

## Pyrochemistry within the FP7 ACSEPT Project-Program and Objective

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**Abstract** – Actinide recycling by partitioning and transmutation is considered as one of the most promising strategies to reduce the inventory of radioactive waste, thus contributing to make nuclear energy sustainable. To make advances beyond the current state of the art in pyrochemical separations processes, the Domain 2 (DM2) of ACSEPT has been built on considering a process approach based on system studied. Four work packages that represent the main steps of a process block diagram have been identified: head-end steps, core process development, and salt treatment for recycling and waste conditioning. The results obtained in this domain will be integrated in DM 3 (Process) in order to orientate the R&D studies of DM2 and to propose and validate flowsheets at the end of the project. The state of the art on pyrochemical separation within the European Community and the working program of ACSEPT in pyrometallurgy are presented in this work.

### INTRODUCTION

In the 50-60s, the development of the Molten Salt Reactor (MSR) and Breeder Reactor concepts led to the development of the associated pyrochemistry in order to treat spent fuels. In the 70s, the selection of the Pressurised Water Reactor concept, associated to the Purex process, was a break point in this development. Today, some experimental spent fuels or some Gen IV reactor fuels might not be compatible with current hydrometallurgical processes. Therefore pyrochemical processes could provide alternative strategies for their treatment.

Indeed, pyrochemical processes are not sensitive to radiolysis, and obviously to temperature effects, and could afford to treat fuels after a short cooling period, even at high concentrations. They are suitable for treatment of highly refractory materials and the wide temperature range amplifies the differences in thermodynamic stability that control the separation factors among compounds. Conversely, the process media are highly aggressive to process equipment. The high reactant melting points result in a risk of fouling of transfer systems and damage to process reactors in the event of an accidental temperature drop. Some of these processes are also difficult to develop for continuous operation, and moreover, technological and process waste requires suitable treatment.

A pyrochemical process includes actually several basic steps: head-end steps, core of process, conversion of final products, decontamination of

process waste for recycling salt and metal fluxes, conditioning of waste materials in accordance with their chemical and radiological properties, decontamination of technological waste and of all process off-gases.

After a presentation of the state-of-the art of the results obtained within the FP5 PYROREP and FP6 EUROAPRT Projects, the work program of the FP7 ACSEPT Project will be described.

### STATE OF THE ART

#### Basic Studies

Transient techniques and e.m.f. measurements were used to determine diffusion coefficients, apparent standard potential, and then some thermodynamic properties.

In chloride media, the electrochemical behaviour of U, Pu, Am, Th [1-4] and Np [5] for actinides and La, Ce, Pr, Y, Nd [6], Gd, Sm and Eu [7-9] for lanthanides as well as Mo and Ru were determined. For each chloride, MCl<sub>x</sub>, the diffusion coefficient, the apparent standard potential of the redox couple, the free energy of formation as well as activity coefficient were determined.

Studies in molten fluoride are much less developed. Despite a lot of experiments were done in various molten salts (LiF-NaF, LiF-NaF-KF, LiF-CaF<sub>2</sub>), no thermodynamic data were really determined with accuracy, particularly because of the difficulty of using a reliable reference electrode. It seems clear now that it is not possible to deposit metal Ln in sodium containing salts.

For actinide-lanthanide separation, either by liquid-liquid reductive extraction or by electrodeposition on a liquid metallic cathode, the separation factor ( $An/Ln$ ) is mainly controlled, for the metallic phase, by the ratio of activity coefficients of actinides and lanthanides in the metal. In order to select the best low melting point metallic solvent for an  $An/Ln$  separation, activity coefficients of  $An$  and  $Ln$  were counted in the literature and a specific method was developed to acquire new ones. Experiments on  $Ce$  and  $Pu$  in  $Ga$  were carried out, assessing that, in the temperature range used, aluminium is better than  $Ga$ ,  $Bi$ ,  $Zn$  for the  $An/Ln$  separation.

### Process development.

Among the various initial core of process, selective precipitation was definitively abandoned. To date, the most promising processes are based on electrorefining on solid aluminium cathode in molten chloride salt and on liquid-liquid reductive extraction in molten fluoride salt/liquid metal [9].

#### *Electrorefining on Solid Aluminium Cathode.*

Demonstration of pyrochemical reprocessing of metallic alloy fuel ( $U_{60}Pu_{20}Zr_{10}Am_{2}Nd_{3.5}Y_{0.5}Ce_{0.5}Gd_{0.5}$ ) has been carried out at ITU by electrorefining onto solid  $Al$  electrodes in  $LiCl-KCl$  at  $460^{\circ}C$ . An excellent grouped separation of actinides from lanthanides ( $An/Ln$  mass ratio in the deposit = 2400) was obtained by keeping the cathodic potential above  $-1.25$  V at  $460^{\circ}C$ ; even in conditions simulating high accumulation of  $Ln$  in the salt (corresponding to a long time of electrorefining). Despite a low concentration of  $Am$  compared to  $Ln$  in the salt phase ( $Gd/Am$  mass ratio in the salt = 10), the electrolysis lead to deposits containing 99.9 wt% of  $An$  and a  $An/Ln$  mass ratio of about 30. The maximum  $An$  loading on  $Al$  cathodes has also been investigated by melting the cathode during electrolyses steps. At the end, 3,72 g of actinides were electrodeposited in 4,17 g of  $Al$ , that represents a yields of 47 wt % of  $An$  in the alloy and a total loading (wt  $An$ / wt  $Al$ ) of 80 %.

