Developments in fabrication of annular MOX fuel pellet for Indian fast reactor

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Abstract

Mechanical rotary presses along with adoption of core rod feature were inducted for fabrication of intricate annular Mixed Oxide (MOX) pellets for Prototype Fast Breeder Reactor (PFBR). In the existing tooling, bottom plungers contain core rod whereas top plungers contain a central hole for the entry of core rod during compaction. Frequent manual clean up of top plungers after few operations were required due to settling of powder in the annular hole of top plungers during compaction. Delay in cleaning can also result in breakage of tooling apart from increase in the dose to extremities of personnel. New design of tooling has been introduced to clean up the top plungers online during the operation of rotary press. It leads to increase in the productivity, reduces the spillage of valuable nuclear material and also reduces man-rem to operators significantly. The present paper describes the modification in tooling design and compaction sequence established for online cleaning of top plungers.

1. Introduction

Indian Nuclear Power Programme is based on closed nuclear fuel cycle for efficient utilization of its nuclear resources. This strategy also enables waste classification and minimizes long-lived waste disposal problem. The three stage nuclear programmes envisage indigenous PHWRs in the first stage, Fast Breeder Reactors in the second stage and thorium utilization in the third stage. Fast reactors are essential for India not only for its contribution to nuclear power but for extension of its modest resources. Commissioning of Fast Breeder Test Reactor (FBTR) at Kalpakkam represents our first attempt in this direction. FBTR was fuelled with Mark I mixed carbide fuel of composition $(U_{0.3},Pu_{0.7})C$ for the initial core which was followed by Mark II fuel of $(U_{0.45},Pu_{0.55})C$ for the extended core. The mixed carbide fuel has performed exceedingly well and its burn-up has exceeded 1, 00,000 MWd/Te without any fuel failure.

(U-Pu) MOX fuel was selected as the driver fuel for our Prototype Fast Breeder Reactor (PFBR-500) because of our good technology base for (U, Pu) MOX fuel manufacture for thermal reactors as well as industrial scale reprocessing experience with oxide fuels of PHWRs. The world-wide experience also indicates (U, Pu) MOX fuel has high burn-up potential, excellent safety response and overall acceptability at a higher level in all parts the fuel cycle.

Advanced Fuel Fabrication Facility (AFFF), BARC, Tarapur has been fabricating MOX fuel of various type for thermal and fast reactors such as Boiling Water Reactors (BWRs), Pressurised Heavy Water Reactors (PHWRs) and Fast Breeder Test Reactor (FBTR). Presently, AFFF has taken up responsibility for fabrication of annular MOX fuel for first core of Prototype Fast Breeder Reactor (PFBR). The MOX fuel is being fabricated through powder metallurgical route involving cold compaction and sintering. Annular MOX fuel pellets of two compositions i.e. 21% and 28% PuO_2 are being fabricated for PFBR. A large number of $(U, Pu)O_2$ MOX pellets have to be fabricated for the first core of PFBR.

The fabrication of MOX fuel is carried out in α-leak tight glove boxes line to comply with safety requirements. It creates lot of constraints like space restriction, accessibility, maintainability and handling of material during the fabrication of plutonium based mixed oxide fuel. Hence, consideration of all aspects is required prior to selection of equipment [1]. Fabrication of annular MOX pellets with outer diameter 5.55 mm and annuls of about 1.8 mm with inner diametrical tolerance of less than $\pm$ 0.20 mm without grinding an inner surface is a challenging task. Fabrication of annular pellet demands incorporation of additional tooling i.e. core rod assembly that provides relative motion with respect to bottom plunger. Initially, hydraulic press was inducted with modified tooling for fabrication of intricate annular pellet [2]. The major restrictions in using hydraulic press for final compaction of annular PFBR MOX pellet was complex tooling design due to requirement of core rod, complicated tool changing and maintenance. Hence, it is generally preferred to adopt a press having easy core rod adoption facility. Rotary press has been inducted for final compaction of MOX pellet over hydraulic press due its high rate of production, simple design of tooling, easy way of tool changing, easy adoption of core rod feature and no chance of Oil leakage.

This paper deals with technology developed for fabrication of annular MOX pellet. It also describes modification carried out in tooling design and compaction sequence established for instantaneous online cleaning of top plunger during operation of rotary press.

2. Fabrication

The flowsheet for fabrication of MOX fuel fabrication along with the quality control checks at different process steps is shown in Fig. 1. Uranium dioxide and plutonium dioxide powder along with organic binder as Polyethylene Glycol and lubricant as Oleic acid were first weighed and then milled together in an indigenously developed attritor to get the required enrichment and homogeneity. Proper choice of binder and lubricant has a considerable significance in achieving desired specification of pellets [3-5]. The milled material was pre-compacted and the pre-compacts were granulated in the size range of 500-1200 µm. These granules were used in final compaction to make the green pellets. Final compaction of MOX annular pellets was carried out in a rotary press. Sintering of green pellets was done in a batch type resistance heating furnace under reducing atmosphere (mixed N_2-7% H_2 gas) at 1600^oC for 4-6 h. Oversize pellets were ground to acceptable size by a dry centerless grinder. Physical and chemical specifications of sintered pellets for PFBR are given in Table 1. The inspected pellets were loaded into clad tubes for encapsulation.

Table 1 Physical and Chemical Specification of PFBR MOX fuel.

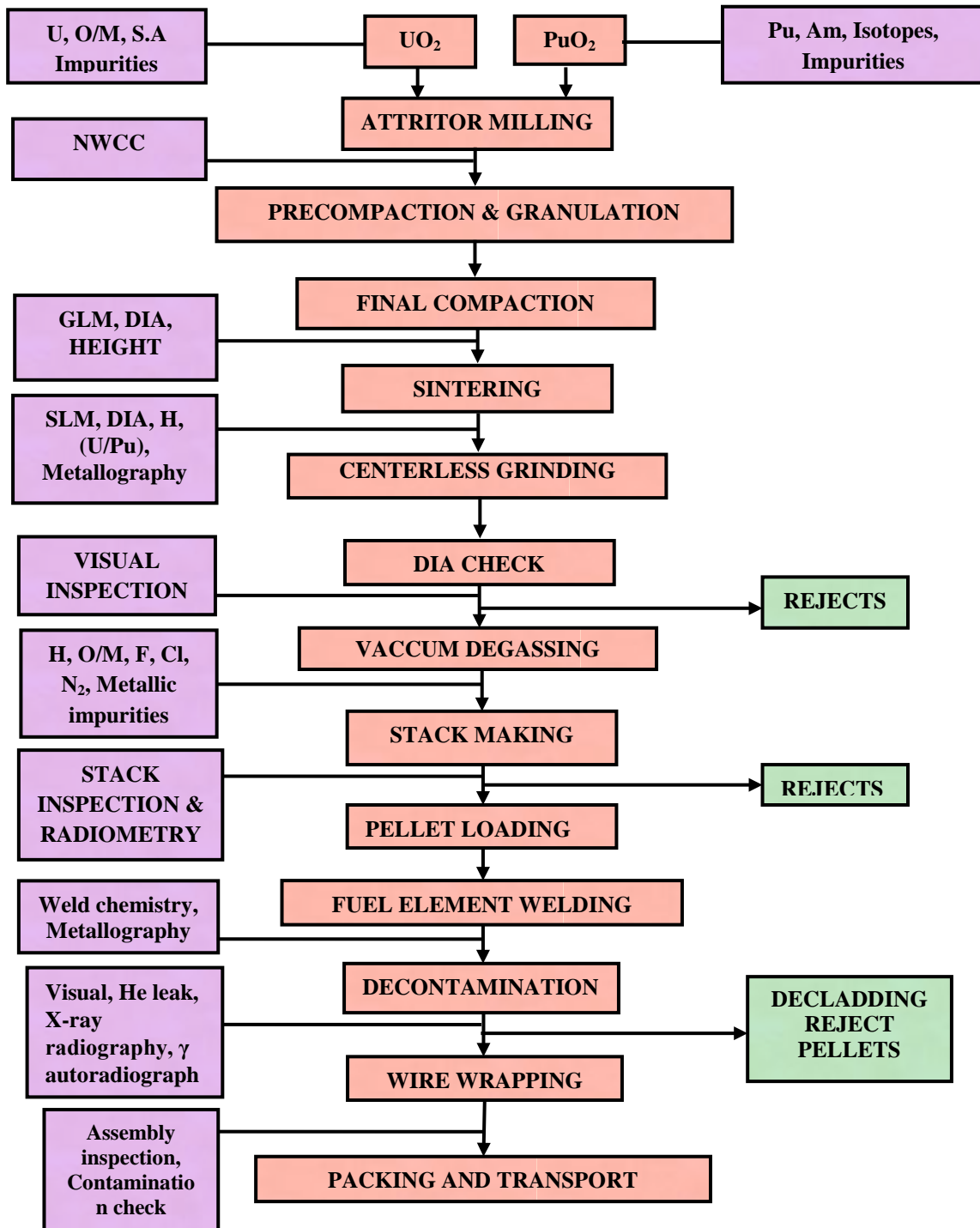|	
Outer Diameter of pellet	5.55 ± 0.05 mm
Inner diameter of pellet	1.8 ± 0.2 mm
Length of pellet	7.0 mm (nominal)
Linear Mass of pellet	2.25 ± 0.15 g/cm
PuO_2 enrichment (nominal)	$21 \pm 1\%$ & $28 \pm 1\%$
Equivalent Hydrogen Content	< 3 ppm
Total Concentration of Impurities	< 5000 ppm

Fig.1 Flowsheet for fabrication of MOX fuel.

3. Annular pellet fabrication technique for PFBR

Depending on the feed material, die fill, final compact shape and dimension, compacting pressure, the type of press, the tooling is designed. Various techniques for the fabrication of annular pellet and the sequence of operation are available in literature [6].

Technology for fabrication of annular pellet using indigenous rotary press has been developed at Advanced Fuel Fabrication Facility (AFFF). Annular pellet fabrication demands incorporation of additional tooling i.e. core rod assembly that provides relative motion with respect to bottom plunger as compared to solid pellet fabrication. Core rod assembly is consists of core rod and core rod holder. Core rod is prone to failure due to misalignment or incomplete die filling, which causes eccentric loading. It is also subjected to wear during the operation. Hence proper selection of core rod material should be done to increase the life of the tooling. The core rod with sufficient toughness can be used to overcome the non-uniform stresses developed during compaction and should also be capable of resisting the ejection loads imposed. Core rod dimension play vital role in achieving inner diameter specification, since it is not easy grind inner surface of an annular pellet.

3.1 Constraint during fabrication of PFBR annular pellets

1. All the fabrication steps had to be carried out in the gloves boxes.
2. Existing facilities and equipment like press without core rod facility etc. had to be used.
3. Fabrication of pellets with small annulus annuls of about 1.8 mm with inner diametrical tolerance of less than $\pm$ 0.20 mm without grinding an inner surface.

4. Experimental

4.1 Granules preparation

Uranium dioxide and plutonium dioxide powder along with Polyethylene Glycol and Oleic acid were first weighed and then milled together in attritor. Milled MOX powder was precompacted at 120 MPa. The precompact so obtained were granulated in oscillatory granulator.

4.2 Annular pellets from rotary press

The granules were final compacted in rotary press at 300 MPa. Initially, experiments were carried out with tooling design having core rod feature in bottom plunger along with central hole in top plunger. Subsequently trials were conducted using MOX granules with modified top plungers in rotary press so as to fabricate PFBR size annular pellets. Experiments with modified tooling experiments were carried out for optimizing tooling size and height of the core rod. Compaction sequence of the rotary press using modified tooling was also established. The final compacted pellets were sintered at 1600°C for 4 h in reducing atmosphere N_2-7% H_2.

5. Result and discussion

The PFBR annular pellets fabricated using modified tooling were free from defects and met desired specification. The results of PFBR annular pellets fabricated in rotary press are given in Table 2.

Table 2: Details of sintered annular MOX pellets

| Sr. NO	Mass (gm)	Av. OD (mm)	ID (mm)	Height (mm)	SLM (g/cm)	Sintered density (g/cc)
1	1.585	5.514	1.65	7.052	2.24	10.34
2	1.611	5.541	1.63	7.129	2.25	10.27
3	1.674	5.551	1.60	7.014	2.34	10.76
4	1.627	5.550	1.61	6.965	2.33	10.54
5	1.594	5.570	1.67	6.941	2.30	10.36

5.1 Tooling design for fabrication of annular pellets

Initially tooling of rotary press used for the fabrication of PFBR annular fuel pellets consist of bottom plungers containing core rod along with top plungers having central hole for the entry of core rod during compaction of powder. The tooling of rotary press used for the compaction of MOX powder to fabricate annular fuel pellets for PFBR is given in Fig. 2.

Top plunger   **Bottom plunger**   **Core rod**
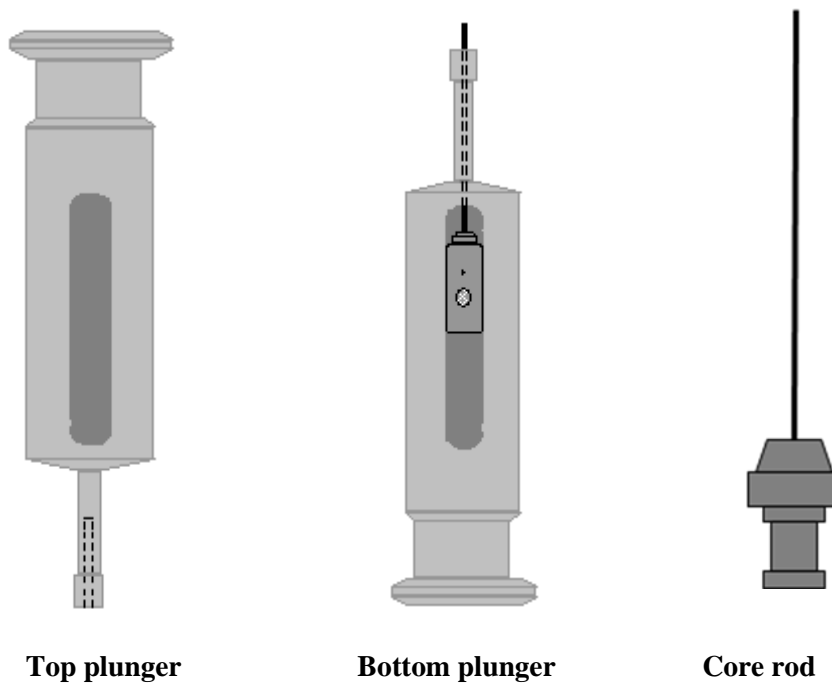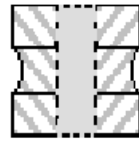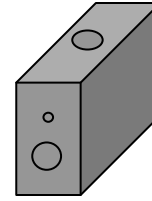
Die   **Core rod holder**

Fig.2 Tooling design for fabrication of annular MOX pellet.

5.2 Problem associated with existing tooling design

In the existing tooling of rotary press used for the fabrication of PFBR annular fuel pellets, a little quantity of powder get settled in the hole of top plungers after few numbers of operations. Frequent manual cleaning of top plunger is required due to settling of powder in annular hole of top plunger during final compaction. Delay in cleaning of top plunger leads to breakage of tooling which further increase man-rem to operator due to increase in maintenance time.

Problems associated with manual cleaning of top plungers
  - Reduces the productivity of the press
  - Increases personnel exposure drastically
  - Increases spillage of valuable strategic nuclear material

5.3 Modification in tooling design

To avoid the problem associated with manual cleaning of top plunger modification in the top plunger were carried by providing core rod, fixing movement of core rod and optimizing height of the core rod.

5.3.1 Adoption of core rod in top plunger

Modified top plunger used in rotary press for final compaction of annular MOX pellets is shown in Fig. 3. Efforts are initiated to clean the top plungers instantaneously by providing a core rod in top plungers. The material and diameter of core rods used in both type of plungers are same. This core rod solves the purpose of top plunger cleaning while top plunger move upward during ejection sequence of rotary press.
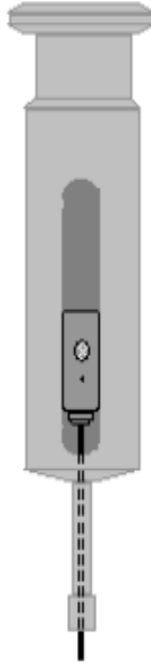
Fig.3 Modified top plunger

5.3.2 Fixing movement of core rod

The compaction sequences established in the rotary press with modified top plungers to fabricate PFBR size annular fuel pellets are given in Fig. 4. The position of core rods in both type of plungers are fixed in such a fashion that they should not interact with each other in any sequence of operation during compaction of powder. The core rod of bottom plungers is flushed with upper platform of the die whereas the core rod of top plungers is 3 to 4 mm projected from the top plungers. The up and down movement of top and bottom plungers are governed by separate cam arrangements. The modified top plungers used in rotary press move downwards during compaction sequence create vacant space in the central portion of top plungers for the easy entry of core rod of bottom plungers. The core rod of top plunger will enter in the vacant space of central portion of top plungers while top plungers move upwards during ejection sequence. This action does the job of instantaneous cleaning of top plungers.
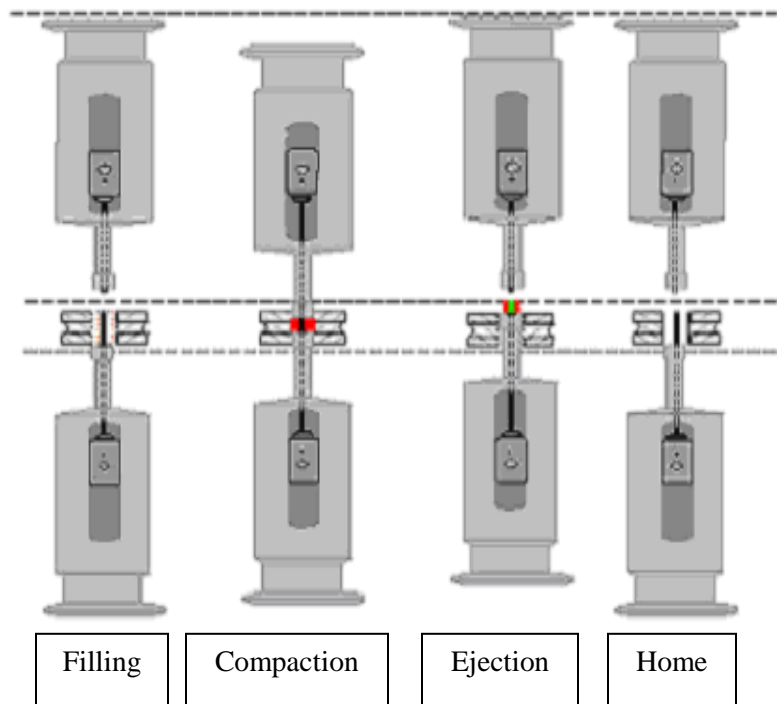
| Filling | Compaction | Ejection | Home |

Fig.4 Compaction sequence in rotary press with modified tooling

5.3.3 Optimizing height of the core rod

The height of core rod and tooling size was decided on the basis of experiments. In this modification, the height of core rod used in top plunger is very crucial. If height of core rod used in top plunger is less then the required, it will come out from the central hole of top plunger during compaction sequence of rotary press resulting in misalignment during ejection sequence of rotary press. If height of core rod used in top plunger is more then the required, it may clash with core rod used in bottom plunger. To circumvent this type of scenario, a number of experiments were carried out to finalise the height of core rod used in top plunger. Height of core rod may vary with different size of tooling sets.

6. Conclusion

Technology has been developed successfully for large scale production of annular MOX pellet. Large quantity of annular MOX pellets meeting desired specification has been fabricated successfully for PFBR using modified tooling in rotary press. Rotary press can be used for continuous production of intricate annular MOX pellet due to easy core rod adoption facility and simplified tooling as compared to hydraulic press.

It has been demonstrated that in the rotary press the cleaning of top plunger is taking place instantaneously after each operation as a result of modification in top plunger. Replacement of manual

cleaning with online cleaning enhances the productivity of the press and reduces man-rem to operators drastically. Moreover, this modification plays key role in reduction of the spillage of valuable strategic material.

Acknowledgement

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TECHNOLOGICAL DEVELOPMENTS IN SAFE AND EFFICIENT FABRICATION OF FAST REACTOR FUEL ELEMENTS

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Abstract.

The Fuel for 500 MWe Prototype Fast Breeder Reactor (PFBR) coming up at Kalpakkam, India consists of Mixed Oxide (MOX) fuel containing PuO_2 and UO_2.The fabrication MOX fuel elements for this reactor core is a challenging task as it involves issues related to radiological safety due to Plutonium handling, radiation exposure concerns and issues like efficient production and quality assurance. This paper deals with the technological developments carried out and their incorporation in the fabrication line to achieve higher throughput with low man-rem consumption. Vibratory bowl and linear feeders are being utilized for arranging the stack of small size i.e 5.5 mm diameter pellets and loading the stack inside the clad tube. Inactive bottom end plug welding has been successfully implementd using laser welding technique. The top end plug welding is carried out inside specially designed chamber in a glove box using TIG welding technique. The top end plug welding by laser welding technique has been demostrated successfully and is going to be implemented shortly. Ultrasonic and laser decontamination techniques have been used to reduce transferable contamination on welded fuel pins. Issues related to radiological and criticality safety , safe handling of fuel elements and measures taken for exposure control are also discussed in this paper.

