account a grouped recovery of actinides (at least all the TRU elements in a first time). The evaluation has to be completed with experiments on Am, Np, Cm and Np+Pu+Am+Cm mixtures.

The Am(III) electrolytic extraction on liquid cadmium in LiCl-KCl eutectic at 500°C has been assessed at g-scale and its chemical feasibility has been demonstrated last year in Atalante

facility [2]. However the Liquid Cadmium Cathode (LCC) design has to be improved for reaching high current density and recovery yield. Work for its purpose is especially undertaken through international collaborations (European contract, ANL).

In parallel, other experimental media (melt, metallic solvent as liquid cathode) are studied, for a given actinide, in order to increase the selectivity of An/Ln separation. Firstly efforts are made to compare fluoride medium with chloride one. If the standard potentials for actinides and fission products are known in various chloride melts it is not true in molten fluoride melt yet [7].

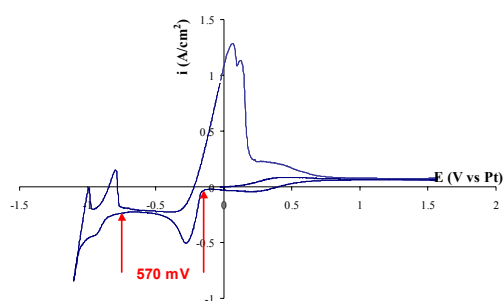


Fig. 3. Cyclic voltammogram in LiF-CaF₂+ UF₄ (1.35 wt%) + U + NdF₃ (0.67 wt%) at 810°C on Mo, $v=0.1$ V/s.

Electrochemical studies in LiF-CaF₂ eutectic at 810°C (Figure 3) show that the melt is promising for U/Ln separation for the equilibrium potential difference (for $i=0$) is about 570 mV; thermodynamically such a difference should allow us to recover more than 99.99 wt% of U without Nd pollution (Neodymium is one the most awkward lanthanide in fluoride melt).

APPLICATION INVESTIGATIONS

Liquid-Liquid Contactor Development

Works started with the study of the flow of fluids with high surface and interfacial tensions which generate capillarity phenomena. They are firstly simulated by room temperature system (gallium/room temperature ionic liquids) in a mock-up prefiguring a high temperature contactor. Preliminary results show that it would be probably not possible to miniaturize as well as

done for high activity hydrometallurgical processes. In parallel, corrosion studies are carried out in dedicated apparatus, especially for molten fluorides.

Physical Properties Data Acquisition

The properties of importance in molten salt applications are the density, the viscosity and the surface and interfacial tensions as previously mentioned. The first one can be obtained by differential pressure measurement. As for the viscosity, it is required to use a rheometer which allows measurements for various speed gradients because the fluids are not Newtonian ones. The major trouble is obviously to adapt the apparatus for temperatures up to 800-900°C.

The measurements of surface and interfacial tensions will be made by methods based on drop detachment; the drop volume is depending on surface tension for gas-liquid system, and on interfacial tension for liquid-liquid system. Experiments have started with room temperature systems and will be adapted for 800-900°C.

CONCLUSION

The impetus for further investigations of the pyroprocesses is renewed at CEA/DEN by ambitious challenges : (i) the reprocessing of irradiated targets or dedicated fuels coming from minor actinides transmutation (if multiple recycling is considered), (ii) the reprocessing of Generation IV fuels.

Lab-scale research is conducted for assessing the performances of these processes for a co-extraction of actinides with sufficient fission product decontamination. Up to 2006 it includes basic research on actinides in molten chlorides and fluorides, exploration of promising options and consolidation of the knowledge of well-known concepts developed abroad. If a right combination (medium and separation technique) is available for the assigned aims, it will lead to the initiation of a more comprehensive development program.

REFERENCES

1. E.E. MOTTA, *Proc. Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, pp. 596-603 (1955).

2. J. LACQUEMENT et al., *Proc. Int. Conf. GLOBAL'03*, New Orleans, pp. 976-80 (2003).
3. F. LEMORT, R. PICCINATO, R. BOEN and M. ALLIBERT, *Proc. 9th Int. Conf. High Temperature Materials Chemistry*, p 307 (1997).
4. L. RAULT,, M. HEUSCH, M. ALLIBERT, F. LEMORT, X. DESCHANEL, R. BOEN, *Nuclear Technology*, **139**, 167 (2002).
5. O. CONOCAR et al., *Journal of Alloys and Compounds*, paper accepted (2004).
6. J. WILLIT, W.E. MILLER and J.E BATTLES, *J. Nucl. Mater.*, **195**, 229-49 (1992).
7. L. MARTINOT, "Molten Salt Chemistry of Actinides", in *Handbook on the Physics and Chemistry of the Actinides*, edited by A.J. Freeman and C. Keller, Elsevier Science Publishers B.V, pp. 241-79 (1991).