#### *Liquid-Liquid Reductive Extraction.*

An experimental device and a protocol have been developed to study the distribution of  $An$  and  $Ln$  in molten fluoride/liquid metal medium. With a salt composition  $LiF - AlF_3$ , 85 -15 mol%, up to 99% of  $Pu$  and  $Am$  could be recovered in a single stage, with  $Ce$  and  $Sm$  separation factors exceeding 250.

The results obtained with individual elements were confirmed by demonstrative experiments in more realistic conditions (Table I). Two runs have been done at  $830^{\circ}C$  with  $LiF-AlF_3$  (85-15 mole%) as salt phase and  $Al-Cu$  alloy (78-22 mole%) and pure  $Al$  as metallic phases to check the influence of  $Cu$  both in term of performances and in term of implementation of the process. For each test, the initial concentrations in the salt were the following (wt%):  $PuF_3$  (11),  $AmF_3$  (0,2),  $CeF_3$  (2,5),  $SmF_3$  (0,5),  $EuF_3$  (0,5) and  $LaF_3$  (0,5). In the test without copper, the distribution coefficient of  $Cm$  (trace concentration in  $Am$  starting material) has been measured for the first time; it is very close to those of other actinides ( $U$ ,  $Np$ ,  $Pu$ ,  $Am$ ). Distribution coefficients of the  $Ln$  are low and allow high separation factors with  $An$ . These tests assess the chemical feasibility of the  $An/Ln$  group separation by liquid-liquid.

Table I.  $An/Ln$  Mass distribution coefficients – Separation factors with  $Am$

Al-Cu (78-22 %mole)			Al		
<i>M</i>	<i>DM</i>	<i>SAm/M</i>	<i>M</i>	<i>DM</i>	<i>SAm/M</i>
$Pu$	197	0.73	$Pu$	273	0.8
$Am$	144	1	$Am$	213	1
			$Cm$	185	1.5
$Ce$	0.42	1014	$Ce$	0.62	1315
$Sm$	0.62	2323	$Sm$	0.44	4954
$Eu$	<0.13	>11000	$Eu$	<0.3	>7100
$La$	<0.6	>2400	$La$	0.3	7100

### Decontamination of Spent Salt for Recycling.

Carbonate or phosphate precipitations and zeolite ion-exchange are considered for salt clean-up. Both processes involve the selective removal of fission product from a molten salt to allow the salt to be recycled or disposed as low level waste.

Several efforts have been addressed to the study of the precipitation of  $Ln$  as oxides or oxychlorides by CIEMAT. Chlorides of other FPs,  $Ru$  and  $Mo$ , have also been investigated. Attempts to obtain oxides and phosphates of alkaline and alkaline earth metals, such as  $Ba$  and  $Sr$ , individually or together, in  $LiCl-KCl$  molten salt have also been performed, however, its precipitation is not possible neither as oxides nor as phosphates. For  $Ln$ , phosphate precipitation, experiments showed ~100% under stoichiometric conditions. The precipitate, however, entrained salt (~70%) which requires removing prior to immobilisation of the phosphate.

NEXIA Solutions performed zeolite ion-exchange experiments with Nd, La, Sr and Rb in LiCl-KCl. The ability of zeolites to act as an immobilisation medium for salts was also tested by occlusion experiments. Results showed a decrease of Sr, Nd and La concentrations in the eutectic salt. Lanthanides have the slowest equilibration time, but the strongest affinity for ion-exchange into the zeolite. A fairly rapid clean-up of Sr was observed, but the partitioning of Rb is weak.

### Salt waste conditioning

Particular attention has been devoted to the synthesis and characterisation of sodalite, to incorporate chloride salt by CEA and ENEA. Two synthesis methods have been studied: the former, which starts from nepheline, the latter, starting from kaolinite or metakaolinite. Pollucite has also been evaluated by ENEA as optimum matrix for containment of Cs.

A preliminary study on the preparation of sodalite  $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$  at atmospheric pressure using hydrothermal-microwave-assisted-synthesis technique lead to crystalline, fine powders of sodalite produced in a short time. The good thermal stability of these sodalites together with water insolubility, are essential properties for confinement of nuclear waste based-halide salts.