Introduction

The fuel for 500 MWe Prototype Fast Breeder Reactor (PFBR) coming up at Kalpakkam India consists of Mixed Oxide (MOX) fuel containing PuO_2 and UO_2 . Advanced Fuel Fabrication Facility, BARC Tarapur is engaged in fabrication of the above mentioned fuel. The whole reactor core contains 181 subassemblies and each subassembly contains 217 fuel elements. The core has subassemblies of two enrichments (21% & 28% PuO_2) for power flattening . The sketch of the fast reactor fuel element is shown in Figure 1. The detail of the fuel element and subassembly is summarized in Table 1. The fabrication of fuel elements for the whole core is a challenging task. There are issues related to radiological safety and radiation exposure due to plutonium oxide handling. There are also issues related to productivity and quality to be addressed as the fabrication is carried out inside alpha tight glove boxes. Earlier, Advanced Fuel Fabrication Facility has fabricated MOX fuel elements for thermal reactors (BWRs & PHWRs) and have also handled $^{233}UO_2$ and ThO_2 for fabrication of experimental fuel elements for research reactors[1]. The fabrication of fast reactor fuel elements is more complex because of higher percentage of fissile (PuO_2) in the MOX, smaller size of the pellets , huge quantity of pellets to be handled , both axial blanket and MOX core pellets in the same fuel element , lesser tolerances in the fuel assembly. Based on inputs from the past experience and keeping in view the requirement and the issues related to fabrication of fuel elements for Prototype Fast Breeder Reactor a new fabrication line has been designed , installed and commissioned at Advanced Fuel Fabrication Facility[2]. In this paper the layout of the new fabrication line has been discussed. It also describes the technological developments which have been incorporated in this line.
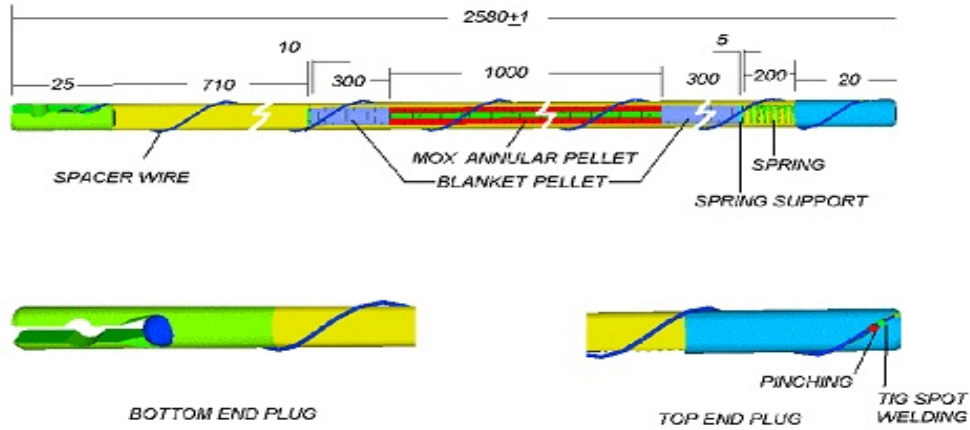
FIG. 1. Sketch of Fast Reactor Fuel Element

Table 1. Details of Fuel Element and Fuel Sub assembly

Material of the clad tube	D9 Stainless Steel
O.D of the clad tube	6.6+/-0.02 mm
Thickness of the clad tube	0.43 mm(min)
Length of clad tube	2650 mm
Diameter of Pellet	5.55 +/- 0.5 mm
Length of Pellet	6 to 8 mm
Number of Pellets in MOX Stack	145 approx.
Number of Pellets in axial blanket Stack	45 approx.
Number of Fuel elements in a sub assembly	217
Number of subassemblies in the core	181
Total Number of Fuel elements in the core	39277
Total Number of Pellets in the core	5695165

Fabrication Flowsheet

The fabrication flow sheet developed for fabrication of PFBR fuel elements is shown in Figure 2. Firstly, degassing of MOX fuel pellets , axial blanket UO_2 pellets and other hardwares is carried out. The hardwares consist of one end welded clad tube, plenum spring, spring support and top end plugs. The degassing of hardwares is an inactive operation. One end welded degassed clad tube is introduced inside the glove box train for loading of MOX pellets, Deeply Dipleated UO_2 $DDUO_2$ pellets and other hardware. The top end plug welding is carried out in the welding station and finally the fuel element is taken out from glove box train after decontamination.
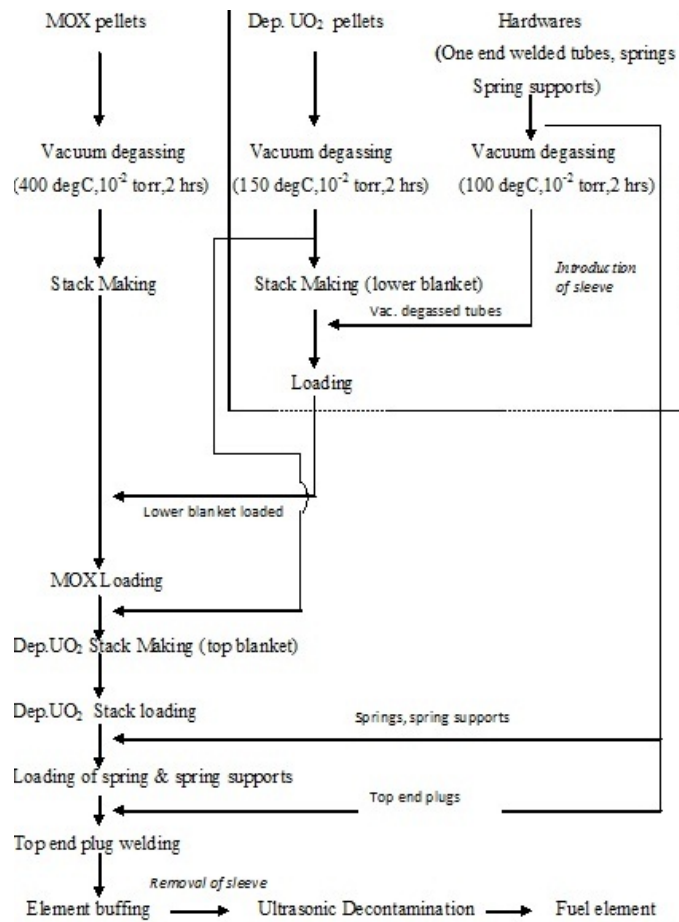

FIG. 2. Fabrication Flow Sheet of MOX Fuel Elements

Layout of the Fabrication Line

Figures 3 and Figure 4 show the top and side views of the layout inside the glove box train. Attached to this train is a specially designed fume hood which is used for loading/unloading of fuel elements from the glove box and ultrasonic decontamination of the fuel elements. The glove box train houses the degassing furnaces for fuel pellets , linear and bowl vibratory feeders for stacking of pellets , stack length measuring device, end plug welding stations, weighing balances. Conveyors are used for movement of fuel pellets and a remotely operated trolley is used for the movement of clad tubes/ fuel elements. A partition in the glove box train separates pellet handling area with tube /element handling area. The fuel element handling area is relatively clean in terms of contamination in comparison to the pellet handling area.
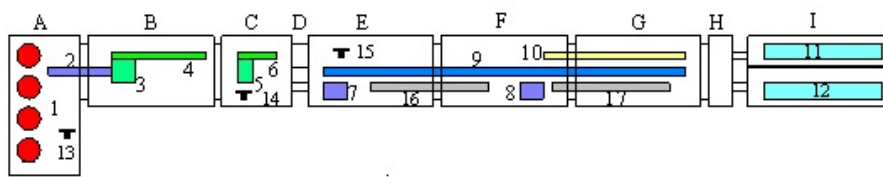
A,B,C,E,F,G and H – Standard Glove Boxes, D –Tunnel, I - Custom made Fumehood

1-Degassing Furnace	10- Element buffing
2-Conveyor	11,12- Ultrasonic cleaning tank
3,5 -Vibratory bowl feeder	13,14,15-Weighing balances
4- Liner feeder for MOX stack	16,17- Element storage
6-Linear feeder for UO$_2$ stack	
7,8- Welding stations	
9- Trolley for tube/element handling	

FIG. 3. Equipment layout in the glove box train for fabrication of PFBR fuel elements.(top)
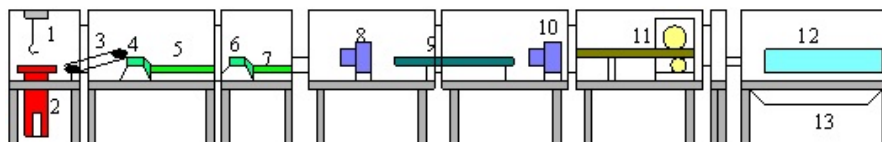
1- Crane	8,10 - Welding station
2- Degassing Furnace	9- Element storage
3- Conveyor	11- Buffing machine
4,6 - Vibratory bowl feeder	12- Element handling unit
5- Linear feeder for MOX stack	13- Ultrasonic cleaning tank
7- Linear feeder for UO$_2$ stack	

FIG. 4. . Equipment layout in the glove box train for fabrication of PFBR fuel elements.(side)

Degassing of Pellets

The degassing of pellets both MOX and DDUO$_2$ is carried out at 200 degrees centigrade in vacuum atmosphere. The furnace for degassing is a resistance heating pit type mounted on the base of the glove box. The furnaces are installed in such a way that the door opens inside the glove box and the body with heating elements, water cooling jacket etc are outside the glove box. A monorail runs above the furnace for loading and unloading of pellet container into the furnaces. For evacuation the furnaces are connected to vacuum pump via a HEPA filter and a diaphragm valve, all connected with flexible stainless steel bellows. The vacuum pump is outside the glove box and the exhaust of the vacuum pump is connected to glove box exhaust line.

Stacking and loading of pellets

After degassing the pellets are fed into the vibratory bowl feeders through a conveyor. The vibratory bowl feeder aligns the pellets in the straight line which are then fed on a vibratory linear feeder. The fuel stack is made in the following way. Both the bowl and linear feeder are switched ON so that pellets move from the bowl to the linear feeder. At one end of the linear feeder a stopper is placed to prevent the movement of the pellets further. Pellets coming from the bowl feeder are collected on the linear feeder till the desired column of the pellets is made. Both the feeder are then switched OFF. Stack length is then measured using a automatic measuring device which consists of a calibrated linear magnetic scale. It is contact type and the probe is made to touch the flat surface of the last pellet of the stack for measurement. The measured stack is then pushed inside the clad tube using vibratory linear feeder. Figure 5 and Figure 6 show the vibratory bowl and linear feeders.
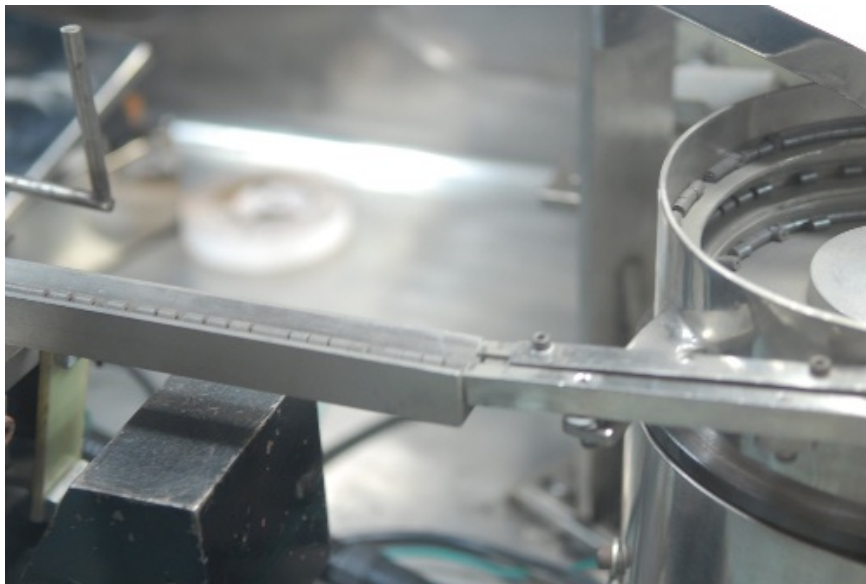

FIG. 5. Vibratory Bowl Feeder

FIG. 6. Vibratory Linear Feeder

End Plug Welding

The clad tube is welded at one end in the inactive condition and then it is introduced inside the glove box for loading of pellets. The end plug weld is carried out using TIG welding process[3]. Recently, Pulsed Laser welding has been successfully introduced in the production line for bottom end plug welds. The main advantages of the Pulsed laser welding process low heat input and consistency in penetration. Figure 7 shows the consistency in penetration in pulsed laser end plug weld. The top end plug weld is carried out in a specially designed welding chamber which is housed in the glove box train. Gas Tungsten arc welding technique is used with helium gas as the inert gas. The welding system has features like automatic loading of end plugs, camera to observe weld joint and the sequence of operation is controlled by programmable logic controller (PLC). The top end plug welding by pulsed laser has been demonstrated successfully and it will be introduced shortly in the fabrication line .The welding chamber which is used for gas tungsten arc welding has been retained for the laser welding . The only modification is replacement of the Tungsten torch with a window which allows the laser beam to enter the welding chamber. Figure 8 shows the scheme of the laser welding being adopted for top end plug welding inside the glove box.
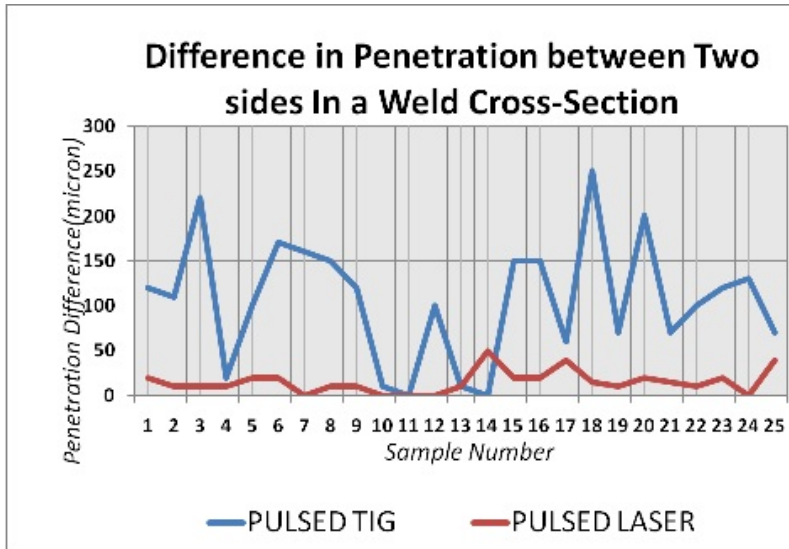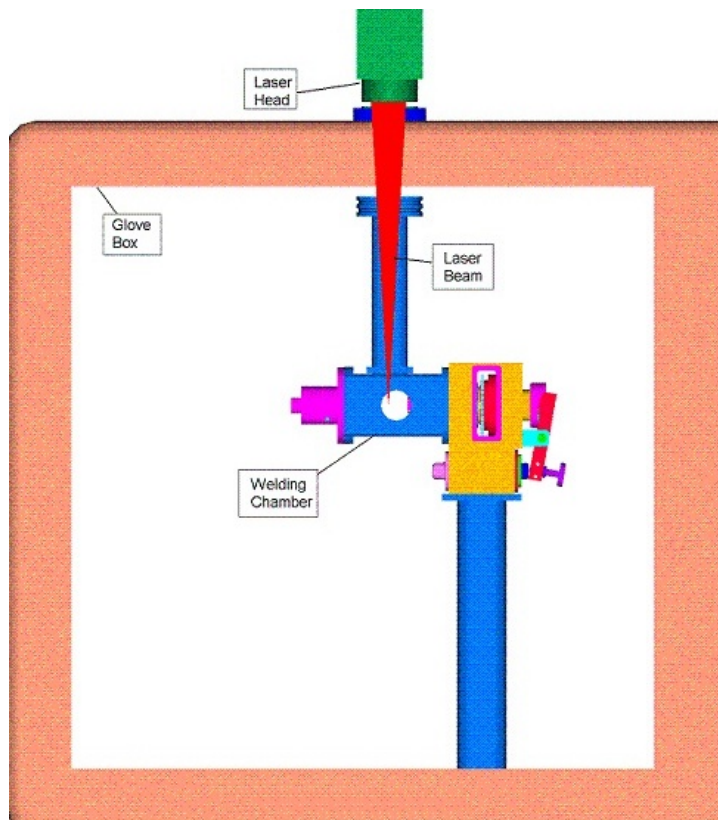
FIG. 7. Pulsed TIG V/S Pulsed Laser

FIG. 8. Scheme for top end plug welding by Laser

Decontamination of MOX Fuel Elements

It is important that finished fuel elements should not contained any transferable contamination on the surface beyond safe limits applicable for unrestricted release as later it moves for inspection. Utmost care is taken to avoid any transferable contamination on the surface of the fuel element. However it is observed that pellet loading and evacuation of the fuel element during top end plug welding results in some cross contamination on the tube surface near the edges.

Decontamination is done to remove loose contamination from the tube surface .It is carried out by using ultrasonic method with de-mineralized water as transfer medium. Recently, decontamination using laser have been successfully introduced in the fabrication line . It is a dry process therefore less secondary waste is generated inside the glove box. Laser assisted decontamination being non contact process minimizes the exposure levels.

Radiological safety

The metallurgical operations for fabrication of MOX fuel elements involve large quantities of plutonium in the form of MOX and are carried out in train of glove boxes. Radiological safety is given top most priority in such operations. Radiological safety surveillance program consists of area monitoring, personal monitoring and environmental monitoring apart from radiological safety related to systems and its operation. All glove boxes are shielded using a composite shield consisting of lead embedded in stainless steel to reduce external radiation exposure at least by a magnitude of 3 in order to minimize personal exposure. Glove ports, bag in /out ports, platforms, panels, floor etc are continuously monitored. All jobs involving bag in / out operations and replacement of gauntlets are given special attention in terms of monitoring of activity. High volume air samplers are used in such cases. All glove box trains are provided with online air sampling points. Installed radiological safety monitors such as plutonium in air monitors, continuous air monitors, area gamma monitors, palm monitors, neutron monitors and criticality monitors provide vital online monitoring of radiological conditions.

All personnel involved in work are monitored for external exposure using TLD, digital personal dosimeters, personal neutron badge. Lead impregnated aprons and gloves are used for reducing personal exposures for jobs such as contact maintenance, decontamination operations and routine jobs involving significant personal exposures. Powered air purifying respirator , full face mask , half face mask, fresh air respirator are widely used for preventing internal exposure for jobs involving potential for activity release. All personnel are subjected to internal monitoring such as lung counting and bio assay periodically for estimation of intake if any.

Criticality safety is implemented by mass control during various metallurgical operations. Total number of fuel elements that can be taken for ultrasonic decontamination is restricted to prevent criticality. Fuel elements are safely stored in a specially designed storage racks where spacing between them is restricted to avoid criticality.

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> **Comment [BU1]:** References are required to be mentioned at appropriate places in the text

Radioactive waste produced from Integral Fast Reactor: Comparisons to Light-Water Reactors

M. Abdel Geleel

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Abstract. The main goal of this study was to compare between radioactive waste that produced from Integral Fast Reactor (IFR) and Light-Water Reactors (LWR). The radioactive waste produced from IFR reactors either have a short halflife, which means that they decay quickly and become relatively safe, or a long halflife, which means that they are only slightly radioactive. The primary argument for pursuing IFR-style technology today is that it provides the best solution to the existing nuclear waste problem because breeder reactors can be fueled from the waste products of existing reactors as well as from the plutonium used in weapons. Depleted uranium (DU) waste can also be used as fuel in IFR reactors. IFR-style reactors produce much less waste than LWR-style reactors, and can even consume other waste as fuel. The total volume of fission products is 1/20th the volume of used fuel produced by a light water plant of the same size, and considered to be waste. 70% of fission products are either stable or have half lives less than one year. Technetium-99 and iodine-129, which constitute 6% of fission products, have very long half lives but can be transmuted to isotopes with very short half lives (15.46 seconds and 12.36 hours) by neutron absorption within a reactor, effectively destroying them. Zirconium-93, another 5% of fission products, could in principle be recycled into fuel-pin cladding, where it doesn't matter that it is radioactive. The remaining high level waste from reprocessing, about 200kg per GWe-yr, is less radiotoxic than mined uranium within 400 years. The radioactivity of the waste decays to levels similar to the original ore in about 200 years.

1. Introduction

Global movements against greenhouse gases have put developed countries in a difficult position, in which they are pressured to reduce greenhouse gas emissions drastically. Yet there are currently few effective alternatives to the cheap sources of electricity: coal and natural gas. Nuclear technology offers the prospect of clean, abundant power for many generations.[1] The International Atomic Energy Agency (IAEA) believes that, to meet the rising demand for emission-free energy, nuclear power will be necessary.[2] If this is case, however, problematic issues do inhibit the growth of nuclear power in the areas of proliferation, safety, and waste management. Any viable nuclear solution must address these issues.While thorium-based fuels present a short-term solution by providing a new source of fuel for nuclear reactors, they ultimately contribute to a major issue for nuclear power: an abundance of hazardous waste. LWRs only use a small portion of the fissile material in their fuel. After it has been fissioned, the material is not reprocessed and is sent to a repository. These once-through cycles employ uranium resources very inefficiently.[3] Initially, PUREX was used to reprocess LWR spent fuel, but in the 1970s, the PUREX process was halted because U.S. experts began to view the plutonium separated during the process as a proliferation threat.[4] Since 1984, one possible solution has been in development in the Argonne National Laboratory: the integral fast reactor (IFR). This reactor possesses the unique ability to recycle its plutonium and LWR fuel until it is fissioned away.[4] The Integral Fast Reactor (IFR) is a fast nuclear power reactor design developed from 1984 to 1994. The design includes both a new reactor and a new nuclear fuel cycle. The reactor is called the Advanced Liquid Metal Reactor (ALMR). The ALMR is a "fast" reactor that is, the chain reactions between fissile materials is maintained by high-energy unmoderated neutrons. The fuel cycle is

distinguished by being closed; meaning that the fuel is produced, the power is generated, the fuel is reprocessed utilizing pyroprocessing, and the waste is managed all on site, reducing the risk of accidents during delivery and the risk of proliferation from theft of the nuclear material.[2]

For the discussion of high-level waste management, it is convenient to categorize the nuclear waste constituents into two parts: fission products comprised of hundreds of various isotopes, and actinides comprised of uranium and the transuranic elements—neptunium, plutonium, ameridum, curium, ate. Fission products are produced by fissioning of heavy atoms, and transuranics are produced as a result of neutron capture reactions.

A fast reactor system with pyroprocess technology is one of the most promising options for electricity generation, with an efficient utilization of uranium resources and a reduction of radioactive wastes[5].

The technologies for the FR cycle can not only achieve dramatically efficient utilization of uranium resources but also burn minor actinides recovered through reprocessing of spent nuclear fuels. The latter can reduce the amount of high level radioactive waste and improve the proliferation resistance. If such FR cycle technology can be available in a safe and economical manner similar to that of light water reactor (LWR) technology, it may contribute to sustainable human development as well as a stable energy supply. Safety and waste are two key factors that influence the public acceptance of nuclear power and, hence, determine the extent to which nuclear power contributes to meet the long-term energy substitution as well as future demand growth.

The aim of this paper was oriented to show the advantage of the IFR radioactive waste production compared with LWR.

2. Integral Fast Reactor

IFR is cooled by liquid sodium or lead and fueled by an alloy of uranium and plutonium. The fuel is contained in steel cladding with liquid sodium filling in the space between the fuel and the cladding. A void above the fuel allows helium and radioactive xenon to be collected safely without significantly increasing pressure inside the fuel element. The IFR's hard neutron spectrum causes all actinides and plutonium isotopes to fission at the same efficiency level. Even at LWR plants that recycle spent fuel, only a few cycles are practical, whereas an IFR can completely destroy plutonium and all the most dangerous radioactive isotopes. The IFR introduces a safer solution that lowers processing costs, fissions plutonium, is completely proliferation resistant, and uses resources efficiently.[6] Pyroprocessing involves a pyrometallurgical and electrochemical process that efficiently recovers actinide elements, while recovering no plutonium. Because no plutonium is separated in the process, the fuel can be considered proliferation resistant.

3. Advantages of IFR

A major advantage of the IFR comes from pyro-processing, a new method of processing fuel developed for the IFR. Pyroprocessing involves a pyrometallurgical and electrochemical process that efficiently recovers actinide elements, while recovering no plutonium. Because no plutonium is separated in the process, the fuel can be considered proliferation resistant. An electrorefiner separates the spent fuel mixture into useful fuel through electrochemical means. Two cathodes are present in the mix; the impure fuel is put on the anode. When a powerful electric current is applied, pure uranium is collected at one cathode and a mix of plutonium, americium, neptunium, curium, uranium, and some rare-earth fission products collect at the other cathode. The other few remaining products remain in the salt solution. This separation process is quite accurate and, through thermodynamics, can be predicted very precisely.[6] During this step, dangerous transuranic isotopes with long-lived radiological toxicity can be dumped in the refinery along with weapons -grade plutonium and actinides recovered from the spent fuel from LWRs.[6] The material that collects at the cathode is then injected into closed-end molds and rapidly cooled. After being capped, the rods are inspected.

The pyroprocessing facility, conceived by the Chemical Technology Division of the Argonne National Laboratory, led by J. J. Laidler, was housed at the same site as the reactor. Their designs made it a completely remote facility requiring no human intervention. Since the plant and its operations are completely contained and isolated in a highly shielded remote facility, it is considerably safer than other plants that utilize reprocessing techniques. Furthermore, this makes the plant even more proliferation resistant.[5] Along the same line of thought, the plant is a "zero-release" plant since everything, including the coolant, is self-contained. This means that there will be no radioactive wastes from corrosion; the only waste released has been processed by the plant. Furthermore, the plant only produces high-level, low volume waste.[6]

A unique and attractive characteristic of IFRs is that they can use spent LWR fuel as fresh fuel after a round of processing. Estimates from J. J. Laider's study predict that approximately 40,000 tons of LWR spent fuel will be in retrievable storage in the U.S.[7] This is a prime fuel source for IFRs. Not only could IFRs employ this as a source, but it also seems necessary for them to do so. Predictions from the 2002 joint study led by C. Rodriguez, sponsored by General Atomics and the Los Alamos National Laboratory, show that the planned Yucca Mountain repository lacks sufficient capacity for all the spent fuel that will have accumulated by the time it is finished. In fact, these researchers believe that the U.S. will need a new Yucca Mountain-sized repository every 20-30 years.[8] One percent of LWR spent fuel contains material that can be used for fuel in IFR reactors and 96% of the spent fuel can be employed as makeup feed to the IFR. Currently, there is enough output from LWRs in the U.S. to provide 1500MWe (Megawatt Electric) of IFR generating capacity annually.[6]

Furthermore, IFRs could be used to reduce the U.S.'s vast plutonium reserves. During the Cold War, many tons of plutonium were produced for warheads that have now been dismantled. Large, scattered stockpiles of plutonium are hard to guard; material not in use is difficult to control and monitor. It is a large proliferation risk, because even hundreds of years after the material has continuously decayed, much of it still remains suitable for weapons.[9] Fast neutron reactors, such as the IFR, can efficiently fission plutonium. In 1997, the US had 1000 tons of plutonium with a growth rate of 70 tons a year. IFRs could be powered on this fuel, reducing the need to guard the plutonium safely and greatly reducing nuclear proliferation risks.[8] According to a study sponsored by the U.S. Department of Energy, performed at Argonne National Laboratory by W. H. Hannum and D. C. Wade, a single IFR would burn through only 50 tons per four years, so this supply could provide an energy source sufficient for many thousands of MWe.[9]

4. Safety

In traditional light water reactors (LWRs) the core must be maintained at a high pressure to keep the water liquid at high temperatures. In contrast, since the IFR is a liquid metal cooled reactor, the core could operate at close to ambient pressure, dramatically reducing the danger of a loss-of-coolant accident. The entire reactor core, heat exchangers and primary cooling pumps are immersed in a pool of liquid sodium or lead, making a loss of primary coolant extremely unlikely. The coolant loops are designed to allow for cooling through natural convection, meaning that in the case of a power loss or unexpected reactor shutdown, the heat from the reactor core would be sufficient to keep the coolant circulating even if the primary cooling pumps were to fail.

The IFR also has passive safety advantages as compared with conventional LWRs. The fuel and cladding are designed such that when they expand due to increased temperatures, more neutrons would be able to escape the core, thus reducing the rate of the fission chain reaction. In other words, an increase in the core temperature will act as a feedback mechanism that decreases the core power. This attribute is known as a negative temperature coefficient of reactivity. Most LWRs also have negative reactivity coefficients; however, in an IFR, this effect is strong enough to stop the reactor from reaching core damage without external action from operators or safety systems. This was demonstrated in a series of safety tests on the prototype.

5. Radioactive Waste

IFRs do need to release waste, but they produce significantly less waste than LWRs and that waste is friendlier to the environment. Most of the released heat comes from fission products with half-lives of 30 years or less, which is much less than that of the spent fuel from LWRs. This difference allows for repositories to be built to lesser specifications. A repository holding IFR waste would only need to house each waste package for a few hundred years versus a repository for LWR waste that would need to store each waste package for hundreds of thousands of years. Furthermore, no proliferation risk is associated with IFR fuel, so security would not need to be as tight. Such shorter holding times also decrease the risk of environmental contamination. Also, because the packages are cooler, they can also be placed closer together, increasing repository capacity.[8] Clearly, IFRs can be part of a much longer-term strategy for U.S. nuclear energy, since they provide a cheap, efficient way to dispose of waste that is proliferation resistant. Ultimately, it appears that the research for IFRs is nearly completed and the only hurdle left is government funding and implementation. Advantages of IFR waste compared with LWR waste are summarized in table 1.

Table 1 Summarize some of the advantages of the waste produced from IFR compared to LWR

	IFR	LWR
Waste	IFR reactors either have a short halflife, which means that they decay quickly and become relatively safe, or a long halflife, which means that they are only slightly radioactive	LWR have both short and long halflife
Waste release	produce significantly less waste	produce more waste
Heat release	released heat comes from fission products with half-lives of 30 years or less	heat comes from spent fuel
Repository	repository holding IFR waste would only need to house each waste package for a few hundred years	repository for LWR waste that would need to store each waste package for hundreds of thousands of years
proliferation risk	no proliferation risk is associated with IFR fuel, so security would not need to be as tight	proliferation risk is associated with LWR fuel, so security would need to be as tight
packages	because the packages are cooler, they can also be placed closer together, increasing repository capacity	can not be placed waste package closer together.

IFR-style reactors produce much less waste than LWR-style reactors, and can even consume other waste as fuel.

The primary argument for pursuing IFR-style technology today is that it provides the best solution to the existing nuclear waste problem because breeder reactors can be fueled from the waste products of existing reactors as well as from the plutonium used in weapons. Depleted uranium (DU) waste can also be used as fuel in IFR reactors.

The waste products of IFR reactors either have a short halflife, which means that they decay quickly and become relatively safe, or a long halflife, which means that they are only slightly radioactive. The total volume of fission products is 1/20th the volume of used fuel produced by a light water plant of the same size, and considered to be waste. 70% of fission products are either stable or have half lives less than one year. Technetium-99 and iodine-129, which constitute 6% of fission products, have very long half lives but can be transmuted to isotopes with very short half lives (15.46 seconds and 12.36 hours) by neutron absorption within a reactor, effectively destroying them. Zirconium-93, another 5% of fission products, could in principle be recycled into fuel-pin cladding, where it doesn't matter that it is radioactive. The remaining high level waste from reprocessing, about 200kg per GWe-yr, is less radiotoxic than mined uranium within 400 years.[10]

Edwin Sayre has estimated that a ton of fission products, reduced to metal, has a market value of $16 million.[11]

The two forms of waste produced, a noble metal form and a ceramic form, contain no plutonium or other actinides. The radioactivity of the waste decays to levels similar to the original ore in about 200 years.[12]

The on-site reprocessing of fuel means that the volume of nuclear waste leaving the plant is tiny compared to LWR spent fuel.[13] In fact, in the U.S. most spent LWR fuel has remained in storage at the reactor site instead of being transported for reprocessing or placement in a geological repository. The smaller volumes of high level waste from reprocessing could stay at reactor sites for some time, but are intensely radioactive from medium-lived fission products and need to be stored securely. Repository capacity is constrained not by volume but by heat generation, and heat generation from medium-lived fission products is about the same per unit power from any kind of fission reactor, limiting early repository emplacement.

"Despite the million-fold reduction in radiotoxicity offered by this scheme,[14] some believe that actinide removal would offer few if any significant advantages for disposal in a geologic repository because some of the fission product nuclides of greatest concern in scenarios such as groundwater leaching actually have longer half-lives than the radioactive actinides. These concerns do not consider the plan to store such materials in insoluble Synroc, and do not measure hazards in proportion to those from natural sources such as medical x-rays, cosmic rays, or natural radioactive rocks (such as granite). These persons are concerned with radioactive fission products such as technetium-99, iodine-129, and cesium-135 with half-lives between 213,000 and 15.7 million years.[15]

6. Conclusion

From this study we concluded that:

- The IFR has passive safety advantages as compared with conventional LWRs.

- IFR-style reactors produce much less waste than LWR-style reactors, and can even consume other waste as fuel.

- A unique and attractive characteristic of IFRs is that they can use spent LWR fuel as fresh fuel after a round of processing.

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Transmutation in ASTRID

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Abstract. Within the scope of the French Act of 28 June 2006 on managing long-lived radioactive waste, one of the objectives of the ASTRID (Advanced Sodium Technological Reactor for Industrial Demonstration) reactor is to demonstrate the capacity to transmute minor actinides (MA) on an industrial scale. Demonstration scenarios currently focus on two modes of transmutation: a homogeneous mode using a standard fuel with low MA content, and a heterogeneous mode where the minor actinides are loaded in the radial blanket around the core, known as the minor-actinide-bearing blanket (MABB) concept. With different initial MA concentrations for the two modes of transmutation, we have estimated their impact on the performance and safety of the ASTRID reactor core. The consequences on the dimensions of the storage means, the handling systems and the fuel sub-assembly transport packaging are also reviewed in order to identify the limits beyond which significant design changes to the core and nuclear steam supply system (NSSS) would be required. Analysis of the results has made it possible to identify the most suitable irradiation conditions and initial contents to demonstrate transmutation in ASTRID, with the main aim of achieving a balance in the minor actinide flows without significantly changing the reactor design:

- Americium (Am), a main contributor to the heat and the radiotoxicity of radioactive waste after the decay of fission products, will be treated as a top priority,
- Part of the americium can be overridden by neptunium (Np) without any impact on the design and performance,
- Curium (Cm) is not considered; it's too penalising in the handling of new sub-assemblies,
- Possible weight levels for the demonstration: 2% of Am in the fuel for the homogeneous mode and 10% of Am in the blanket for the heterogeneous mode.

Whatever the chosen mode of transmutation, it will be necessary to conduct experimental programmes in ASTRID to validate and qualify the behaviour of fuels until the optimal conditions are found, i.e. target irradiation, manufacturing and separation processes implemented in the facilities of the ASTRID material cycle.

1. Introduction

The ASTRID project was launched within the scope of the French Act of 28 June 2006 on the management of long-lived radioactive waste. The reactor will be designed with the capacity to transmute radioactive waste in order to continue demonstrating the industrial feasibility of this technique for reducing the volume and radiotoxic lifetime of ultimate waste. After a review of the transmutation objectives, this paper presents the results which set the initial minor actinide levels and define the irradiation conditions for the demonstration of transmutation in ASTRID. Focus is placed on achieving a balance in the minor actinide flows in the fuel cycle without impacting the core performance, safety, the dimensions of the spent fuel storage and handling systems, and the transport of fuel sub-assemblies.

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2. Objectives of minor actinide transmutation

Analysis of how much the various elements contributes to the radiotoxicity and the residual power of a spent fuel (Figures 1 and 2) shows that it is worth considering the following three elements for transmutation (in decreasing order):

- Americium (Am),
- Curium (Cm),
- Neptunium (Np).

Together with a plutonium recycling strategy, the transmutation of these elements could help to reduce both the radiotoxicity and the volume of waste. The surface covered by the storage facility (which involves reducing the residual power of the vitrified waste packages) could also be given following the decay of fission products (200 years).

The objective of transmutation is to recycle these elements so they can be transformed into radioelements with shorter half-lives after their separation from spent fuels, which means they have a reduced impact on waste. To do this, we must encourage the fission of isotopes contained in these elements. Studies on transmutation physics [1] have shown that fast neutron spectra are much more inclined to share the surplus of available neutrons and fission/capture ratios maximised in the core of ASTRID-type reactors.
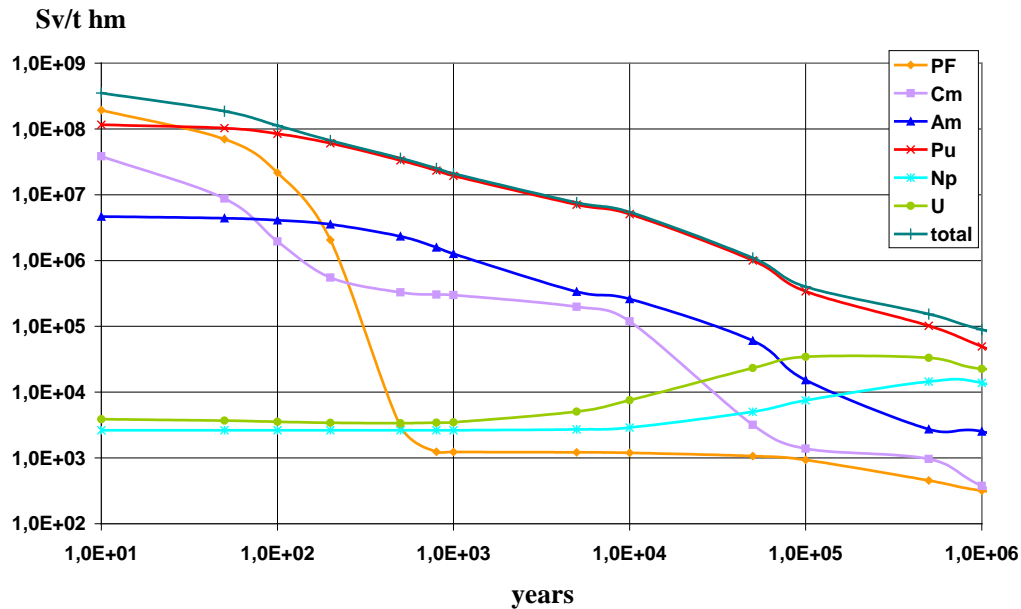

Figure 1: Contribution of the different elements (including decay products) to the radiotoxicity (ingestion) of UOX spent fuel (60 GWd/t)
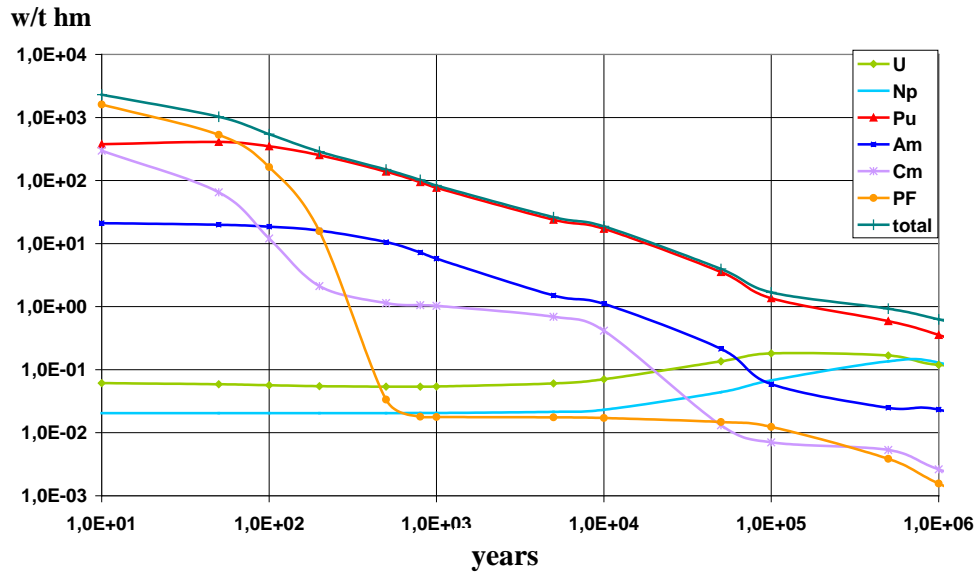
Figure 2: Contribution of the different elements (including decay products) to the decay heat of UOX spent fuel (60 GWd/t)

3.   Transmution modes

Minor actinides (MA) can be recycled in the core of fast neutron reactors in two different ways:

- Homogeneous mode where the MAs are mixed with the fuel in the whole core (Figure 3),
- Heterogeneous mode where the MAs are mixed with depleted uranium and introduced in the radial blanket around the core. This is known as the MABB (Minor-Actinide-Bearing-Blanket) concept (Figure 4).

In homogeneous mode, the minor actinides to be transmuted are diluted in the fuel. We will adjust the initial content of the minor actinides to minimise the effects on the core characteristics. This means introducing low initial levels of minor actinides, which then reduces the specific transmutation capacity in the core. This mode has the disadvantage of aligning the duration of MA irradiation with the fuel and of introducing these MAs in all fuel cycle operations.

In the case of heterogeneous recycling, the minor actinides are concentrated in a specific area of the core (radial blanket) with a much higher level than that used in the homogeneous mode. The number of sub-assemblies and the initial MA content can both be adjusted to minimise the impact of transmutation on the core characteristics. Mass transmutation is a more feasible option using the MABB concept. The heterogeneous mode has the advantage of limiting the number of sub-assemblies containing MAs and of dissociating the standard fuel cycle from the transmutation cycle.
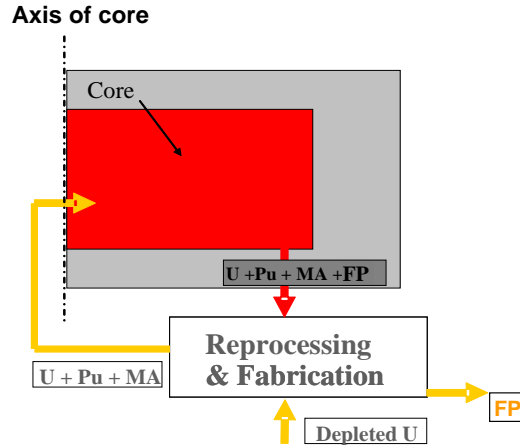
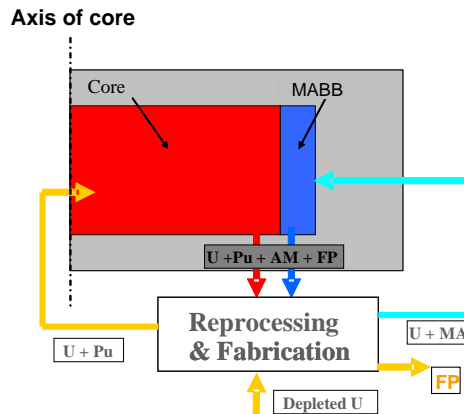**Figure 3: Schematic diagram of transmutation in homogeneous mode**

Figure 4: Schematic diagram of transmutation in heterogeneous mode

4. Transmutation potential in ASTRID

4.1. Assumptions

The following assumptions were taken into account in the analysis of the transmutation potential for ASTRID:

- Reactor: spent fuels handled in sodium pot, external vessel storage tank (in sodium), fuel handling with and without ventilation during transfers for clean-up, and a spent fuel storage pool,
- Reference core (CFV 1500 MWth AIM1 described in Chapter 4.2): the Pu reference is given in Table 1. This table is used as input data for the ASTRID core design studies. The composition of the separated Am is given in Table 1.

As seen in Chapter 2, the transmutation of americium (Am) is to be treated as a priority, in particular to reduce the thermal content of the waste packages and the surface covered by the storage facility [2].

The assumptions applied to the two modes of Am transmutation are as follows:

- Homogeneous mode: the residence time of the $(U,Pu,Am)O_2$ fuel in the core is 1,440 EFPD (effective full power days) broken down into 4 cycles of 360 EFPD each,
- Heterogeneous mode: the residence time of the $(U,Pu)O_2$ fuel in the core is 1,440 EFPD broken down into 4 cycles of 360 EFPD each. Blanket assemblies (66 positions on a full ring) with americium are irradiated for 5 cycles of 360 EFPD, i.e. a total residence time of 1800 EFPD.

Isotope	Reference Pu		Separated Am
Pu^{238}	2.59	Am^{241}	81.04
Pu^{239}	55.2	Am^{242m}	0.11
Pu^{240}	25.85	Am^{243}	18.85
Pu^{241}	7.27		
Pu^{242}	7.87		
Am^{241}	1.22		

Table 1: Isotopic composition (%) of original Pu and Am separated for recycling

4.2. *Reference core: CFV V1 1500 MWth AIM1*

The reference core ASTRID CFV V1 1500 MWth [3] is based on a core concept with a low void effect which makes it possible to minimise (sometimes even negative) sodium void coefficient in the core. To do this, the concept is based on a geometric configuration combining axial and radial heterogeneities (see Figure 6):

- Axial heterogeneity: the internal fissile core has a fertile plate,
- Radial heterogeneity: the external fissile core has a homogeneous fissile height greater than the internal core,
- Each fuel zone has a fairly extensive sodium plenum,
- The top neutron protection, located above the plenum, contains a neutron-absorbing material,
- AIM1 cladding,
- Two core areas are equipped with lower axial blankets for a breeding gain close to zero.

Figure 5 shows a radial cross section of the core with different areas; based on the assumption of transmutation in heterogeneous mode, the radial blanket with minor actinides is positioned immediately after the external core instead of the first row of steel reflector assemblies; axial and radial core configurations are shown in Figure 6.
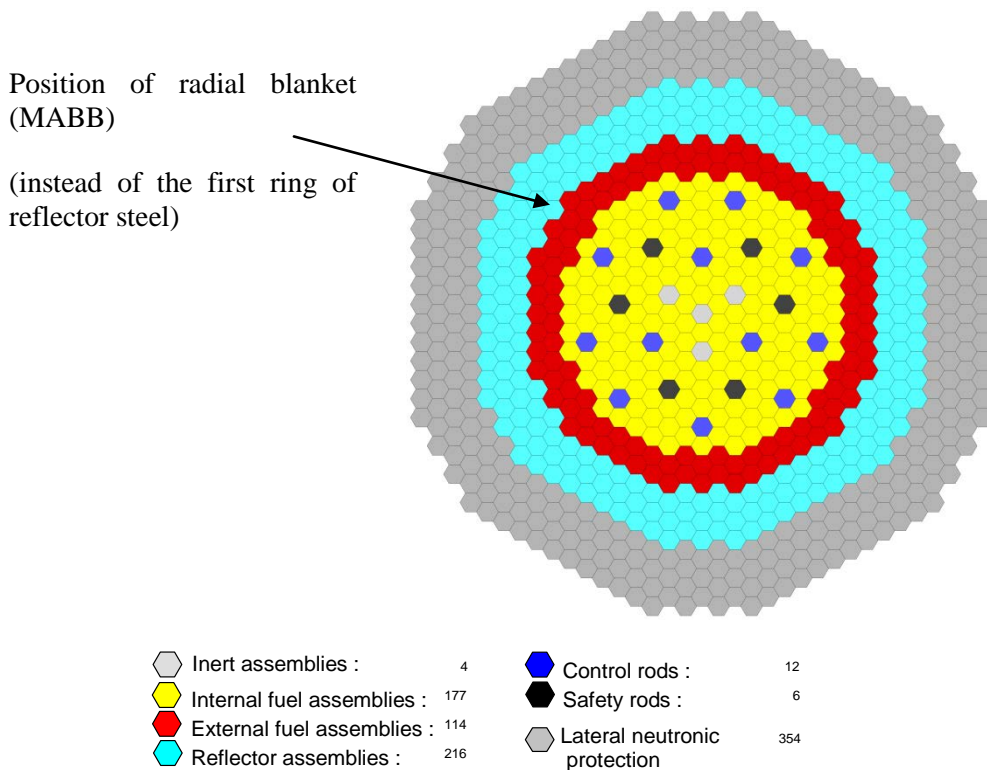

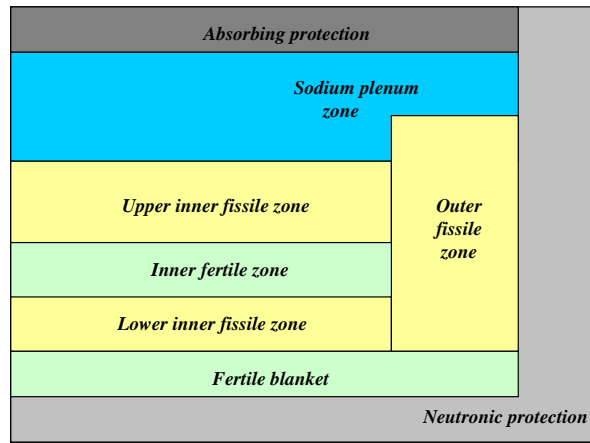**Figure 5: Radial cross section of the CFV V1 AIM1 1500 MWth core**

Figure 6: Axial and radial configurations of the CFV V1 AIM1 1500 MWth core

4.3. *Transmutation of americium in ASTRID*

The parametric study on the initial levels of americium helped to establish the Am limits for two modes of transmutation that achieve the main objective of burning the minor actinides produced by the standard $(U,Pu)O_2$ fuel in ASTRID. The initial volume level of Am should be:

- In homogeneous mode, 2%
- In heterogeneous mode 10%.

Table 2 shows how much of each minor actinide is burned (kg/TWhe) and the sum of the three minor actinides (Np+Am+Cm) at the end of irradiation and after 5 years of cooling. The burn-up for each type of sub-assembly is calculated as follows:

$$C = (M_f(MA) - M_i(MA))/E$$

C: burn-up (kg/TWh) up to cooling t_{ref},

$M_f(MA)$: final mass (kg) of the minor actinide or the sum of the three MAs, up to cooling t_{ref},

$M_i(MA)$: initial mass (kg) of the minor actinide or the sum of the three MAs, at the start of the irradiation,

E: energy produced (TWh) during irradiation.

Negative values indicate that the configuration leads to the full burn-up of the relevant minor actinide.

Kg/TWh	(U,Pu)O$_2$		Homogeneous 2%		Heterogeneous 10%	
Cooling (years)	0	5	0	5	0	5
Np	0.67	0.50	0.72	0.64	0.17	0.28
Am	2.70	5.16	-5.73	-3.48	-5.46	-5.62
Cm	0.67	0.39	2.40	1.40	1.27	0.74
MA	4.03	6.06	-2.61	-1.44	-4.02	-4.60

Table 2: Transmutation performance for Am in homogeneous mode

- In homogeneous mode, the total burn-up of americium is about 3.5 Kg/TWh after a 5-year cooling period for the fuel before treatment and an overall minor actinide burn-up (Np + Am + Cm) of about 1.4 Kg/TWh with a different distribution between the minor actinides compared with the standard $(U,Pu)O_2$ fuel. The transmutation of Am results in a significant production of Cm.
- In heterogeneous mode, the total burn-up of americium is around 5.6 Kg/Twh after a 5-year cooling period for the MAAB before treatment; the production of americium in the core fuel is 5.1 Kg/TWh after the same cooling time. The overall burn-up was equivalent to about 4.6 Kg/Twhe (Np+Am+Cm); production in the core fuel was about 6.1 kg/TWh with a different distribution between minor actinides; the balance between production and burn-up in minor actinides would be reached after a spent fuel cooling period of about 3 years.

The two initial levels of Am selected therefore meet the fixed objective of burn-up in the ASTRID core. We then checked the impacts on:

6

➢ **Core safety :**

Table 3 gives the criteria used to assess the impact of incorporating americium on the core safety.