The nepheline route was used to try to synthesize LiCl-KCl containing sodalite by initiating a reaction between nepheline, LiCl and KCl in stoichiometric conditions. The reaction product consisted exclusively of sodalite. The possibility of loading fission products (Sr, Ba, Cs and Rb) in the sodalite structure was also evaluated under the same conditions. The resulting powder appeared to consist mainly of sodalite. The XRD characterizations demonstrate that Cs and Rb do not enter into the sodalite structure. The main conclusions of this work are that 1) pollucite is an excellent matrix for containment of Cs, 2) its hydrothermal synthesis does not present any significant problem and the product obtained can withstand pellettisation, 3) synthetic pollucite is resistant to high temperature ( $T_{\text{max}} 1250^\circ\text{C}$ ), and stable under critical thermal conditions, 4) the leachability is very low, even for calcinated samples.

### System studies

To date, the development of pyrochemical separation technologies suitable for advanced reprocessing of spent fuel is still mainly at the basic laboratory level. Therefore, the definition

of general fuel cycle scenarios defining the role and position of individual pyrochemical partitioning technologies is necessary, particularly for the further aiming of present-day experimental research.

Two basic P&T concepts corresponding to two scenarios were studied by individual partners, supplemented by approaches done at ENEA concerning the pyrochemical reprocessing of spent fuel from the US Integral Fast Reactor.

The first scenario is the Double Strata scenario with ADS in the second stratum. This concept, evaluated by CEA, considers the exclusive use of current and advanced hydrometallurgical technologies in the first stratum and the use of pyrochemical technologies for the advanced reprocessing of ADS spent fuel in second stratum. The second concept, evaluated by NRI considers the use of Molten-Salt Transmutation Reactor (MSTR) as the final transmuter. Design of flowsheets, complemented by calculation of main mass fluxes, represents a fundamental criterion for mutual comparison. Flowsheets represent also one of the main outputs of process system studies and purveys the decisive information for process feasibility studies and for final process design.

## ACSEPT WORKING PROGRAMME

### Head-end Steps

This Work Package foresees to link the fuel and the potential separation core processes through head-end processes. As far as fuel dissolution is concerned, a lot of data are already available in chloride but very few in fluoride media. Some efforts will then be put on this later part. The electrorefining process is dedicated to metallic fuels. In a double strata concept, it could be of interest to go from an oxide fuel to a metallic one to make the link between the two strata. Then direct electroreduction from oxide to metal will be studied in correlation with worldwide studies to acquire a European experience. To enhance core of process performances and to simplify the further salt purification step, it could be efficient to remove as much volatile fission products as possible prior to the core of process step, by an appropriate thermal treatment. It is envisaged to run these experiments on irradiated fuels.

### Core of the Process Development

Former studies on core of process pointed out some important ancillary steps to be

assessed. First, the electrorefining process needs a further exhaustive electrolysis to increase and guarantee the overall actinide recovery yield. In particular, the recovery yield of Curium together with the other actinides must be clearly evaluated. In parallel, another objective is to recover pure actinides from the metallic aluminium phase, which is a common step for the two reference processes. In addition, the development of alternative electrochemical processes in fluoride media will be explored with the aim to suggest a proper chemical system in which the feasibility of An separation can be demonstrated. The work on liquid-liquid reductive extraction performances in molten chloride will be finalized.

### Salt Treatment for Recycling

The pyrochemical treatment of spent nuclear fuel must aim to produce as little waste as possible in order to demonstrate industrial feasibility. Carbonate or phosphate precipitation was demonstrated to be efficient to remove rare earth elements in molten chloride but leads to an increase of the volume of the salt loop, and consequently requires a bleed-off increasing the volume of waste. Some studies will then be carried out to find gaseous reagents which do not increase the volume of the loop. In parallel, alternative decontamination processes based either on electrochemical methods or on filtration on zeolite or zeolite like materials will be developed. Attention will also be paid to fluoride salt decontamination where few data are available.

### Waste conditioning

This work package foresees to assess confinement matrices suitable for conditioning chloride and fluoride, and metallic waste issued from pyroprocess, with the aim at minimizing the waste volume and coupling with the criteria for storage and disposal. A definitive answer will be given on the potentiality of the Li, K sodalite as a confinement matrix (relatively to sintering and leaching properties). Then the same work will be done on chloroapatite. The specific case of the confinement of metallic fission products recovered either in salt or metal phases will be studied. Attention will also be paid to matrix process development such HIP or cold crucible technologies either on chloride or fluoride waste.

### Conceptual studies.

If down selection of processes and narrowing of flowsheet options is important, no issue should

be ignored and process options will remain open unless showstoppers were identified in terms of process industrialisation. International collaboration and cross-fertilisation of nuclear and non nuclear industries will be initiated so that the engineering constraints can be accounted for early.

### Science and Engineering Integration

Some aspects of process operation and online monitoring in molten salts will be addressed. In molten salts, also, corrosion issues are of a great importance. Analyses tools for corrosion as well as material behaviour will be studied.

### CONCLUSIONS

Based on pyrochemical separation results obtained during the FP5 PYROREP and FP6 EUROPART projects, a new European Project has been built. Four work packages, going from head-end steps to waste conditioning, have been identified. Close links with DM3, process, are expected to be achieved in order to make advances towards a possible industrialization of a pyrochemical separation process.

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