		(U, Pu)O$_2$	Homogeneous 2%	Heterogeneous 10%
Void coefficient (EC)	$	-1.05	-0.54	-1.05
Margin to melting	°C	>300	>300	>300
k		-1.84	-1.70	-1.81
g		-0.89	-0.80	-0.87
h		-4.86	-4.42	-4.57
Max. temperature of Na (ULOF)	°C	908	909	904
Temperature neutron choking	°C	737	729	725
δρ max insert (UTOP)	pcm	243	221	228

Table 3: Impact of Am on the core behaviour

o The substitution of uranium by americium degrades the sodium void coefficient but it nonetheless remains negative for an Am content of 2% in homogeneous mode. In heterogeneous mode with blankets with very little power, the sodium void coefficient in the core is almost equal to the reference case (U,Pu)O$_2$,

o The margin before fuel melting remains above 300°C (criterion used at this stage of the design) during irradiation,

o The global coefficients k, g and h are representative of the core's thermal feedback. They correspond to the reactivity effect generated by a variation in the core inlet temperature (Tec), a variation in the core heating (ΔCT), and a variation in the core power (P0) respectively. They are related by the following relationship:

δ(Tec) . k + δ(ΔTC) . g + δ(P0)/P0 . h + Δρext = Δρtot,
with: Δρext: reactivity inserted, Δρtot: total reactivity.

It is possible to analytically calculate the main criteria reflecting the natural behaviour of the core under accident transients. The following information can be given for transients such as: Unprotected Fast Loss of Flow (ULOF), Unprotected Loss of Heat Sink (ULOHS), and Unprotected Transient of Power (UTOP):

• The maximum temperature of the sodium during an ULOF is not impacted by the introduction of Am regardless of the mode of transmutation,

• The neutron choking temperature (reached when the neutron power becomes zero) decreased slightly but remains comparable to that of the standard case (U,Pu)O$_2$,

• The admissible maximum reactivity level prior to fusion of the fuel decreased, mainly due to the reduction of the Doppler effect. The decline was not significant for the two Am contents selected.

The results for the two modes of transmutation show that the core safety coefficients are not impacted, including a sodium void coefficient that remains negative.

➢ **Handling fuel sub-assemblies: fresh and spent fuels**

Table 4 lists the impacts resulting from the introduction of Am on the relevant physical characteristics (thermal power and radiation, γ and neutron, sources) for the different stages of fabrication, transport and handling of the fuel sub-assemblies (fresh and spent fuels). The sodium pot is used to handle spent fuels during their transfer to an external vessel storage tank; the target residual power during handling is 40 kW for spent fuel. Handling out of the external storage is done in gas. Two target values on the maximum power of spent fuels are considered, the first with ventilation of the sub-assemblies: 7.5 kW (active cooling), the second without ventilation: 2.2 kW (passive cooling); This power also corresponds to the current value that can be achieved for the transport of spent fuel; the R&D work in progress for future transportation packages aims to increase this value to about 5 kW.

Table 4 also provides the following information for spent fuels at the maximum irradiation:

• The time needed to reach 40 kW; the neutron and γ radiation sources are provided,

- The time needed to reach 7.5 kW and 5 kW,
- The time needed to reach 2.2 kW; the neutron and γ radiation sources are provided.

	(U, Pu)O$_2$	Homogeneous 2%	Heterogeneous 10%
New sub-assembly, aging time 2 years			
Power (kW)	0.39	0.55	0.95
Neutron sources (10^7 n/s)	1.96	2.39	2.56
γ sources (10^4 γ/s)	0.83	2.31	8.65
Spent fuels			
Time to reach 40 kW	< 1 day	1 day	< 1 day
Neutrons sources (10^9 n/s)	0.75	2.5	7.6
γ Sources (10^{17} γ/s)	2.9	2.8	0.95
Time to reach 7.5 kW (days)	68	168	350
Time to reach 5 kW (days)	123	291	485
Time to reach 2.2 kW (days)	456	687	1 898
Neutrons sources (10^9 n/s)	0.45	1.3	3.0
γ Sources (10^{15} γ/s)	3.6	2.8	1.1

Table 4: Impact of Am transmutation on handling, cleaning and transportation of spent fuels

- The power of the new fuel sub-assemblies is less than the value target of 2.2 kW for transport and handling in gas of new sub-assemblies,
- Time to reach 40 kW – limit for transferring the sodium pot to the external vessel storage tank – remains less or equal to 1 day,
- Time to reach target decay heat values for handling in gas and cleaning spent fuels (with or without ventilation) remains compatible with external storage capacities,
- Time to achieve a decay heat of 5 kW or 2.2 kW, remains compatible with the of pool water storage capacity before transport to the waste treatment plant,
- Despite the increase in the sources of radiation, there is little impact on the radiological areas around the handling areas for new fuel sub-assemblies in gas or spent fuels in the sodium pot.

The results for the two modes of transmutation show that new and spent fuel sub-assembly handling systems are not impacted; the external storage and interim pool storage capacities make it possible to increase the residence time to compensate for the increased decay heat from the spent fuels.

4.4. Taking into account neptunium and curium

4.4.1. Transmutation of neptunium in ASTRID

For the same initial volume contents in homogeneous and heterogeneous mode, we replaced 40% of americium by neptunium (Np237). Table 5 shows the burn-up (kg/TWh) for each minor actinide and the sum of the three minor actinides at the end of the irradiation and after a 5-year cooling period.

Kg/TWhe	(U,Pu)O$_2$		Homogeneous 2%		Heterogeneous 10%	
Cooling (years)	0	5	0	5	0	5
Np	0.67	0.50	-2.69	-2.84	-2.11	-2.06
Am	2.70	5.16	-2.41	-0.09	-3.31	-3.41
Cm	0.67	0.39	1.70	0.99	0.77	0.45
AM	4.03	6.06	-3.40	-1.94	-4.65	-5.02

Table 5: Transmutation performance for (Np + Am) in homogeneous and heterogeneous mode

- In homogeneous mode: the table indicates the overall burn-up of neptunium, americium and the sum of the minor actinides in the core for the two considered cooling times,
- In heterogeneous mode: the initial content of 10% in (Np + Am) makes it possible to burn the Np produced in the core with both cooling times for the standard $(U,Pu)O_2$ fuel and the "MABB-NpAm". The burn-up of the sum of the minor actinides produced in the core is reached after around 4 years of cooling for the standard fuel. To burn the americium produced by the core, the standard $(U,Pu)O_2$ fuel needs to be reprocessed before 5 years of cooling. It is also possible to modify the ratio between Np and Am to find the optimum level where the Np and Am burn-up is higher than their production in the core.

The substitution of part of the americium by neptunium has no impact on the various analysis criteria.

To summarise, the replacement of americium (40%) by neptunium – in homogeneous or heterogeneous mode – has no additional impact regarding the criteria taken into account in the analysis of the transmutation potential in ASTRID; a content of 2% in homogeneous mode or 10% in heterogeneous mode would ensure the self-recycling of Np, Am and all of the minor actinides.

4.4.2. *Taking into account curium*

Curium (Cm) – mainly Cm-244 – is a strong neutron emitter and is the source of neutron radiation which contributes to about 90% to the dose rate. This corresponds to a factor of 30 for the homogeneous mode with 2% of Am and Cm and a factor of 130 for the heterogeneous with 10% of the same actinides. This increase would result in a change of radiological area compared with the standard $(U,Pu)O_2$ fuel and would have a significant impact on the design of the handling system within ASTRID, as well as on the manufacturing facility. Curium was not retained for the transmutation demonstration in ASTRID.

4.5. *Summary and future prospects for incorporating minor actinides in ASTRID*

The analysis presented in this document demonstrates the potential of minor actinide transmutation on an industrial scale in the CFV V1 core of ASTRID on the basis of different criteria taken into account. The objective of ensuring a balance in the minor actinide flow in the ASTRID fuel cycle may be obtained without any impact on the design of the core and handling systems for the management of the new and spent fuel sub-assemblies. For both modes of transmutation, americium is treated as a priority; the substitution of part of the americium by neptunium has no effect on the impact on the various analysis criteria. Curium is not taken into consideration in the transmutation demonstration of ASTRID.

a) **Homogeneous mode**
The initial content volume in Am is of 2%, which gives a mass content of 2.25% by adding the Am241 produced during aging of Pu; the residence time of the fuel $(U,Pu,Am)O_2$ in the core will be adapted to the design data of the core retained to ASTRID, in the study presented in this note, it is 1440 EFPD (equivalent full power days) over 4 cycles of 360 EFPD.

b) **Heterogeneous mode**
The maximum initial content in Am is 10% in the MABB radial blanket. In the study, the residence time of the fuel $(U,Pu)O_2$ in the core is 1,440 EFPD divided into 4 cycles of 360 EFPD. Radial blankets with americium are irradiated for 5 cycles of 360 EFPD each without flipping, or 1,800 EFPD.

To achieve the industrial demonstration of transmutation in ASTRID, it will be necessary to conduct several experimental phases in the reactor implementing different transmutation scenarios using homogeneous and heterogeneous modes. This will require the availability of facilities involved in the ASTRID material cycles (Figure 7).
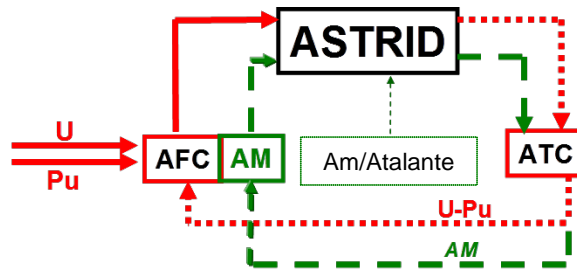
Figure 7: Cycle of materials for ASTRID

The behaviour under irradiation of fuels or MABBs exploited for minor actinide transmutation might prove to be quite different from that of standard fuels, due mainly:

- The incidence of minor actinides on the physical properties of the material (thermal conductivity, fusion, potential of oxygen, etc..),
- The process associated with the transmutation of minor actinides (especially the high production of helium due to americium),
- Special irradiation conditions. This is particularly true for areas of the radial blanket using the MABB concept where neutron flux gradients are important and where the initially low linear power increases significantly during irradiation.

The lack of knowledge on the behaviour of these fuels under irradiation requires implementing a qualification process covering the fissile material, the fuel element (pin with sheath, fissile column and internal structures) and the complete sub-assembly (external structure, pin with spacer wire beam) in support of the studies, design and sizing of the fuel elements and sub-assemblies.

The considerable amount of data required to design a fuel pin is accessible via experimental irradiations:

- Changes under irradiation of the fuel characteristics: composition, density, stoichiometry, r, etc.,
- Changes under irradiation of the physical and chemical properties: oxygen potential, thermal conductivity, mechanical properties, etc.,
- Fuel swelling under irradiation linked to the onset of helium and solid and gaseous fission products,
- Fission gas releases and helium production rates,
- Cracking and fuel relocation ,
- Changes under irradiation of the characteristics and properties of the cladding material.

The development and qualification plan for a fuel concept involves several phases that range from designing the fuel to qualifying the product in its industrial environment (supply, manufacturing, irradiation, reprocessing), including the analytical validation and qualification of a prototype with representative reactor conditions. These different phases require conducting irradiation experiments at various scales of which the majority will be conducted in ASTRID to supplement those [4] already conducted in the MTR and in the Phenix reactor.

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Analysis of Spent Fuel Characteristics in Different Scenarios of Closing the Nuclear Fuel Cycle

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Abstract. Calculation analysis of the isotope and radiation-migration characteristics of spent nuclear fuel (SNF) in the open fuel cycle of thermal reactor VVER-1000 and in closed cycle of fast reactor with lead-bismuth coolant has been fulfilled. Effects of including an accelerator-driven system (ADS) into the system for transmutation of minor actinides (MA) into the cycles studied on the SNF characteristics has been reviewed. The application of ADS-burner of MA symbiotically with operating VVER-1000 reactors has been shown to decrease the high-level wastes' activity approximately 20 times within the interval from the end of cooling in reactor to 105 years; in this case the principle of radiation-migration balance of activity in the underground burial for ~500 years is met as well. The calculation analysis gives grounds to conclude that the use of ADS for burning minor actinides in closed fuel cycle of fast reactors with lead-bismuth coolant, where U, Pu, and MA are recycled, with natural uranium as a makeup fuel, does not provide any special advantages in terms of radiation and migration characteristics of spent fuel and its wastes.

1. Introduction

In order to organize a closed nuclear fuel cycle, it is necessary to analyze both radiation safety and technological conditions at every phase of management and disposition of spent nuclear fuel. This includes phases of SNF unloading and cooling down, the phase of its reprocessing and manufacturing of new fuel with recycling of the most part of fissile elements, formation of high-level wastes (HLW) followed by their final disposal.

The long-term radiation activity of spent fuel is determined, primarily, by isotopes of plutonium (Pu) and minor actinides (Np, Am, Cm). A radical solution for the MA problem is their "burning" (transmutation) in various nuclear facilities, i.e., under neutron flow the MA nuclei are transformed into relatively short-lived fission fragments.

An accelerator-driven system with lead-bismuth coolant has been studied as a specialized burner of MA. The MA extracted from SNF of VVER-1000 reactor, as well as from SNF of fast critical reactor (120 kg/year) serve as a makeup fuel for this system. A detailed description of the concept of ADS-system based on the experience of designing the fast critical nuclear reactor SVBR with lead-bismuth coolant [2,3] can be found in Ref. [1].

Codes such as MCNPX [4], ORIGEN2 [5], and code complex REACTOR were used in complex calculations for determining the SNF characteristics [6]. The input information for calculating the VVER-1000 reactor fuel cycle is taken from Ref. [7].

The comparative analysis was based on the following options of fuel cycle.

1) Open fuel cycle for thermal reactor VVER-1000.

2) Open fuel cycle of VVER-1000 with MA from SNF of the reactor dispatched to ADS for transmutation.
3) Closed nuclear fuel cycle (CNFC) of critical reactor with lead-bismuth coolant, where U, Pu, and MA are recycled into the composition of new fuel, and natural uranium serves as makeup fuel.
4) CNFC of the fast reactor with Pb-Bi coolant, with an ADS-system specially included for the MA transmutation.

2. Comparative analysis of HLW radioactivity in different cycles of VVER-1000 reactor and the ADS-burner of MA.

Proceeding from the contemporary estimations of wastes volumes, it is assumed for the comparative analysis that in the SNF reprocessing, approximately 0.1 per cent of U, 0.1 per cent of Pu, and 1% of MA remain from their initial masses in high level wastes. It will be supposed that fission products (FP) from SNF and HLW can be disposed completely therefore they are not considered in the calculations.

In case of power output of 50 GW·day/t h.a., after 1-year cooling the SNF from VVER-1000 reactor contains ~ 1.12% of plutonium and 0.12 % MA (Np, Am, Cm).

Three options of HLW formation in the fuel cycle of VVER-1000 have been considered:

1. Open fuel cycle, where entire SNF is considered to be the HLW;
2. The cycle in which U and Pu are extracted from the fuel in its reprocessing, with 0.1% U, 0.1% Pu, and all MA transferred to the wastes.
3. The cycle when U, Pu, and MA are extracted from the VVER-1000 fuel in its reprocessing, and the minor actinides extracted act as the makeup fuel for the ADS-burner of MA (Fig. 1). It was assumed that amounts of 0.1% U, 0.1% Pu, and 1% of MA get into the HLW both in the reprocessing of SNF from VVER-1000, and in the reprocessing of ADS fuel.
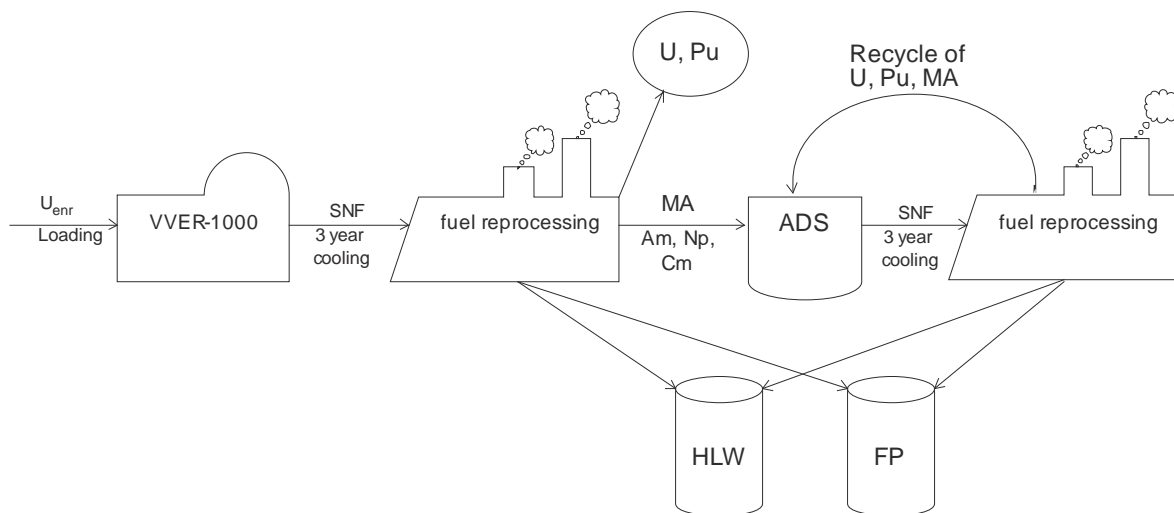

FIG. 1. Open fuel cycle of VVER-1000 reactor with ADS.

Calculations of wastes activity in these three cycles are presented in Table 1. It is obvious, also corroborated by the calculation results, that the HLW radioactivity in the 3-rd cycle is considerably smaller, because transmutation reduces the MA content in the fuel cycle. All values have been normalized for 1 ton of SNF from VVER-1000.

Table 1. Radioactivity of high level wastes in different cycles of reprocessing the SNF from VVER-1000 reactor, Ci/t

Time of SNF cooling, years	VVER-1000 reactor	VVER-1000 reactor	Joint cycle of VVER-1000 and the ADS–burner of MA		
	Initial radioactivity of HLW (activity of SNF without FP)	HLW contaning 0.1% U, 0.1% Pu, and 100% of MA of VVER-1000 fuel	HLW contaning 0.1% U, 0.1% Pu, and 100% of MA of VVER-1000 fuel	HLW containing 0.1% U, 0.1% Pu, and 100% of MA of the ADS fuel	Total for HLW of VVER-1000 and ADS
3.00E+00	1.660E+05	7.653E+03	2.348E+02	1.708E+02	4.056E+02
4.00E+00	1.583E+05	6.883E+03	2.190E+02	1.509E+02	3.699E+02
5.00E+00	1.514E+05	6.553E+03	2.091E+02	1.432E+02	3.523E+02
6.00E+00	1.448E+05	6.322E+03	2.005E+02	1.387E+02	3.392E+02
7.00E+00	1.386E+05	6.119E+03	1.925E+02	1.353E+02	3.278E+02
8.00E+00	1.326E+05	5.927E+03	1.849E+02	1.325E+02	3.174E+02
9.00E+00	1.270E+05	5.742E+03	1.776E+02	1.299E+02	3.075E+02
1.00E+01	1.216E+05	5.565E+03	1.706E+02	1.275E+02	2.981E+02
5.00E+01	2.023E+04	1.665E+03	3.505E+01	7.434E+01	1.094E+02
1.00E+02	9.531E+03	1.030E+03	1.872E+01	5.886E+01	7.758E+01
2.00E+02	6.566E+03	8.049E+02	1.376E+01	4.359E+01	5.735E+01
5.00E+02	3.892E+03	5.247E+02	8.584E+00	2.183E+01	3.041E+01
1.00E+03	2.238E+03	2.818E+02	4.757E+00	9.444E+00	1.420E+01
5.00E+03	7.516E+02	6.582E+01	1.338E+00	1.326E+00	2.664E+00
1.00E+04	5.394E+02	4.494E+01	9.394E-01	9.214E-01	1.861E+00
2.00E+04	3.127E+02	2.328E+01	5.195E-01	5.075E-01	1.027E+00
5.00E+04	1.129E+02	7.389E+00	1.784E-01	2.125E-01	3.909E-01
7.00E+04	7.280E+01	5.457E+00	1.213E-01	1.808E-01	3.021E-01
1.00 E+05	4.606E+01	4.613E+00	8.721E-02	1.696E-01	2.568E-01

It can be seen from the analysis of results that the extraction of U and Pu in reprocessing of 1 ton of spent fuel from VVER-1000 provides a 10 - 20 times reduction of radioactivity level in reprocessed HLW during the time interval from the end of fuel cooling in reactor to 105 years, and the MA transmutation in ADS-burner results in an additional ~20-fold reduction of activity.

Analysis of radiation-migration balance of radioactivity (RMBA) was performed for all options of fuel cycle studied.

The equivalent radiation-migration radioactivity was estimated by the following expression:

$$A_{m\ r\ eq} = \sum_i \frac{a_i(t)\xi_i}{K_{migr,\ i}\ \ K_{rad,\ i}}$$

where

$a_i(t) -$ specific activity of the i-th nuclide at the moment of time t, Ci/t;

$K_{rad,i}$- radiation coefficient of the i-th nuclide;

$K_{mig,i}$- migration coefficient of the i-th nuclide;

ξ_i – mass fraction of the i-th nuclide.
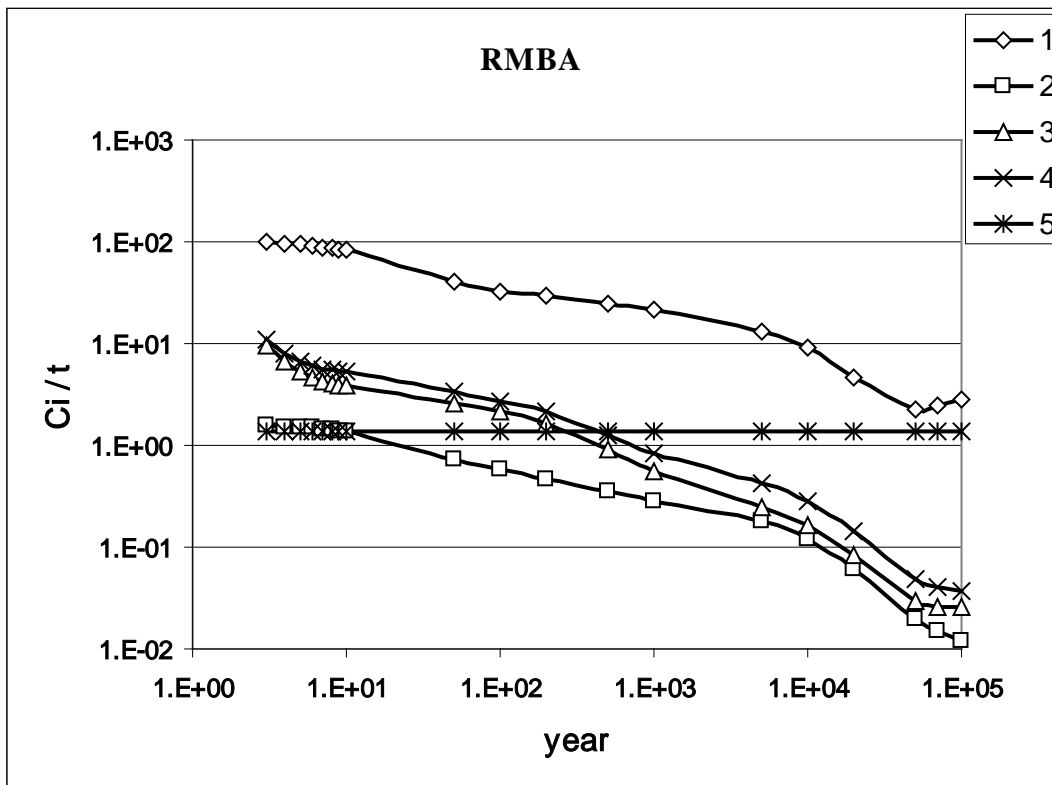
FIG. 2. RMBA of HLW for VVER-1000 reactor and ADS-burner of MA.

1 – activity of HLW of VVER-1000 containing 0.1% U, 0.1% Pu, and 100% MA;
2 – activity of HLW of VVER-1000 containing 0.1% U, 0.1% Pu, and 1% MA;
3 – activity of HLW of ADS containing 0.1% U, 0.1% Pu, and 1% MA;
4 – total activity of wastes from VVER-1000 and ADS (total of curves 2 and 3);
5 – activity of 1 ton of natural uranium.

The radiation coefficient Krad,i reflects the extent of a separate nuclide's effect on man compared to natural uranium; migration coefficient Kmig,i reflects different degrees of mobility of a separate nuclide in hard rocks as related to uranium. Coefficients Krad,i, Kmig,i from Ref. [8] were used in the calculations. The activity of natural uranium extracted from ore is assumed to be equal to 1.37 Ci/t. This value is inferred from the analysis of natural radiation series for 235U and 238U, which are in secular equilibrium [9].

Figure 2 presents a comparison of equivalent radiation-migration activities of high level wastes generated in the reprocessing of 1 ton of SNF from VVER-1000 for different options of fuel cycle.

The calculation results give evidence that in approximately 500 years the radiation-migration activity of high level wastes formed in the reprocessing of one ton of SNF from VVER-1000 in a joint operation with the ADS-burner of MA becomes smaller than radioactivity of one ton of natural uranium. Without application of ADS, this balance of radioactivity cannot be reached even for the time period of 105 years.

In the third option of fuel cycle with ADS-burner of MA, HLW buried in underground structures in stable geological environment for the time comparable with the period when major radioactivity of fission products is decreased (~300 years) begin to meet the principle of radiation-migration balance of radioactivity [8], whereas activity of wastes from the SNF reprocessing and activity of the input nuclear raw materials become equal, i.e., the wastes after achievement of such equilibrium do not violate natural radiation background any more, and further final disposal of these wastes can proceed without special control.

3. Comparative analysis of SNF and HLW from fast reactor with Pb-Bi coolant and ADS-burner of MA

Two strategies of closing the fuel cycle for the fast critical reactor with Pb-Bi coolant have been analyzed considering the following conditions:

a) in closed nuclear fuel cycle with complete recycling of U, Pu, MA, i.e., only fission products are disposed in the fuel reprocessing (an ideal fuel cycle CNFC1);

b) in closed nuclear fuel cycle when only U and Pu are recycled (Fig. 3), whereas fission products and minor actinides are disposed, the MA separated being directed to the ADS-burner for transmutation (CNFC2).

In both cases it is natural uranium which serves as the makeup fuel for the fast critical reactor in the equilibrium mode. For the ADS, minor actinides from SNF of fast reactor serve as makeup fuel as well. Similar power levels are chosen for the critical reactors in both cases studied and that for ADS-burner − 330 MW, with inter-reloading periods of four years.

Table 2 shows the equilibrium compositions of SNF after 3-year cooling for the fast reactors for two strategies of closing the fuel cycle. Like in previous cases, fission products are not included into analysis.
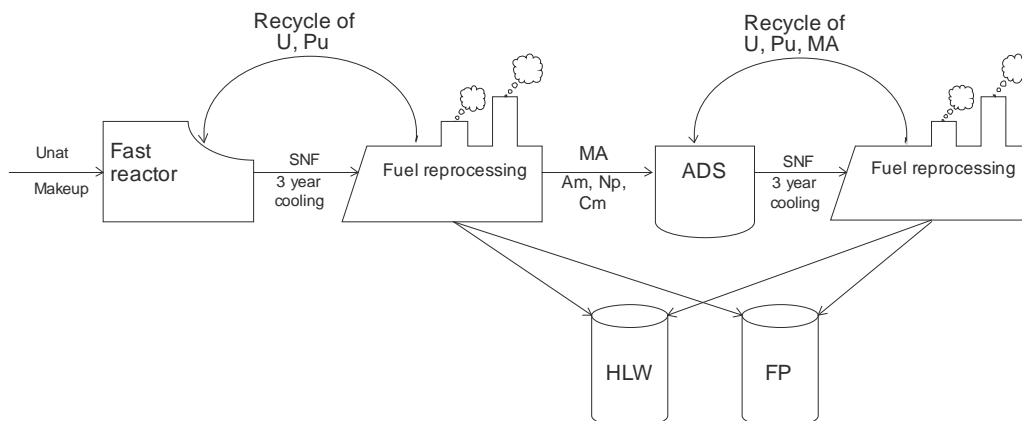

FIG. 3. Closed fuel cycle for fast reactor with ADS.

Table 2. Composition of SNF of fast critical reactor and ADS (without FP)

Composition	Critical reactor, recycling U, Pu, MA		Critical reactor, recycling U, Pu		ADS, makeup fuel - MA of fast reactor	
	mass, kg	% weight	mass, kg	% weight	mass, kg	% weight
U-234	2.68E+00	4.9E-02	1.87E+00	3.4E-02	1.25E+02	5.7E+00
U-235	4.08E+00	7.5E-02	4.06E+00	7.4E-02	2.81E+01	1.3E+00
U-236	6.58E+00	1.2E-01	6.59E+00	1.2E-01	2.88E+01	1.3E+00
U-238	4.52E+03	8.3E+01	4.54E+03	8.3E+01	2.61E-02	1.2E-03
NP-237	5.85E+00	1.1E-01	2.21E+00	4.0E-02	1.89E+02	8.6E+00
NP-239	3.10E-05	5.7E-07	2.97E-05	5.4E-07	1.09E-04	5.0E-06
Pu-236	7.65E-05	1.4E-06	2.00E-05	3.7E-07	2.84E-03	1.3E-04
PU-238	1.37E+01	2.5E-01	4.50E+00	8.2E-02	5.53E+02	2.5E+01
PU-239	5.94E+02	1.1E+01	5.96E+02	1.1E+01	1.27E+02	5.8E+00
PU-240	2.43E+02	4.5E+00	2.48E+02	4.5E+00	2.10E+02	9.5E+00
PU-241	2.81E+01	5.1E-01	2.95E+01	5.4E-01	2.30E+01	1.0E+00
PU-242	1.23E+01	2.3E-01	1.15E+01	2.1E-01	1.67E+02	7.6E+00
AM-241	1.99E+01	3.6E-01	9.40E+00	1.7E-01	5.20E+02	2.4E+01
AM242M	5.47E-01	1.0E-02	7.60E-02	1.4E-03	2.20E+01	1.0E+00
AM-243	3.10E+00	5.7E-02	1.25E+00	2.3E-02	1.26E+02	5.7E+00
CM-242	1.00E-02	1.8E-04	2.00E-03	3.7E-05	3.29E-01	1.5E-02
CM-243	9.30E-02	1.7E-03	9.00E-03	1.6E-04	3.68E+00	1.7E-01
CM-244	1.14E+00	2.1E-02	1.33E-01	2.4E-03	6.15E+01	2.8E+00
CM-245	1.81E-01	3.3E-03	7.00E-03	1.3E-04	9.74E+00	4.4E-01
CM-246	4.60E-02	8.4E-04	1.61E-04	2.9E-06	2.71E+00	1.2E-01
CM-248	8.00E-03	1.5E-04	6.96E-05	1.3E-06	9.20E-01	4.2E-02
Total	5.46E+03	1.0E+02	5.46E+03	1.0E+02	2.20E+03	1.0E+02

Table 3 shows specific radioactivity levels and residual decay heat both for separate fractions of SNF, and for all actinides (U,Pu,MA).

Table 3. Specific characteristics of spent fuel after 3-year cooling

Fuel fraction	Specific activity					
	Critical reactor, recycling U,Pu,MA		Critical reactor, Recycling U,Pu		ADS, makeup fuel – MA of fast reactor	
	Ci/kg	%	Ci/kg	%	Ci/kg	%
U,Pu	5.95E+02	94.0	5.83E+02	98.5	5.14E+03	68.8
MA	3.81E+01	6.0	9.38E+00	1.5	2.33E+03	31.2
U,Pu,MA	6.33E+02	100	5.92E+02	100	7.47E+03	100
	Specific energy release					
	W/kg	%	W/kg	%	W/kg	%
U,Pu	1.76	59.3	9.15E-01	74.3	1.16E+02	53.2
MA	1.21	40.7	3.13E-01	25.6	1.02E+02	46.7
U,Pu,MA	2.97	100	1.23E+00	100	2.18E+02	100

It follows from the data presented that the separation of MA in the second strategy of fuel cycle closure during the phase of fast reactor fuel reprocessing does not result in a radical improvement of the SNF characteristics. The actinides' activity is 6.5 per cent smaller, with energy release 58.6 per cent lower. For the organization of remote industrial scale reprocessing of fuel from fast reactors, such difference in characteristics is unlikely to be significant.

It follows from the results obtained that to provide the makeup fuel for one ADS from MA of fast reactor, synchronized operation of approximately 37 fast critical reactors is needed (further, all calculations are presented for 36.7 reactors). The radioactivity levels and residual energy release for such system within the fuel cycles studied can be found in Table 4.

Table 4. Total radioactivity and residual energy release of spent fuel after 3 years of cooling in closed fuel cycles (without FP)

Fuel fraction	CNFC1	Double strata closed fuel cycle CNFC2		
	37 reactors with recycling U,Pu,MA	37 reactors with recycling of U,PU	1 ADS with makeup fuel from MA	Total for 37 reactors + 1 ADS
	Activity, Ci			
U,Pu,MA	1.38E+08	1.29E+08	1.99E+07	1.49E+08
	Residual energy release, W			
U,Pu,MA	6.47E+05	2.68E+05	5.82E+05	8.50E+05

In the implementation of the second strategy of CNFC, there appears the need to reprocess additionally the ADS fuel, its specific activity by actinides being 11.8 times higher, and specific

residual energy release 73.4 times larger than those for fuel in the second strategy of closed fuel cycle. Relative mass fraction of the ADS fuel in total mass amounts to 1.2%; however, this fraction covers 13.4% of actinides activity, and corresponding value for energy release is 68.5%. Probably, development of a separate technology for reprocessing this fraction of spent fuel will prove necessary.

Total activity as an accompanying factor of the SNF reprocessing in the frame of CNFC2 strategy appears to increase compared to the first cycle by 8%, and total residual energy release – by 31.4%.

It is assumed again for the comparative analysis of radioactivity values in HLW in different strategies of closed nuclear fuel cycle that in CNFC1, with recycling of U, Pu, and MA, the amounts that get into high level wastes are 0.1% U, 0.1% Pu, and 1% of MA contained in the SNF from critical reactor. Total mass of such wastes from 37 fast reactors equals to 211.4 kg. In the second strategy of CNFC, when the MA from critical reactor are dispatched to transmutation to ADS, the quantities that are released into the wastes include also 0.1% U, 0.1% Pu and 1% contained both in the reactor SNF, and in the SNF of ADS. The mass of wastes in CNFC2 from 37 reactors is 204.8 kg, and from one ADS - 10.0 kg (total 214.8). The quantities of radioactivity of these wastes calculated in the time interval from the moment of end of cooling time in reactor up to 105 years are cited in Table 5.

Table 5. Specific radioactivity of wastes in cycles, Ci

Time of cooling, year	37 fast critical reactors	Joint cycle of 37 critical reactors and ADS–burner of MA		
	Wastes 0.1% U, 0.1% Pu, 1%MA, 211.4 kg	Wastes 0.1% U, 0.1% Pu, 1% MA, 204.8 kg from 37 reactors	Wastes 0.1% U, 0.1% Pu, 1% MA, 10.0 kg from 1 ADS	Total for wastes in the cycle of 37 reactors + 1 ADS
3.00E+00	1.99E+05	1.32E+05	7.03E+04	2.02E+05
4.00E+00	1.85E+05	1.25E+05	6.22E+04	1.87E+05
5.00E+00	1.77E+05	1.20E+05	5.89E+04	1.79E+05
6.00E+00	1.71E+05	1.16E+05	5.72E+04	1.73E+05
7.00E+00	1.65E+05	1.11E+05	5.56E+04	1.67E+05
8.00E+00	1.60E+05	1.07E+05	5.46E+04	1.62E+05
9.00E+00	1.55E+05	1.03E+05	5.35E+04	1.57E+05
1.00E+01	1.50E+05	9.95E+04	5.24E+04	1.52E+05
5.00E+01	5.54E+04	2.82E+04	3.06E+04	5.87E+04
1.00E+02	4.10E+04	1.97E+04	2.42E+04	4.39E+04
2.00E+02	3.19E+04	1.59E+04	1.80E+04	3.38E+04
5.00E+02	1.85E+04	1.05E+04	8.99E+03	1.95E+04
1.00E+03	9.78E+03	6.44E+03	3.88E+03	1.03E+04
5.00E+03	2.92E+03	2.62E+03	5.46E+02	3.16E+03

1.00E+04	2.12E+03	1.90E+03	3.78E+02	2.27E+03
2.00E+04	1.24E+03	1.12E+03	2.08E+02	1.32E+03
5.00E+04	4.36E+02	3.86E+02	8.71E+01	4.74E+02
7.00E+04	2.73E+02	2.27E+02	7.42E+01	3.01E+02
1.00E+05	1.61E+02	1.17E+02	6.96E+01	1.86E+02

Therefore, the MA removal in the reprocessing of fast reactors' fuel provides a ~1.5 - 2.0 fold decrease of radioactivity of wastes from fast reactors in the time interval under 103 years, and a 1.1-1.4 fold decrease – in the interval from 103 years to 105 years. However, with the wastes from reprocessing of the ADS fuel accounted for, total radioactivity of HLW in the second strategy of fuel cycle is somewhat higher (2-10%), than radioactivity in the first strategy of CNFC in entire time interval under review.

The differences in isotope composition of HLW in two strategies of CNFC in this analysis considerably influence the results of radioactivity calculation using the principle of radiation-migration balance. Figure 4 shows the radioactivity levels of wastes equivalent to natural uranium for the CNFC strategies analyzed. The results are normalized for 1 ton of fuel of 37 fast reactors. The activity of 1 ton of natural uranium is taken for comparison.
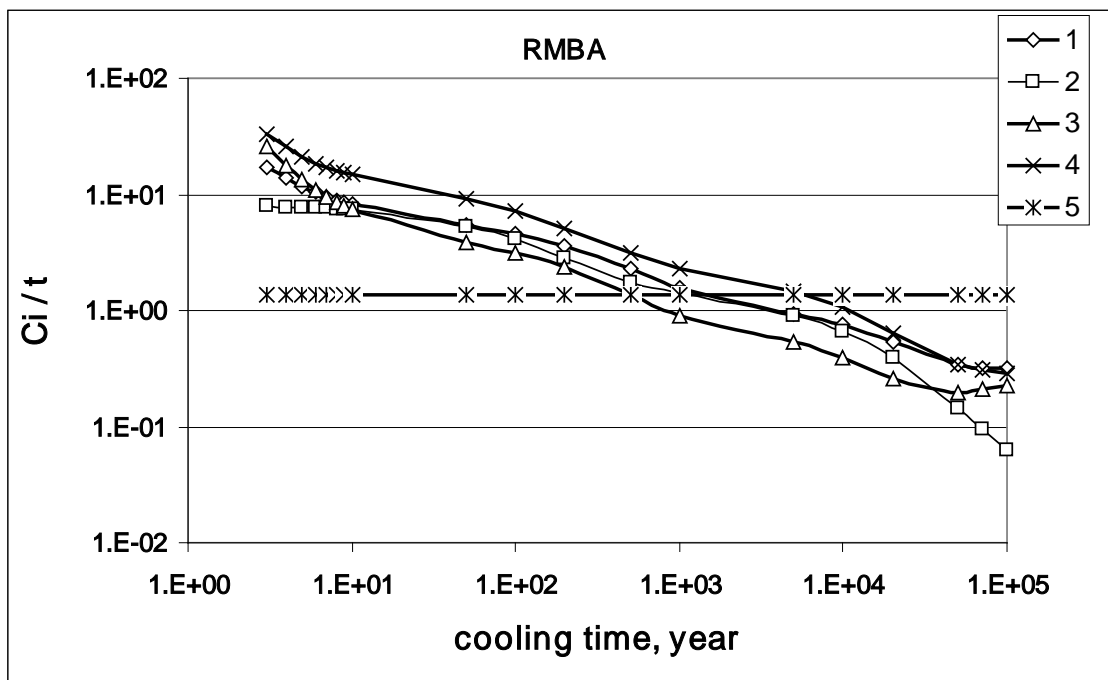
FIG. 4. RMBA of wastes for critical fast reactor and ADS-burner

    1. – activity of wastes from critical reactor in CNFC1;
    2. – activity of wastes from critical reactor in CNFC2;
    3. – activity of wastes from ADS in CNFC2;
    4. – total activity of wastes from critical reactor and ADS in CNFC2;
    5. – activity of 1 ton of natural uranium.

The equality (balance) of equivalent radioactivity of wastes corresponding to one ton of natural uranium is established for the first strategy of CNFC in ~ 2000 years and for the second strategy of CNFC with ADS – in ~ 5000 years.

Summarizing the results of calculations for the application of ADS-burner of MA in closed fuel cycle of fast reactors with lead-bismuth coolant, the following conclusions can be made:

- the ADS inclusion of into the CNFC strategy for burning MA does not result in a significant improvement of radiation and power characteristics of spent fuel of fast reactor, where radioactivity and residual energy release are determined to a considerable extent by plutonium recycled. Overall radiation characteristics, with radioactivity of SNF from ADS, prove to be impaired.
- The problem of final disposal of HLW does not become simplified, because the wastes from reprocessing of "dirty" fuel from the ADS itself nullify a certain gain in the characteristics of wastes from fast reactor.

4. Conclusions

Calculation analysis of characteristics of spent nuclear fuel in the open fuel cycle of thermal reactor VVER-1000 and in closed cycle of fast reactor with lead-bismuth coolant has been fulfilled.

It has been shown that the inclusion of accelerator-driven system into open fuel cycle of thermal reactor VVER-1000 makes it possible to decrease activity of HLW approximately 20 times, as well as meet the principle of radiation-migration balance of activity in the underground burial for the time of cooling of ~500 years. Without ADS, the said balance of activity appears not feasible even for the time interval of 105 years.

The option when ADS is used for burning MA in closed fuel cycle of fast reactors with lead-bismuth coolant where all actinides (U, Pu, and MA) are recycled, and natural uranium serves as the makeup fuel does not provide any special advantages in terms of radiation and energy characteristics of spent fuel, neither for spent fuel, nor the HLW.

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Impact of minor actinide transmutation options on geological disposal
The French case

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Abstract. Whithin the framework of June 28, 2006 waste management French Act, an assessment of industrial perspectives of partitioning and transmutation of actinides is provided in 2012. These studies must be carried out in tight connection with GENIV systems development. In this perspective, CEA asked the French waste management Agency (Andra) to assess the impact of high and intermediate level waste as produced by various transmutation options, on the sizing of a geological repository. Andra used repository architectures similar to those employed in the Cigéo project which is under development for current NPPs. Results allow to compare the underground footprint and the excavated volume for each option ; the impact of the interim storage duration is also assessed. Solutions are proposed to optimize the footprint of the repository. An analysis of the advantages and drawbacks of transmutation options is proposed.

1. INTRODUCTION

The French Waste Act of June 28, 2006 provides for three research routes for the long term management of high level and long-lived waste: partitioning and transmutation, (ii) geological disposal with respect to the reversibility principle, (iii) above-ground interim storage. These three routes are not alternatives options but potential complementary waste management tools. In particular partioning and transmutation do not eliminate the need for geological disposal.

Andra and CEA have carried out in partnership an assessment of the impact of waste induced by various transmutation options, on the sizing and the safety of a geological repository. Such transmutation would be implemented in potential IVth generation fast breeder reactors.

Waste produced by possible future reactors are not included in the inventory of Andra's industrial geological repository project "Cigéo" in Meuse/Haute-Marne. Indeed Cigéo is dedicated to waste induced by former and current nuclear facilities. Therefore the study has addressed one or two new hypothetical repositories which would be implemented specifically for future nuclear power fleets. For the purposes of this study, the assumption has been made of a geological setting similar to the one studied in Meuse/Haute-Marne, without prejudice to the future implementation of these facilities.

Transmutation scenarios as well as characteristics, volumes and flows of waste packages were defined by CEA as input data. Three scenarios were selected for this study. The first scenario (F4) is related to the multiple recycling of plutonium (Pu): minor actinides (MA) and fission products (FPs) are then

high level waste (HLW). The second scenario (F1g) considers the multiple recycling of Pu and the partitioning and transmutation of MA: HLW contain only FPs. The third scenario (F1j) relates to the multiple recycling of Pu and americium (Am) ; HLW contain FPs, curium and neptunium.

Nuclear power generation associated to these scenarios is assumed to be constant capacity of 60GWe (430TWhe/y): light water EPR^{TM}-type reactors with a total power of 40GWe would be implemented between 2020 and 2040, followed by sodium fast breeder reactors (SFR) with a total power of 20GWe between 2040 and 2050. The introduction of a second fleet of 40GWe SFR would take place from 2080 to replace the EPR^{TM} at the end of their assumed operating life. Starting in 2100, nuclear power capacity would consist entirely of fast breeder reactors. In scenarios # F1g and F1j transmutation of MA or Am would start in 2040 within SFR. Under these assumptions, HLW and intermediate level long-lived waste (ILW-LL) would be produced between 2038 and 2150 by two successive 60GWe NPP fleets and three reprocessing plants.

For the purposes of this study the packaging process of HLW is assumed to be identical to that used currently in the reprocessing plants at La Hague, namely vitrification and packaging in a stainless steel container (CSD-V). In addition ILW-LL include (i) operational waste from reactors, (ii) waste nuclear fuel structure, (iii) maintenance waste from nuclear fuel manufacturing and reprocessing. Most ILW-LL is considered packaged after compaction in stainless steel containers (CSD-C). Part of the waste issued from fuel manufacturing and reprocessing plants is supposed to be cemented in fiber concrete containers (CBF-C'2).

The study has been conducted in two phases between 2009 and 2012. The main objectives of the first phase (2009-2010) were (i) to compare the underground footprint and the excavated volume of the repository as a function of transmutation scenarios and (ii) to assess the impact of the interim storage period of HLW (70 years or 120 years). Based on the results obtained in 2009-2010, the second study phase (2012) focused on the identification of additional gains for the underground footprint. It included an analysis of the advantages and drawbacks of transmutation options on the long-term performance and safety of the geological repository.

2.   REPOSITORY DESIGN OPTIONS FOR HLW AND ILW-LL

2.1. *Waste disposal packages*

To prevent groundwater to leach vitrified HLW during the thermal phase (defined by a core temperature above 50°C to 60°C), each primary HLW package is placed individually in a watertight overpack. This overpack is made of non-alloy steel with a thickness dimensioned to withstand corrosion and in situ stresses.

To reduce the flow of waste packages transferred underground and facilitate handling, ILW-LL primary packages are grouped into disposal containers prior to their transfer to the underground facility. These parallelepiped concrete canisters ensure mechanical stability of waste packages with regard to their retrievability.

Waste disposal packages are shown on Figure 1.

2.2. *Repository cells*

2.2.1.   *HLW*

HLW repository cells consist of micro-tunnels with a diameter close to that of disposal packages, providing a small clearance for handling (see Figure 2). The repository cells are located in the middle part of the host clay layer. Access is provided by horizontal drifts. The repository cells are cased with a steel tube in order to ensure their dimensional stability. This architecture provides a physical and chemical environment conducive to long-term behaviour of nuclear glass.

An interim storage period is required for HLW to reduce their thermal power prior to disposal in order to limit thermal disturbances.
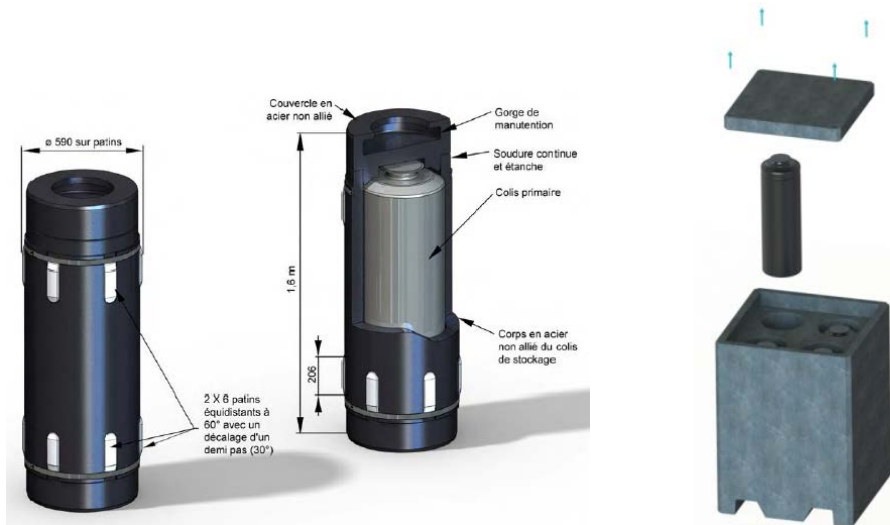

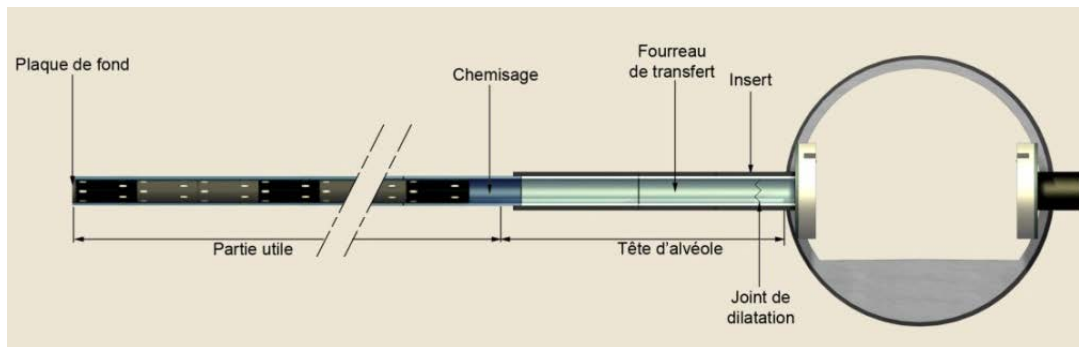**Figure 1 – Waste disposal packages (HLW are shown on the left, ILW-LL right)**

Figure 2 –Cross section of a HLW repository cell

After waste emplacement the heat generated by HLW is removed passively by conduction in the geological formation. As necessary, spacers can be placed between waste disposal packages to evenly distribute the heat flux density. Each cell contains a variable number of HLW packages according to the presence or absence of spacers. Distances between repository cells are ajusted to the thermal power of disposed HLW.

2.2.2. ILW-LL

ILW-LL are disposed of in horizontal tunnels. Because of the low thermal power of ILW-LL, a large number of waste disposal packages can be placed in each tunnel (Figure 3).
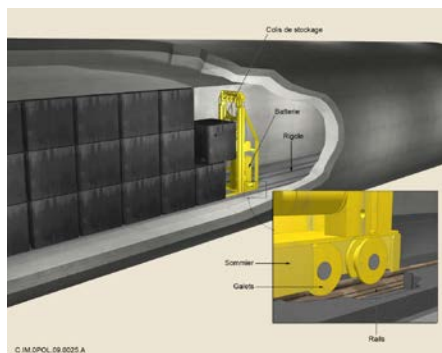
Figure 3 – Disposal tunnel for ILW-LL

2.3. Repository layout

HLW and ILW-W are disposed of in separate underground zones. This arrangement offers independence in terms of (i) the management of the various types of waste and (ii) the phenomenological behaviour of each zone, in view of the specific characteristics of the waste contained.

The repository cells are constructed progressively with waste emplacement, according to a modular architecture with provides for a strict separation between mining and nuclear activities.

The underground facility includes (Figure 4) :

- A common infrastructure built prior to the operational phase of the repository;
- A disposal zone for ILW-LL;
- A disposal zone for HLW.
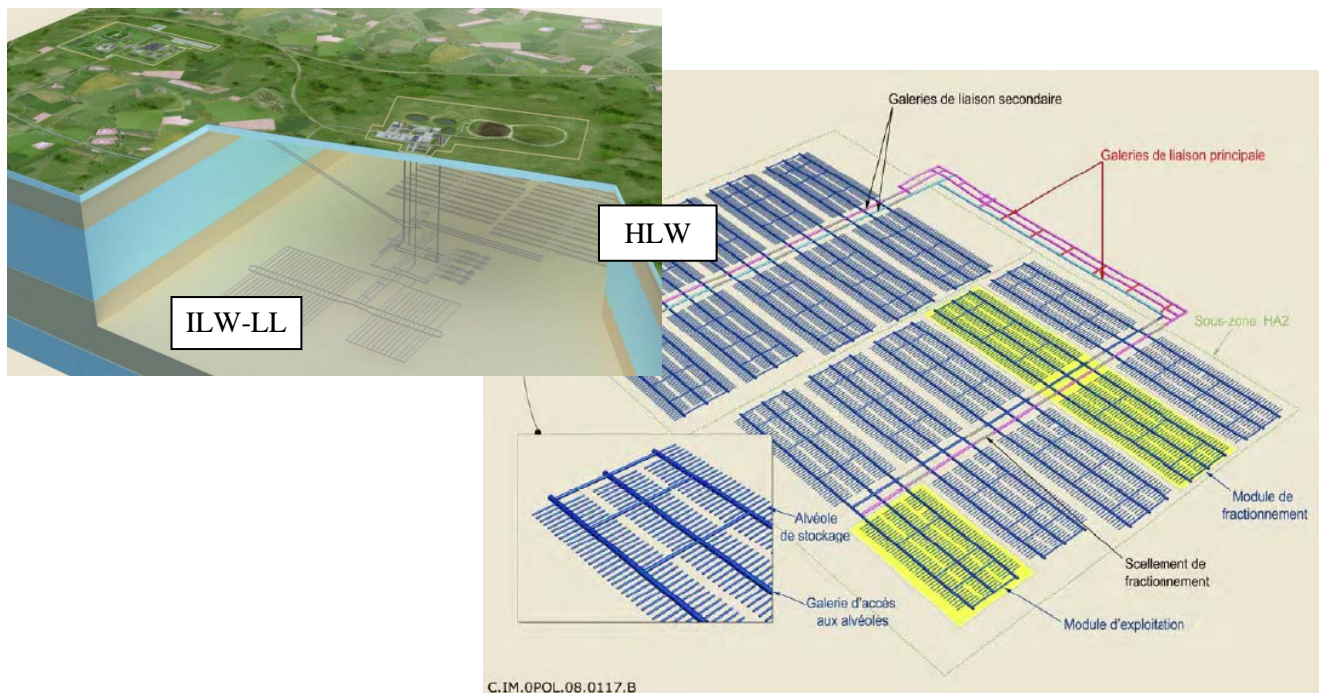
Figure 4 – Potential layout of the repository

3. THERMAL SIZING OF THE REPOSITORY

3.1. Thermal power of HLW

The evolution with time of the thermal power of HLW associated with scenarios F4, F1g and F1j is illustrated in Figure 5.

Differences in HLW thermal power between studied scenarios are mostly due to [241]Am, which is either present or not in the waste. Figure 5 shows that the incorporation of minor actinides in HLW significantly slows the heat decay with time (F4). It should be noted that beyond a storage period of 120 years, the transmutation of minor actinides (F1g) or Am only (F1j) results in a difference of thermal power not exceeding 20W. The radiological profile and thermal power of F4 HLW are close to HLW as produced by the co-reprocessing of UOX/MOX PWR fuels.

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3.2. HLW repository cell design

The temperature of the host rock induced by HLW heat should be limited to avoid disturbances of safety functions. Therefore a maximum temperature of 90°C in contact with the host formation is specified. Sizing of repository cells consists of the determination of the three following parameters with regard to (i) temperature limit, (ii) residual thermal power of HLW after interim storage (Figure 6):

- number (N) of waste packages per repository in relation with their spacing;
- distance between two adjacent cells (Px);
- distance between bottom cells (Dy).

The thermal design is achieved by finite elements calculations. Heat transfer modes taken into account are conduction (predominant in the rock), advection and radiation. N decreases and Px increases with HLW heat. The combination of these parameters provides the footprint of the HLW disposal zone which increases with more exothermic waste.
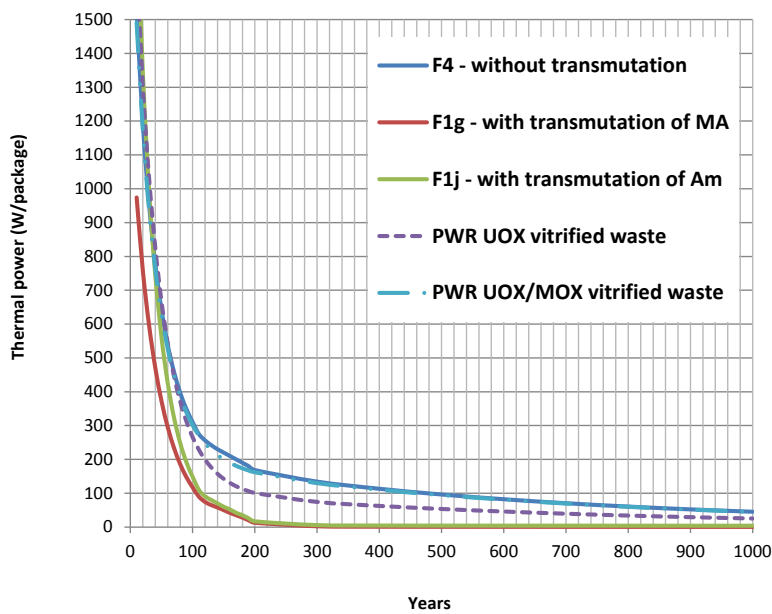
Figure 5 - Residual thermal power of HLW packages (CSD-V)
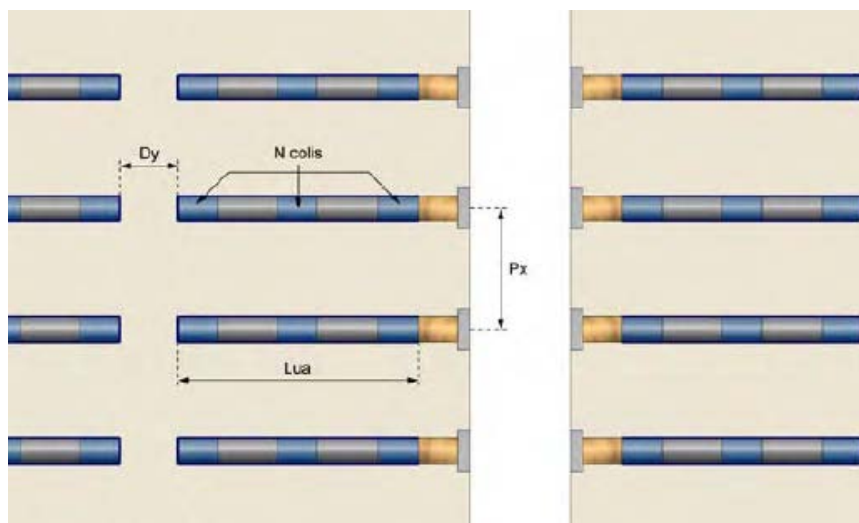
Figure 6 - Thermal design parameters

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4.   REPOSITORY UNDERGROUND ARCHITECTURES

Figure 7 shows underground architectures associated to scenarios F4 and F1g for an interim storage period of 70 years. These results come from the first study phase (2009-2010).

| Whitout transmutation (F4) | With transmutation of MAs (F1g) |
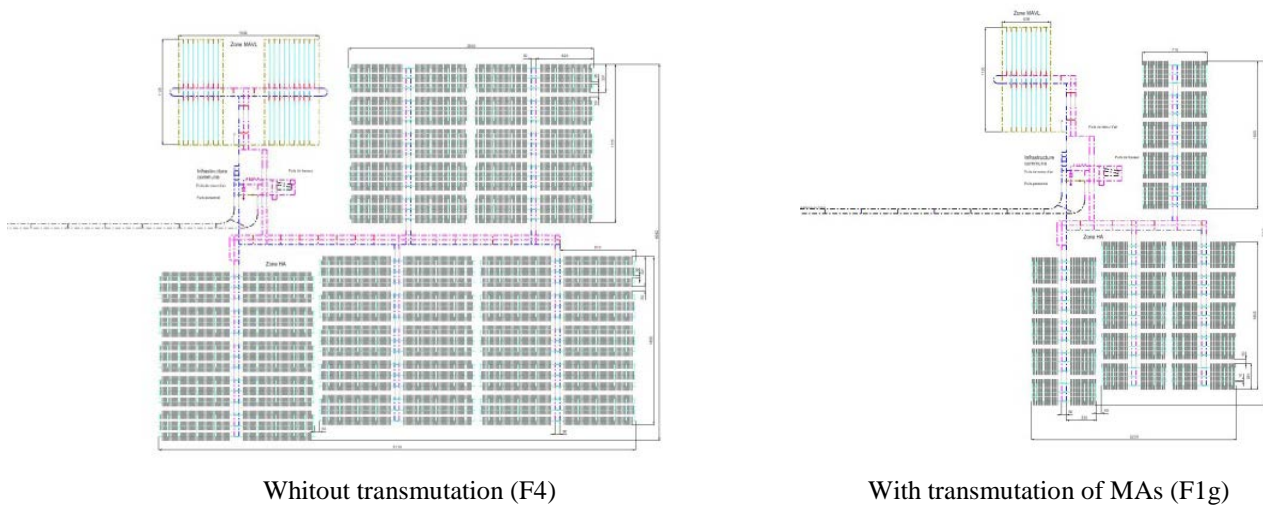
Figure 7 – First study phase: underground repository architectures for various scenarios with an interim storage period of 70 years

Compared to the multiple recycling of plutonium, the partitioning and transmutation of actinides provide (i) a reduction by a factor of 2 (Am) to 2.5 (MAs) of the footprint of the HLW zone, (ii) a reduction of 30% (Am) to 40% (MAs) of the excavated rock volume.

In the F4 scenario, the first study phase concluded that an increase of the interim storage period from 70 to 120 years would provide a gain of 25% on the footprint of the HLW zone and 7 % on the total excavated volume. The presence of americium in the waste restricts the densification of the repository because of a relatively low decay of the thermal power with time due to the long radioactive half-life of americium 241.

In the case of the transmutation of all minor actinides (scenario F1g), the increase of the interim storage period to 120 years allows a larger gain (60%) of the footprint of the HLW zone and 12% of the overall volume excavated.

Based on the results of the first study phase, the second study phase (2012) consisted of a search for ways of optimizing the design with the objective of a more drastic decrease of the repository footprint. This second phase has considered only an interim storage period of 120 years for HLW. Indeed this assumption associated with transmutation scenarios provides a significantly higher gain than a 70 years interim storage period. Such period nevertheless raises the question as follows: is it realistic to consider an interim storage period higher than 100 years?

Figure 8 shows the repository layout as a result of the second study phase.

Compared to the multi-recycling of plutonium in SFR, the transmutation of MAs associated with a design optimization of the repository would provide:
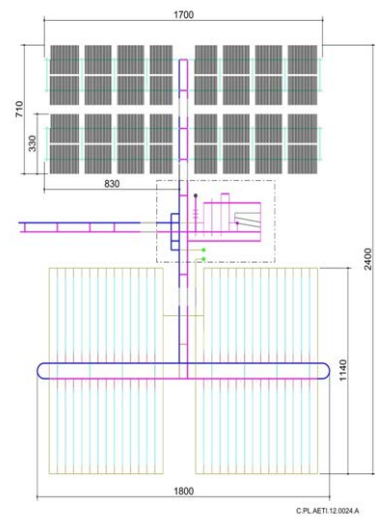
-    a reduction by a factor up to 7.3 (Am) to 9.8 (MAs) of the footprint of the HLW disposal zone after an interim storage period of 120 years;
-    a total reduction by a factor 3 of the repository footprint taking into account ILW-LL and common infrastructures;
-    a total reduction by a factor 2 of the excavated rock volume.

Note that in scenarios F1j and F1g the footprint of the ILW-LL disposal zone is equal to or higher than the optimized footprint of the HLW disposal zone.

Without transmutation (F4)
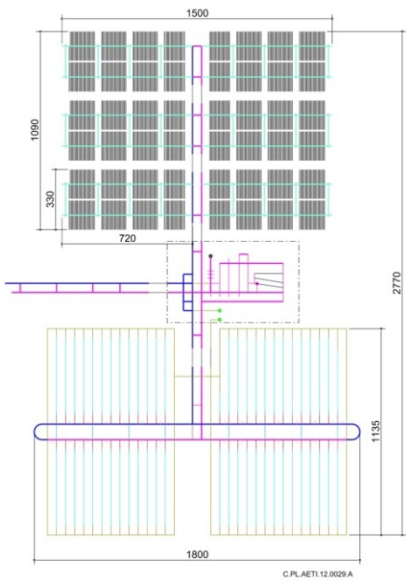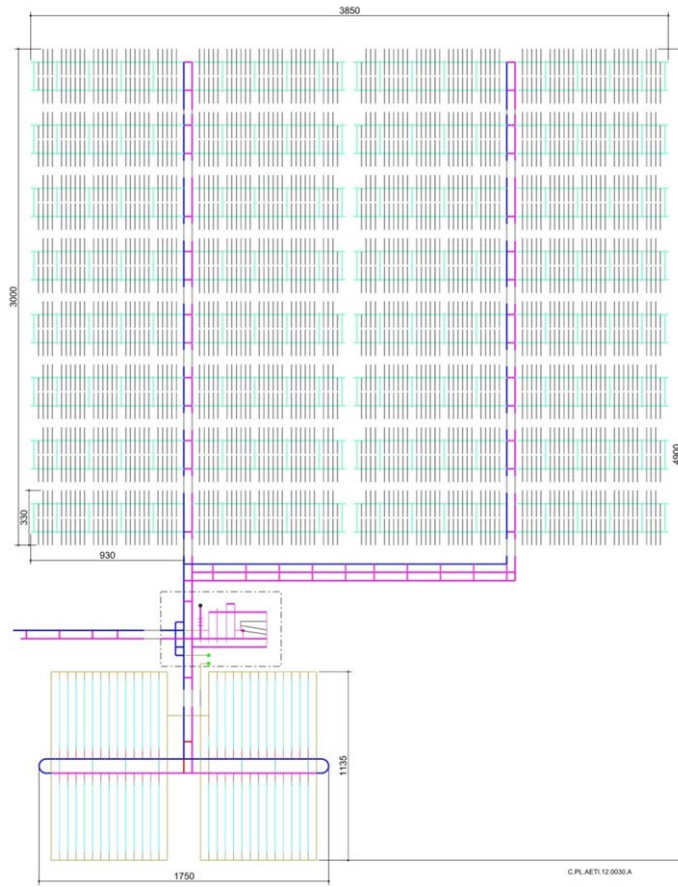
With transmutation of Am (F1j)

With transmutation of MAs (F1g)

Figure 8 – Second study phase: underground repository architectures for various scenarios with an interim storage period of 120 years

5. SAFETY ISSUES

Along with a reduction of the footprint of the HLW disposal zone, the partitioning and transmutation of actinides also decrease the duration of the thermal phase. After an interim storage period of 120 years, the thermal phase is reduced to about 200 years against thousand years without transmutation.

However, this reduction does not result in a significant gain in the energy density delivered by the repository to the host formation. Instead, the long term energy density may increase up to a factor of 2 depending on the scenario.

More generally the consequences of partitioning and transmutation on the long term safety functions of the repository have been assessed in a preliminary approach, taking into account the potential densification of the repository.

The partitioning and transmutation of actinides do not reduce the long term radiological impact of the deep geological repository. Indeed this impact is dominated by long lived fission and activation products (APs) with a higher mobility in the geosphere (iodine 129, chlorine 36).

In the normal long term evolution safety scenario, the study shows that the densification of the repository as allowed by partitioning and transmutation does not significantly change the radiological impact of fission and activation products, despite concentrations in the near field increase with densification.

In an altered evolution scenario such as intrusive drilling, the impact of FPs and APs may increase to some extent because of the densification of the repository. Nevertheless this impact remains acceptable with regard to the dose limit provided by the basic safety guide issued by the French nuclear safety authority (0.25mSv/y).

Modeling of extraction chromatographic reprocessing-partitioning processes

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Abstract. A numerical code was developed to simulate extraction chromatographic reprocessing-partitioning processes. The mathematical model considers axial dispersion in the fixed bed and the two-films approach to represent the mass transfer kinetics. Several correlations to estimate distribution coefficients were used to simulate different extraction systems. The mass transfer coefficients were obtained fitting simulated curves with the experimental data. Simulations of Uranium - Plutonium - HNO_3 - fission products - tri-*n*-butyl phosphate (TBP) extraction chromatographic system were carried out and compared with laboratory experiments using actual irradiated uranium target solution as tracer. The separation and recovery of lanthanides and actinides elements, from simulated raffinate solution containing Am and Eu tracers, in the octylphenyl-N,Ndiisobutylcarbamoylmetylphosphine oxide (CMPO) - tri-*n*-butyl phosphate (TBP) - HNO_3 extraction chromatographic system, was simulated too. The simulated elution profiles were in agreement with the experimental data obtained.

INTRODUCTION

In the development of advanced nuclear fuel cycles, it is necessary to improve spent nuclear fuel reprocessing processes. Partitioning and transmutation strategies based on Fast Reactors cycles systems requires Minor Actinides from Lanthanides separation steps. Several selective extractants and different separation schemes have been proposed to address these objectives[1].

Solvent extraction is the preferred technique employed in spent nuclear fuel reprocessing. Extraction chromatography combines the selectivity of solvent extraction with easer operation and more compact equipments emerging as an alternative to be studied for many process purposes.

Over the last decades, several chromatographic processes has been proposed to the reprocessing of spent nuclear fuels on an industrial scale. Many of them, directly related to the fast reactors fuels reprocessing and partitioning processes. In the early eighties European researchers proposed different flow-sheets for the so called "chromex processes"[2]. More recently Japanese researchers developed many chromatographic processes[3][4]. The ERIX (Electrolytic reduction and ion exchange process for reprocessing spent FBR-MOX fuel) process involves many chromatographic steps including U, Pu and Np recovery using ion chromatography and Minor Actinides MA(III) and Lanthanides Ln(III)

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separation using extraction chromatography. The MAREC process (Minor Actinides Recovery from HLLW by Extraction Chromatography) has been proposed to treat High Level Liquid Wastes (HLLW) in order to separate MA and Ln.

As in any other process operation, it is desirable to have a simulation tool to design and optimize operation parameters and conditions. In this work a numerical code developed to simulate extraction chromatographic processes is presented and its results compared with experimental data.

MODEL DESCRIPTION

In the model axial dispersed flow is considered to describe the mobile phase flow inside the chromatographic column. Along the total length of the column, the axial dispersion coefficient is considered to be constant. The column is assumed to be unidimensional, this means that no radial dispersion is considered. It means that the chromatography is treated as non-ideal and non-linear[5].

The system is considered as isothermal. It is, no thermal effects are having into account and no energy balance are included into the model.

The mass transfer kinetics is described by the use of the linear driving force approximation[8][9]. Two mass transfer coefficients are required in this description. One to represent the mobile phase mass transfer resistant and the other to represent the intraparticle mass transfer into the stationary phase.

GOVERNING EQUATIONS

Differential mass balance equations

Equation (1) represents the differential mass balance along the column. This describes the solutes balance in the mobile phase.

$$\frac{\partial C_i}{\partial t} = D \cdot \frac{\partial^2 C_i}{\partial z^2} + v \cdot \frac{\partial C_i}{\partial z} - E \frac{\partial S_i}{\partial t} \tag{1}$$

Where,

C_i: Mobile phase concentration of the i-th component.
S: Stationary phase concentration of the i-th component..
t: time.
z: Spatial coordinate along the column axis.
D : Dispersion coefficient.
v : velocity of the mobile phase into the inlet of the column.
E : Coefficient of extractant concentration.

The coefficient E express the extractant concentration in the column. Its expression depends on the equilibrium relationship used in each case. If the equilibrium is given based on extractant loaded into the stationary phase the coefficient will be the concentration of the extractant into the column. In the case that the equilibrium is based on the mass of stationary phase, this coefficient will be the apparent density of the fixed bed.
Equation (2) represents the differential mass balance in the stationary phase. This describes the interfacial solute mass transfer between the mobile and the stationary phase.

$$\frac{\partial S_i}{\partial t} = \eta \cdot \left(S_i^* - S_i \right) \tag{2}$$

2

Where,

η: Mass transfer coefficient.
S_i^*: Equilibrium concentration of the i-th component.

$$S_i^* = S(C_1, C_2, ..., C_n) \tag{3}$$

Equation (3) represent the equilibrium relationship between every component. The complete set of equations in the model are n equations (1) plus n equations (2) coupled through equation (3). The solution of this partial differential equations system gives the evolution of the concentration profiles of every component over the time.

In this simulation the equation system is numerically solved using an implicit finite differences scheme. The code was written using Octave language [6].

Initial and Boundary conditions

The boundary conditions adopted are expressed in the equations (4) and (5).

$$z = 0 \; ; \; C_i = C_{inlet} \tag{4}$$

$$z \to \infty \; ; \; \frac{\partial C_i}{\partial z} = 0 \tag{5}$$

Where,

C_{inlet} : Solute inlet concentration.

The initial conditions are expressed in the equation (6).

$$t = 0 \; ; \; C_i(z) = C_{i0}(z) \; ; \; S_i = S_i^*\left(C_{10}, C_{20}, \ldots, C_{n0}\right) \tag{6}$$

Where,

$C_{io}(z)$: Initial concentration profile into the mobile phase.
S_i : Initial concentration profile into the stationary phase.

Equation (6) shows that the initial conditions considers that the stationary phase is equilibrated with the mobile phase at the beginning of the simulation.

Equilibrium relationships

Depending on the processes to be simulated, many different equilibrium relationships has been used. In the case of U-Pu-HNO$_3$-TBP system the correlation described by W. Groenier, et al [7]was tested with good results. To simulate fission products equilibrium, experimental data has been empirically correlated. Zr, Ru and Nb equilibrium correlations were obtained.

In the case of the simulation of the MA-Ln-CMPO-TBP system, Europium and Americium correlations were obtained from batch contact experiments. The contacts contacts were made using Eu-152 and Am-241 as tracers and RE™ resin from Eichrom Technologies, Inc. The batch contacts were maintained 48h in a thermostatic bath at 25ºC constant temperature. Contacts solutions were filtrated and the filtrates were analyzed using gamma ray spectrometry with a HPGe 20% efficiency detector. *FIG. 1* shows the distribution coefficients obtained and the correlation curves fitted in the contact experiences. Data were fitted using an empirical expression using least squares minimization.
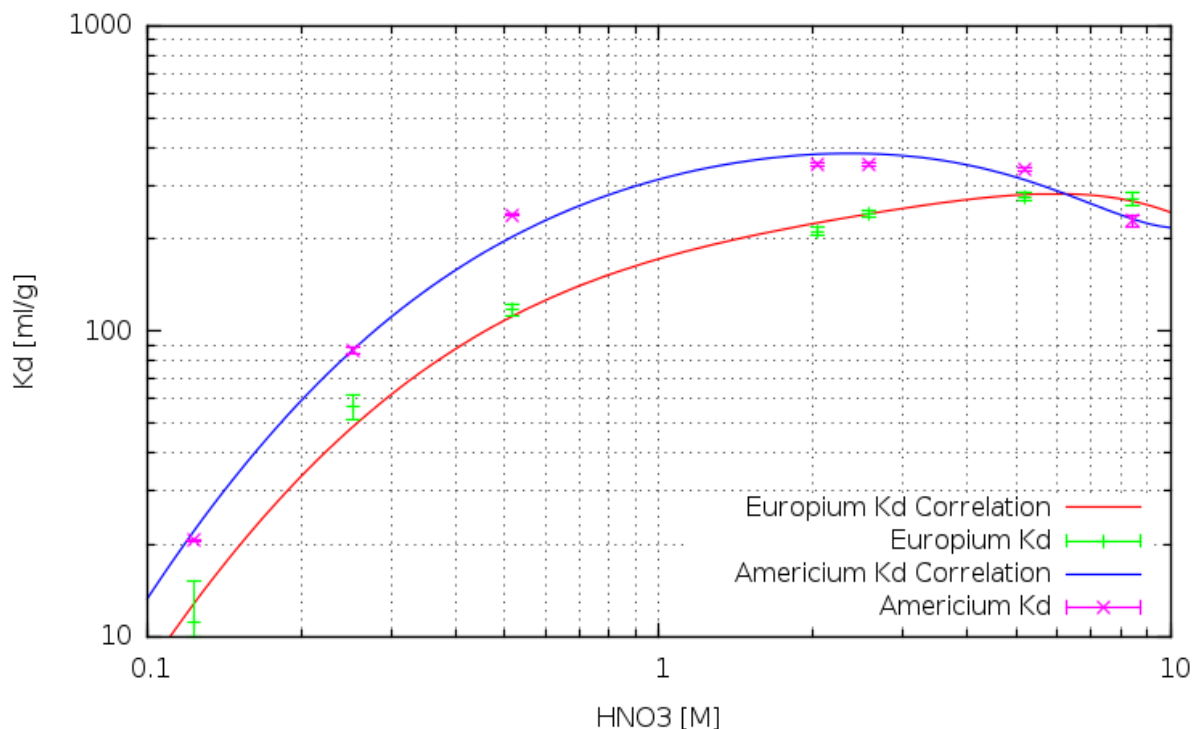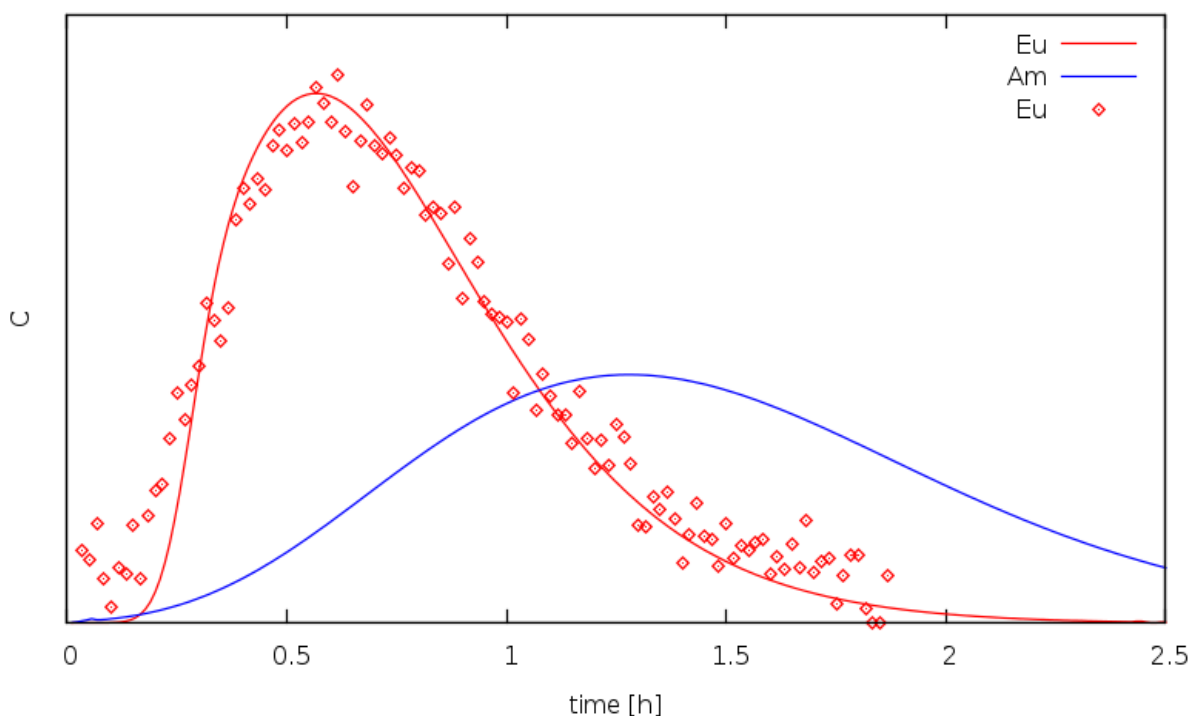
FIG. 1. **Am- Eu- octylphenyl-N,Ndiisobutylcarbamoylmetylphosphine oxide (CMPO) - tri-*n*-butyl phosphate (TBP) - HNO$_3$ distribution coefficients.**

EXPERIMENTAL

In this section two column experiences are described. They were made in order to compare experimental results with the simulation code outputs. The first experience was made to study the behavior of the U-Pu-HNO$_3$-Tri-*n*-butyl-phosphate system using actual irradiated uranium target as fission products tracer solution.

U-Pu-HNO$_3$-Tri-n-butyl-phosphate system

The column used during this experience was packed using a resin prepared with Tri-*n*-butyl-phosphate as extractant loaded in an inert support as stationary phase. The support material chose was Amberlite™ XAD-7 HP from Rohm and Haas Company.

The column was loaded with a solution of UO$_2$(NO$_3$)$_2$ 100 g/l in 5M HNO$_3$. The solution was traced with actual irradiated uranium target solution. After loading the column was washed with 5M HNO$_3$ solution and finally the uranium was eluted with 0,05M HNO$_3$. Between loading and washing the column was left overnight.

During the run, samples were taken. The samples were analyzed using gamma ray spectrometry with a HPGe 20% efficiency detector. *FIG. 2* shows the the data analysis results compared with the code output.

The numerical simulation describe the column behavior very well. The simulation parameters (axial dispersion coefficient, fixed bed porosity and mass transfer coefficients) were adjusted using this experimental results.
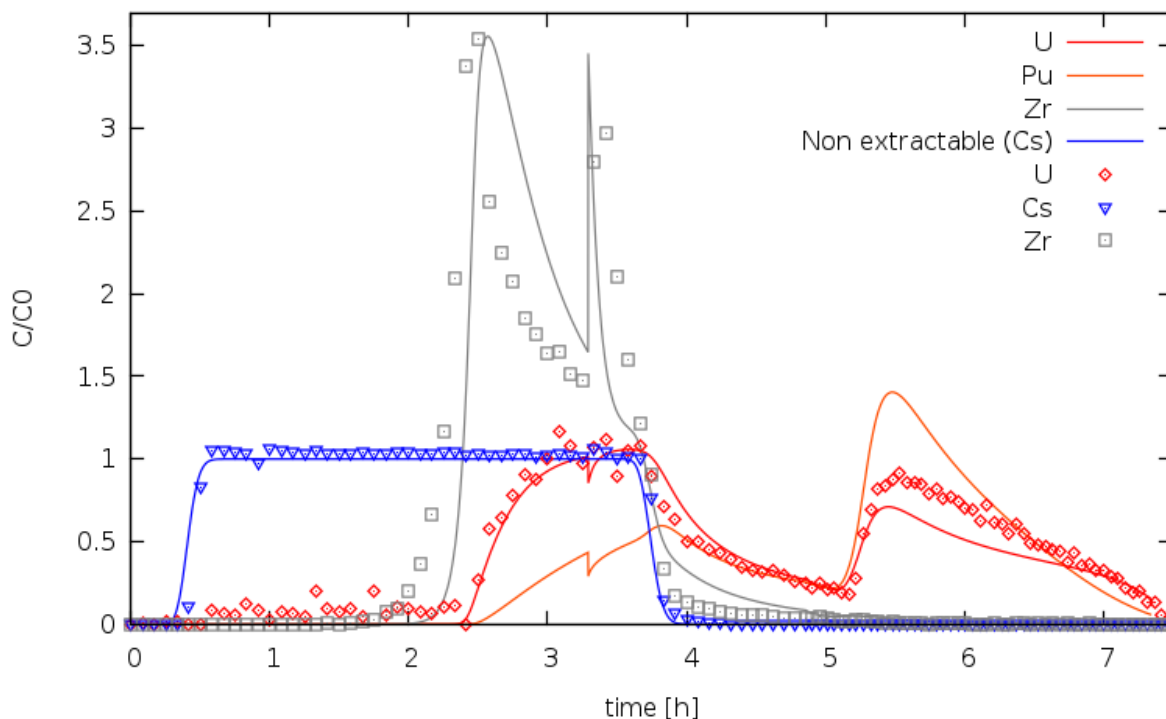
FIG. 2. **U-Pu-HNO$_3$-Tri-n-butyl-phosphate column experience and simulation.**

Simulated HLLW

This experiment was made using a column packed with RE™ resin from Eichrom Technologies, Inc as stationary phase. This resin contains octylphenyl-N,Ndiisobutylcarbamoylmetylphosphine oxide (CMPO) - tri-*n*-butyl phosphate (TBP) as extractants. The was loaded with a 5M HNO$_3$ solution traced with Cs-137, Eu-152 and Am-241 simulating the raffinate obtained in the previous experience.

The column was eluted with 0,5M HNO$_3$ and the elution solution was measured on line with cell-flow and a NaI(Tl) detector system. *FIG. 3* shows the experimental results compared with the simulation code output.

FIG. 3. **Am- Eu- octylphenyl-N,Ndiisobutylcarbamoylmetylphosphine oxide (CMPO) - tri-*n*-butyl phosphate (TBP) - HNO$_3$ column.**

CONCLUSIONS

The numerical simulation predicts the behavior of the extraction chromatographic processes in good agreement with the experimental data. The mass transfer model applied describes very well the phenomena occurring during the processes. No more detailed description of this phenomena seams to be necessary.

The equilibrium relationships used in the examples presented are base on purely empirical correlations of experimental distribution coefficients data. More effort should be devoted to obtain and improve equilibrium correlations. It is desirable to obtain correlations based on a better understanding of the chemical phenomena involved in the processes to be simulated.

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Mock-up Granulation Experiments for the Simplified MOX Pellet Production Process

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Abstract. The Japan Atomic Energy Agency has been developing a granulation system to improve flowability of MOX powder, as a part of project on the simplified MOX pellet production process. In the previous paper, we demonstrated the experimental results obtained by the top-drive agitation granulator of bench-top scale which can granulate powder in a dish used in microwave de-nitration. In this study, the scale of the granulator was enlarged to industrial scale (5kgHM/batch), and the performance of the granulator was investigated with WO_3 powder. The mass of collected granules after the granulation experiments exceeded 90 wt.% of mass of charged powder and sprayed water. The maximum yield of granules of appropriate sizes was obtained at 4 minutes in granulation time, when the moisture content was 15 wt.% and the rotational speed of agitator was 150 min.$^{-1}$. But it was considered to be practically difficult to stop the granulator exactly at the peak time, because the yield curve changed drastically in several tens of seconds around the narrow peak. As an alternative method to obtain granules of appropriate sizes, crushing of over-granulated coarse granules with a sizing machine was examined. The maximum yield of granules of appropriate sizes with the sizing machine was 70.7 wt.%, when rotational speed of rotating ring was 2000 min.$^{-1}$ and the clearance between rotating ring and fixed stator was 0.5 mm. It was found that the performance of the sizing machine changed gradually according to operational conditions. The method with the sizing machine was evaluated to be more realistic than the method without sizing machine from standpoint of stable production.

1. Introduction

As a part of the Fast Reactor Cycle Technology Development Project (FaCT Project), the Japan Atomic Energy Agency has been developing the simplified MOX pellet production process[1][2]. In this process, MOX powder is made from mixed solution of plutonium and uranyl nitrate by a sequential heating process, which is composed of de-nitration conversion based on microwave heating, calcination and reduction. The fine MOX powder smaller than several micrometers in diameter, which is produced by this heating process, is appropriate for sintering of pellets, but it is not easy to fill dies with the fine powder smoothly. It is also difficult to prevent fine powder from scattering in glove boxes.

For purpose of improving flowability of MOX powder, an agitation granulation was applied after the reduction process[3][4]. To minimize scatter of fine powder, we proposed to handle and process MOX powder in a silicon nitride dish for microwave heating until the completion of the granulation process[5]. In the previous paper[6], we demonstrated the calcination and reduction of uranium oxides in a silicon nitride dish successfully. We also developed a specially designed top-drive agitation granulator of bench-top scale which can combine with the dish, and demonstrated granulation of UO_2 powder in the dish successfully.

In this paper, the agitation granulator was enlarged to industrial scale (5kgHM/batch), and a series of parametrical granulation experiments with dummy MOX powder (WO_3) were conducted to know the performance of the granulator. As an alternative method to control size distribution of granules, the

performance of sizing machine to crush over-granulated coarse granules was also investigated with the WO_3 granules, which was fabricated by the agitation granulator. The ability of stable production of granules of the apporoproate sizes with the sizing machine and without the sizing machine were compared.

2. Experimental

2.1 Experimental set up

2.1.1 Top-drive agitation granulator

   Figure 1(a) and **(b)** show a photograph and an outline drawing of the top-drive agitation granulator. The inner diameter of a granulation vessel is 600 mm. The granulation vessel consists of an upper stainless cylinder and a lower detachable de-nitration dish. In this experiment, a stainless dish was used instead of silicon nitride dish which is employed for microwave de-nitration. To reduce attached powder on the wall of granulation vessel, a scraper takes attached powder off the vessel during granulation operations. A binder spray unit was used to add water to powder in the vessel.

(a) Photograph   *(b) Outline drawing*
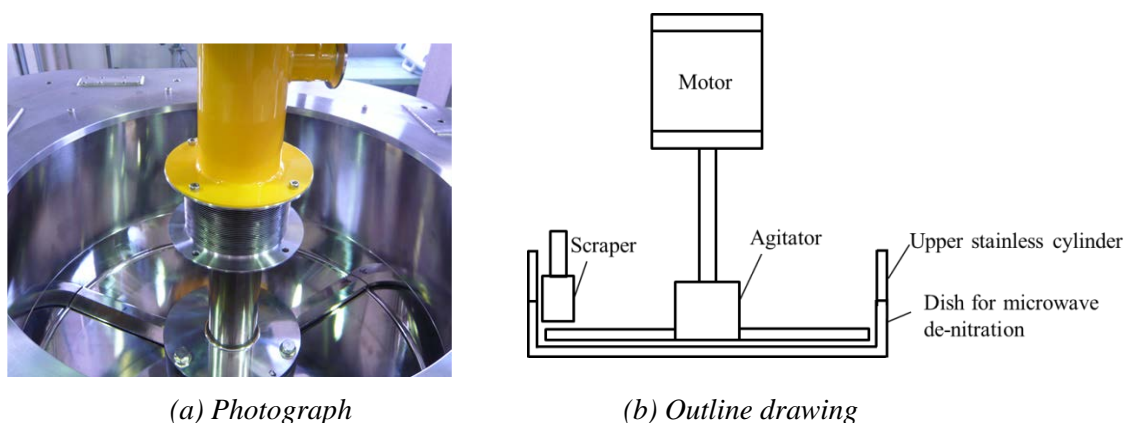
Figure 1. Photograph and outline drawing of the top-drive agitation granulator of industrial scale.

2.1.2 Sizing machine

   A sizing machine (Nara Machinery Co., Ltd. type Nebulasizer NS-20) was employed to adjust sizes of granules after granulation. **Figure 2** shows an outline drawing of the sizing machine[7]. This machine crushes coarse granules by a rotating ring. The granules, whose sizes are smaller than a clearance between the rotating ring and fixed stator, are ejected from an outlet.
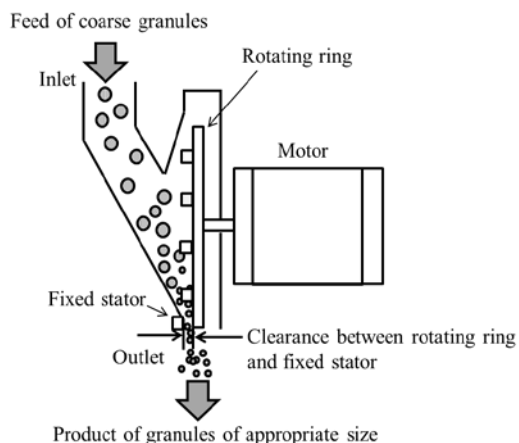
Figure 2. Outline drawing of sizing machine.

2.1.3 Analyzing equipment

An incubator was used to dry granules for size distribution measurements. The size distributions of dried granules were measured by a mechanical shaker (Tanakakagakukikai Corp. type R-1).

2.2 Experimental procedures

2.2.1 Granulation experiments with the top-drive agitation granulator

To investigate the performance of granulator, parametrical experiments were conducted by using the top-drive agitation granulator. The parameters were moisture content, which is defined as ratio of mass of sprayed water to dry mass of charged WO_3 powder, and rotational speed of agitator. The parameters tried in the experiments are summarized in **Table 1**.

Table 1. Experimental parameters of granulation experiments.

Run	Moisture content (wt.%)	Rotational speed of agitator (min.$^{-1}$)
G1	15	150
G2	14	150
G3	13	150
G4	15	200
G5	15	100

At first, 5kg of WO_3 powder (A.L.M.T.Corp. type F1-WO_3) , whose nominal diameter is 0.5-1.2 μm, were poured in the granulation vessel. A nozzle of the binder spray unit was set about 50 mm above the WO_3 powder layer in the granulation vessel. Rotating the agitator at 100 min.$^{-1}$ and the vessel at 20 min.$^{-1}$ in rotational speed, purified water was sprayed from the nozzle at a rate of 150 mL/min. until the moisture content was reached at experimental parameter.

After completion of water spray, granulation operation was started by increasing the rotational speed of agitator up to experimental parameter. To sample WO_3 granules for size distribution measurements, operation of the granulator was intermitted several times during the granulation operation. In each intermission, WO_3 granules of 120 g were sampled with a spatula, which was a mixture of 40 g from 3 different positions in the granulation vessel.

The dish was detached from the granulator after the granulation operation. WO_3 granules were collected by turning over the dish and by sweeping the dish softly with a brush. The weight and the size distribution of the collected granules were measured. Remained attachment in the dish was cleaned up by pressing a dedicated scraper to the rotating dish at 20 min.$^{-1}$ in rotational speed.

2.2.2 Sizing experiments

A series of sizing experiments was carried out to know the performance of the sizing machine by changing the rotational speed of rotating ring and the clearance between rotating and fixed stator. The parameters used in the experiments are summarized in **Table 2**.

Table 2. Experimental parameters of sizing experiments.

Run	Clearance (mm)	Rotational speed of rotating ring (min.$^{-1}$)
S1	0.7	1000
S2	0.7	2000
S3	0.7	3000
S4	0.5	2000
S5	1.0	2000

Wet WO_3 granules of 200 g, which were prepared by the granulator, were fed in the inlet of the sizing machine manually. Supply rate of the WO_3 granules was controlled appropriately by monitoring the value of electrical current and the situation of powder attachment in the machine during operation. The ejected granules, which were processed by the sizing machine, were collected into a stainless container. The measurements of size distribution of the granules were carried out.

3. Results and discussion

3.1 Granulation experiments with the top-drive agitation granulator

Figure 3 shows the change of view inside the granulation vessel with the progress of granulation, when the moisture content is 15 wt.% and the rotational speed of agitator is 200 min.$^{-1}$. WO_3 granules were uniformly distributed on the bottom of granulation vessel at 1 min. An area without WO_3 granules appeared in the center of the granulation vessel at 2 min., and expanded with granulation time. So, the granules had a tendency to move in the direction to wall of the granulation vessel with progress of granulation.
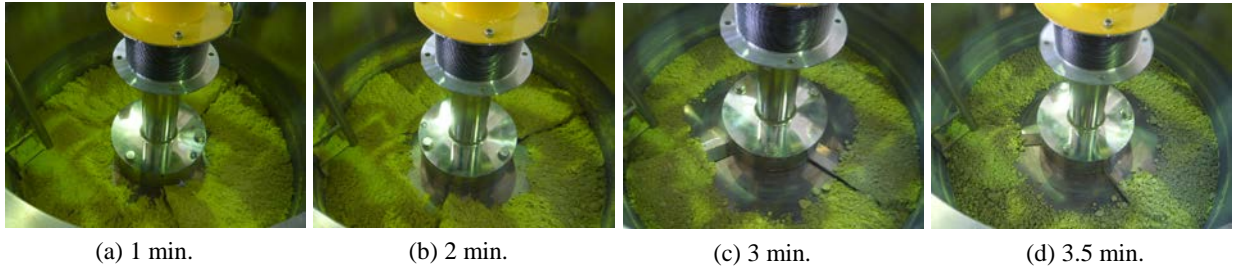
| (a) 1 min. | (b) 2 min. | (c) 3 min. | (d) 3.5 min. |

Figure 3. Change of view inside granulation vessel with progress of granulation time.

Moisture content: 15 wt.%, Rotational speed of agitator: 150 min.$^{-1}$.

Figure 4 (a) and **4 (b)** show the photographs of the granulation vessel after granulation and after collection of granules respectively. It was found that the attachment remained at the corner of the dish and the stop location of agitator.
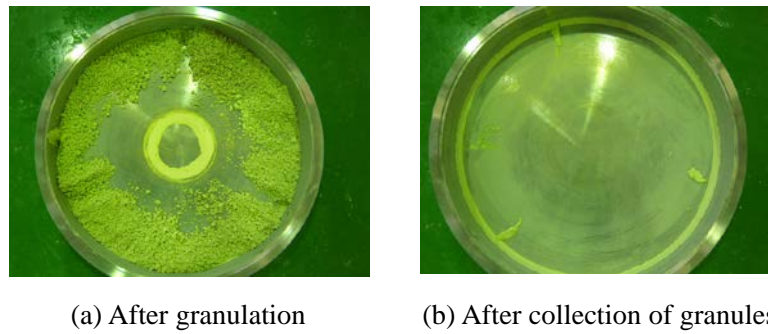

| (a) After granulation | (b) After collection of granules |

Figure 4. Photographs of de-nitration dish

The collection ratio (C) of the granulation experiments is defined

$$C = \frac{M_g}{M_p + M_w}$$

where M_g is mass of collected wet WO_3 granules, M_p is dry mass of charged WO_3 powder before granulation experiment, and M_w is mass of sprayed water. The collection ratio obtained in the granulation experiments are summarized in **Table 3**. All experimental results on the collection ratio exceeded 90%.

Table 3. Collection ratio of granulation experiments.

Run	Collection ratio (wt.%)
G1	94.6
G2	92.6
G3	94.2

G4	94.3
G5	94.6

Figure 5 exhibits the relation between mass median diameter of the WO_3 granules and granulation time, when the rotational speed of agitator is 150 min.[-1]. The median diameter increased as granulation time increased. The curve of 15 wt.% in moisture content increased most rapidly, and the curve of 14 wt.% increased next. In case of 13 wt.%, the granulation was not preceded after 30 minutes of granulation operation, though the granules were obtained in bench-top scale experiments in the previous paper[6]. So the granulation rate tended to be larger as the moisture content increased, and the industrial scale granulator required more moisture content than the bench-top scale granulator.

Figure 6 denotes the mass median diameter dependence on granulation time, when the moisture content is 15 wt.%. The all curves increased with the progress of granulation in order of 200 min.[-1], 150 min.[-1], and 100 min.[-1] in rotational speed of agitator. So the granulation rate was increased with the rotational speed of agitator increased.
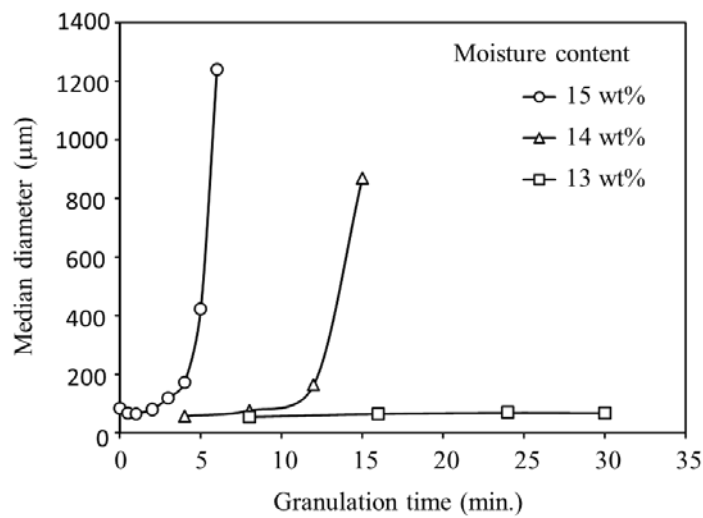
Figure 5. Relation of mass median diameter of WO₃ granules and granulation time.

Rotational speed of agitator: 150 min.[-1].
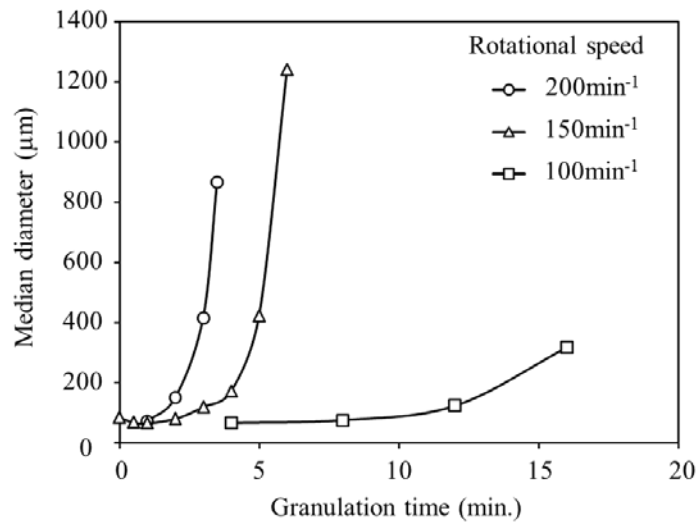
Figure 6. Mass median diameter dependence on granulation time.

Moisture content: 15 wt.%.

The Yield (Y) is expressed

$$Y = \frac{m}{M}$$

where m is dry mass of sampled WO_3 granules which belong to a specific diameter range, M is dry mass of sampled WO_3 granules.

Figure 7 shows the yield of granules of 100-500 μm in diameter as a function of granulation time at 150 min.[-1] in rotational speed of agitator. In this research, we assumed that the granules of 100-500 μm in diameter were suitable to fill annular dies, because fine powder smaller than 100 μm in diameter degrades flowability and coarse granules larger than 500 μm in diameter are too large to fill gap of about 4mm between die wall and center rod. In case of curve of 15 wt.% in moisture content, the yield showed local minimum in the beginning of granulation operation, because fragile aggregates, which were formed by water spray before granulation operation, were pulverized by increasing rotational speed of agitator. Then the yield increased with operation time, because the amount of fine powder decreased with progress of granulation, but the yield decreased after reaching maximum value, because of the accumulation of coarse granules larger than 500 μm in diameter. The curve of 14 wt.% was similar to that of 15 wt.%, but the time of peak value was delayed, and the peak width was enlarged. The yield curve of 13 wt.% in moisture content was almost flat, because growth of granules was not observed.
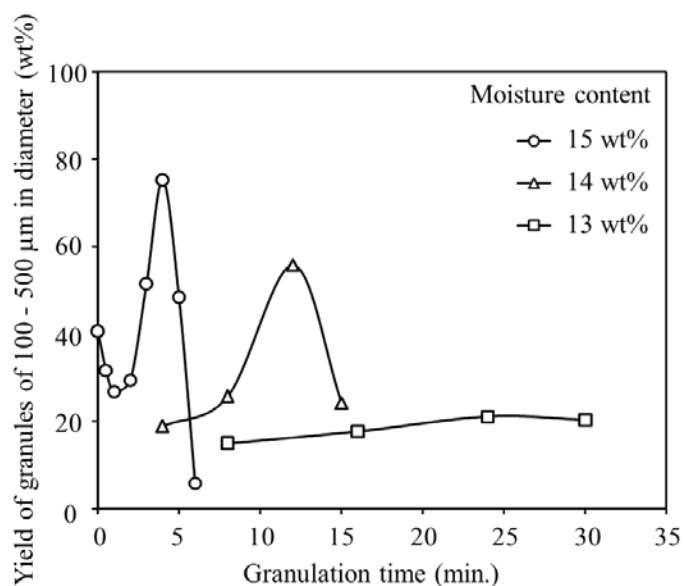
Figure 7. Relation of yield of granules of 100 - 500 μm in diameter and granulation time.

Rotational speed of agitator: 150 min.$^{-1}$.

Figure 8 indicates the relation between the yield of granules of 100-500 μm in diameter and granulation time, when the moisture content is 15 wt.%. In case of the curve of 200 min.$^{-1}$ in rotational speed of agitator, the yield of 100-500 μm increased with the progress of operation time at first and then decreased after peaking. The curve of 150 min.$^{-1}$ was similar to that of 200 min.$^{-1}$, but the peak time was delayed, and the local minimum was observed at a few minutes, because of the pulverization of fragile aggregates. The curve of 100 min.$^{-1}$ increased monotonously, because the operation of the granulator was ended before peaking.

From **Figure 7** and **Figure 8**, the peak time and the peak width of curve tended to be decreased when the moisture content and rotational speed of agitator increased. The maximum yield of granules of 100-500 μm in diameter in a series of the parametrical experiments was 75.2 wt.%, when the moisture content was 15 wt.% and the rotational speed of the agitator was 150 min.$^{-1}$. In this condition, it is expected to produce granules of appropriate sizes effectively, if the granulator is operated for 4 minutes. But it is necessary to control granulation endpoint exactly by such as online monitoring of size distribution of granules in granulation vessel, because the yield curve changed drastically in several tens of seconds around the narrow peak. Besides we have to control moisture content precisely, because only 1 wt.% difference of moisture content influenced much on the yield curves. So, stable production of granules of appropriate sizes in good yield only by the agitation granulator was evaluated to be practically difficult.
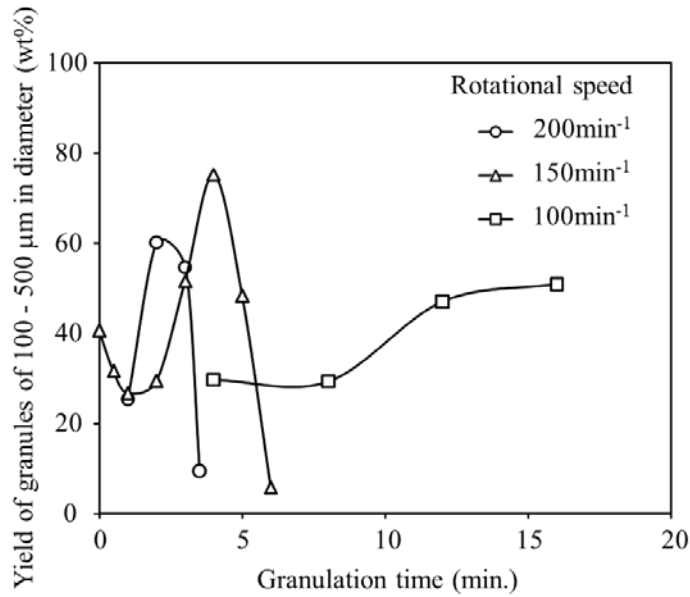
Figure 8. Relation of yield of granules of 100 - 500 μm in diameter and granulation time.

Moisture content: 15 wt.%.

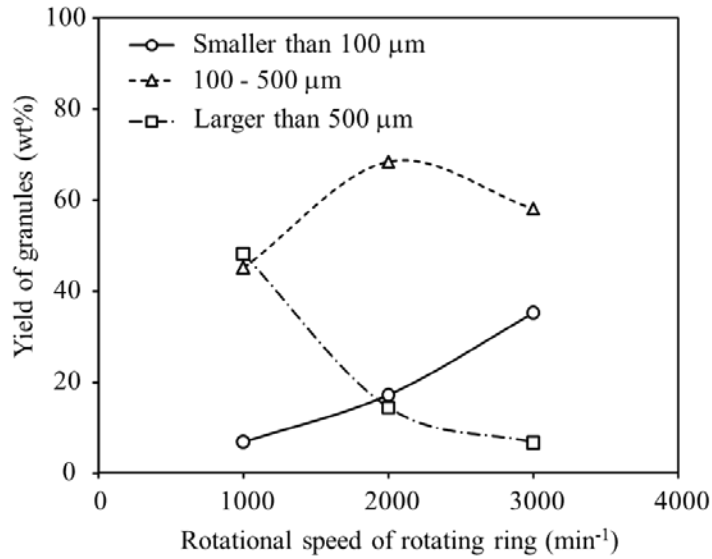3.2 Sizing experiments with WO_3 granules

Figure 9 exhibits influence of rotational speed of rotating ring on yield of WO_3 granules, when the clearance between rotating ring and fixed stator is 0.7 mm. In this figure, the yield is classified by the sizes of WO_3 granules smaller than 100 μm, 100-500 μm, and larger than 500 μm in diameter. The yield of granules of 100 - 500 μm in diameter before sizing was 19.8 wt%, so the yield was improved by the sizing machine. The maximum yield was obtained, when the rotational speed of rotating ring was 2000 min.[-1]. The yield of coarse granules larger than 500 μm in diameter was decreased, and the yield of fine powder smaller than 100 μm in diameter tended to be increased, when the rotational speed of rotating ring was increased.

Figure 9. Influence of rotational speed of rotating ring on yield of WO$_3$ granules.

Clearance between rotating ring and fixed stator: 0.7 mm.

The yield of WO$_3$ granules dependence on the clearance between rotating ring and fixed stator was shown in **Figure 10**. The yield of coarse granules larger than 500 μm in diameter was increased, and the yield of fine powder smaller than 100 μm in diameter was decreased as the clearance was increased. The yield of granules of 100 - 500 μm decreased monotonously with the increase of clearance. The maximum yield of granules of 100 - 500 μm was obtained at 0.5 mm of clearance.
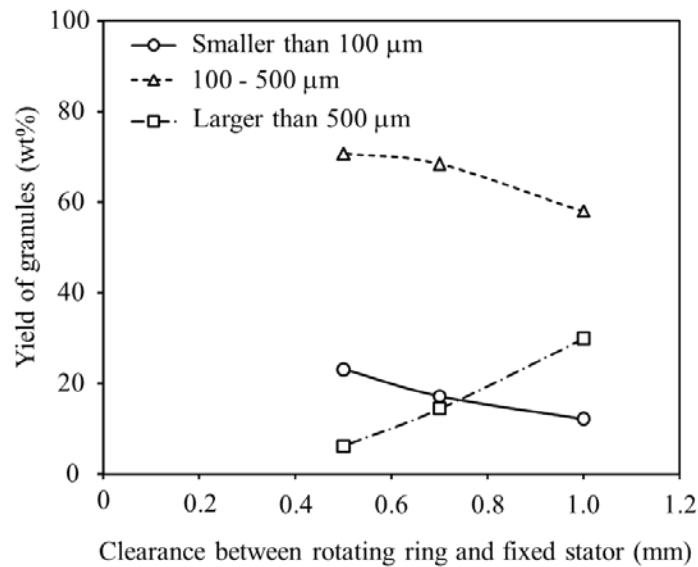
Figure 10. Yield of granules dependence on clearance.

Rotational speed of rotating ring: 2000 min.$^{-1}$.

It was found that the maximum yield of granules of 100-500 μm in diameter in a series of parametrical sizing experiments was 70.7 wt.%, when the rotational speed of agitator was 2000 min.$^{-1}$ and the clearance between rotating ring and fixed stator was 0.5 mm. The maximum yield by the method of crushing over-granulated coarse granules with the sizing machine is smaller than the maximum yield only by the agitation granulator. We also have to take into account powder attachment in the sizing machine. But the method by the sizing machine was considered to be more realistic from standpoint of stable production, because the performance of the sizing machine changed gradually caccording to the operational conditions.

4. Conclusions

Mock-up experiments with WO_3 by the specially designed top-drive agitation granulator and by the sizing machine were conducted. The results of the experiments are summarized as follows.

(1) The granulation rate increased as the moisture content and the rotational speed of agitator increased.

(2) To obtain granules, the industrial scale granulator required more moisture content than the bench-top scale granulator.

(3) The peak time and the peak width of yield curve of granules of 100-500 μm in diameter was decreased when the moisture content and the rotational speed of agitator increased.

(4) The maximum yield of granules of 100-500 μm in diameter in a series of the parametrical granulation experiments was 75.2 wt.% at 15 wt% of moisture content and 150 min.$^{-1}$of rotational speed of the agitator.

(5) The maximum collection ratio of the parametrical granulation experiments was 94.6 wt.%.

(6) In the sizing experiments, the maximum yield of granules of 100-500 μm in diameter in a series of sizing experiments was 70.7 wt.%, when the rotational speed of agitator was 2000 min.$^{-1}$ and the clearance between rotating ring and fixed stator was 0.5 mm.

(7) The method of crushing over-granulated coarse granules with the sizing machine was considered to be realistic from standpoint of stable production, because the performance of the sizing machine changed gradually according to the operational conditions.

We will the continue mock-up experiments with the agitation granulator and the sizing machine, and also develop more attractive granulation system appropriate for the simplified MOX pellet production process.

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Integrated Recycling Test Fuel Fabrication

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Abstract. The Integrated Recycling Test is a collaborative irradiation test that will electrochemically recycle used light water reactor fuel into metallic fuel feedstock. The feedstock will be fabricated into a metallic fast reactor type fuel that will be irradiation tested in a drop in capsule test in the Advanced Test Reactor on the Idaho National Laboratory site. This paper will summarize the fuel fabrication activities and design efforts. Casting development will include developing a casting process and system. The closure welding system will be based on the gas tungsten arc burst welding process. The settler/bonder system has been designed to be a simple system which provides heating and controllable impact energy to ensure wetting between the fuel and cladding. The final major pieces of equipment to be designed are the weld and sodium bond inspection system. Both x-radiography and ultrasonic inspection techniques have been examine experimentally and found to be feasible, however the final remote system has not been designed. Conceptual designs for radiography and an ultrasonic system have been made.

Introduction

The Integrated RecyclingTest (IRT) has been proposed in support of increasing the technical readiness level of a closed fuel cycle utilizing electrometallurgical separations and metal fuel forms as well as examining fuel performance of recycled metal fuel. In this test used light water reator fuel, preferrably with burnup >50 MWd/kg, will be electrometallurgically reduced to metallic form and separated to retreive fissionable material while reducing deleterious fission products to an acceptable level. The recycled fuel feedstock will then be cast into small diameter slugs and encapulated for irradiation testing in the Advanced Test Reactor (ATR) on the Idaho National Laboratory (INL) site. Because it is expected some level of rare earth fission products will be carried over from the separations process, it was initially planned that all fabrication activities would be done remotely in a radiological hot cell. As more laboratory scale work is done and feedstock actual composition and radiation fields known this option may be re-considered in light of the small samples needed for irradition testing. This paper will introduce the basic irradiation test configuration and details of the fabrciation equipment design.

Irradition Test Configuration

The IRT will be done in collaboration with the U.S. DOE Fuel Cycle Research and Development Advanced Fuels Campaign using the AFC-3 series drop in capsules. The general test configuration consists of a sodium bonded metallic fuel slug approximately 4.2 mm diameter x 38 mm length encapsulated in a rodlet (miniature fuel rod or element) that is approximately 5.8 mm OD x 15 cm length. The rodlet is then encapuslated in a secondary containment capsule. The secondary capusle satisfies reactor safety requirements and provides an additional thermal barrier between the fuel and reactor coolant. ATR is a water cooled reactor but the target temperature of the rodlets will be prototypic of a sodium cooled fast reactor therefore the gas gap between the capsule inner wall and rodlet outer wall serves as a thermal barrier allowing the desired temperatures to be reached. Also, reactor safety policy requires these tests to be conatined within a pressure vessel built to the intent of

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[†] Retired

the ASME Boiler and Pressure Vessel Code Section III. A schematic of the test is shown in Figure 1. Target burnup of the rodlets will be 5-10%.

FIG. 1. Schematic of rodlet. Total length is approximately 15 cm with an outside diameter of 0.58 cm.
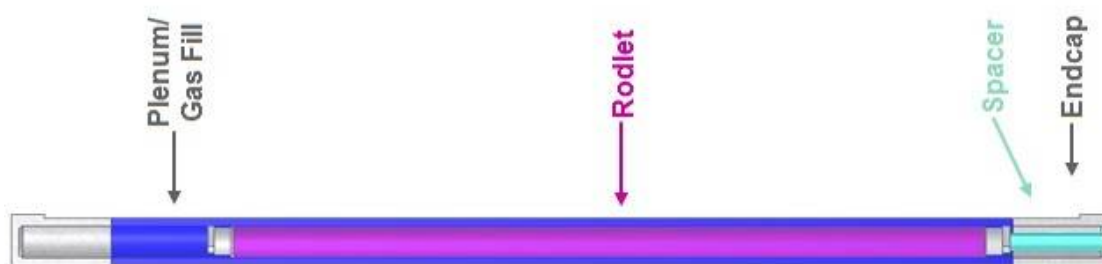

FIG. 2. Schematic of capsule assembly. Total length is approximately 21.6 cm with an outside diameter of 0.71 cm.

Fuel Fabrication Process

Fuel fabrication is a multi-step process which requires several pieces of equipment. The general process starts with fuel casting and trimming to length. The trimmed and inspected slugs are then loaded into the rodlets which have been pre-loaded with sodium and have one end closed. After loading the rodlets are welded and inspected. Weld inspection includes visual inspection as well as a helium leak check followed by radiography. After the welds have been inspected the rodlets are heated up and the fuel slug settled into the sodium, then the temperature is raised and the sodium wet or bonded to the fuel and cladding. After settling and bonding and final dimensional and cleanliness inspection the rodlets are loaded into the capsules and sealed. Capsule fill gas composition must be tightly controlled to ensure the correct thermal barrier. Usually fuelled tests require 100% helium, however, helium-argon mixes can be used. Capsules follow the same inspections as the rodlets with the addition of a dye penetrant inspection on the capsule welds. Although the Experimental breeder Reactor II (EBR-II) made use of recycled fuel during the Fuel Cycle Demonstartion program in the early 1960s and several pieces of equipment were installed and tested for hot cell fuel fabrication during the Integral Fast Reactor program these pieces of equipment are no longer in use for fuel fabrication and are on a scale that is much too large for this size of test. Recent fast reactor fuel irradiation testing done under the FCRD program, although on the appropriate lab scale, only uses fresh fuel and therefore is done utilizing benchtop and glovebox work. In order to fabricate the IRT fuel remotely new equipment must be designed and installed into the hotcell.

Fuel Casting

Casting is the first step in the fuel fabrication process taking the feedstock from it original form and forming it into a usable fuel pin or fuel slug. Throughout the fuel cycle fuel losses must be minimized or eliminated. Casting is the largest source of fuel losses in the fuel fabrication process. Under the IRT losses must be characterized and minimized to the extent possible. During EBR-II fuel fabrication campaigns fuel was cast using a counter gravity injection casting process. In this process quartz molds

are suspended above molten fuel. The furnace chamber and molds are evacuated, then the molds lowered down into the melt, after which the furnace is pressurized which pushes fuel up into the quartz molds. The molds are then shattered to remove the fuel slugs. Although robust and successful this casting process created large recycle and waste streams in the form of casting heels and broken molds. The molds were also a source of fuel losses and because of the dust produced during shattering the molds a source of hot cell contamination. Also because of the low pressures needed casting of minor actinide, such as americium, bearing fuels may be problematic. Recent fuel fabrication for the AFC series irradiation experiments used an arc casting process for casting fuel slugs. Although efficient for lab scale production with little to no losses this process is not feasible for hotcell use and is not scaleable to an engeering or production scale. Because of these reasons new casting process has been proposed and tested and will be installed in the hotcell for the IRT. Fresh fuel furnaces have been designed and fabricated for gravity casting utilizing charges on the order of 300 grams. Previous work has shown gravity casting of long high aspect ratio pins to be feasible although a remote friendly design has not been fully implemented. The furnace designed is re-configurable to allow both gravity pour, with or without pressure differential assist, as well as counter gravity injection casting to be done. The furnace will be heavily instrumented with up to 15 "K-type" thermocouples, 4 "S-type" thermocouples and pressure sensing elements for chamber, internal mold, and crucible pressures. The casting furnace controller will be programmable and be capable of capturing all temperatures, pressures, and power levels.

Casting Furnace Design

Figure 3 shows the overall furnace assembly design. The charge size in the furnace can be as high as 500 grams although this is more than is needed for the irradiation test. A more probable charge is 200-300 grams which will be enough to cast three slugs approximately 4.2 mm in diameter and 250 mm long. The mold and crucible are independently induction heated. The internal parts are contained within a stainless steel chamber which utilizes standard ISO or "NW" style vacuum fittings. Although the furnace can be used for either gravity or counter gravity casting gravity, casting is the reference casting process. By using gravity casting quartz molds are not needed and melt utilization will increase which reduces the recycle stream. The basic design has the graphite crucible with a non-reactive coating applied to the inside diameter, sit directly on the graphite mold. A stopper rod will be installed in the crucible, once the material reaches casting temperatures the stopper rod is lifted using the air driven linear actuator. Material then flows out of the crucible and into the mold. A schematic of the crucible is shown in Figure 3.

The crucible and mold, also made of graphite, have been designed such that the crucible interfaces with the mold to aid in alignment of the system during assembly and casting activities. The mold is composed of two sections, a cup and a cone. The fuel slug cavities are cut on the parting line with small vent holes leading from the bottom of the cavity to the mold cone interior for venting of gas out of the cavity. A schematic of the mold is shown in Figure 3. The challenge of casting the high aspect ratio pins is the molten material freezes very quickly so it must have adequate superheat, although furnace refractory and crucible/melt interaction limit the amount of superheat that can be applied, and flow fast enough to reach the bottom of the mold cavity, otherwise a short pin is cast. However, if too much superheat is applied or the the material flows too fast it will become separated and often solidify before the molten material can re-join, resulting in a pin having large void sections or multiple pieces or segments. Another consequence of improper flow is trapping of gas bubbles in the mold cavities which result in porosity in the cast slug. To control the material velocity the size of the vent hole can be varied. The vent hole allows gas to escape into the inner cone central void area. If the vent is too large flow will be too fast resulting in tears and separations, but if the vent is too small fluid flow is slow and will freeze off before reaching the bottom of the cavity and gas may become trapped leading to porosity.
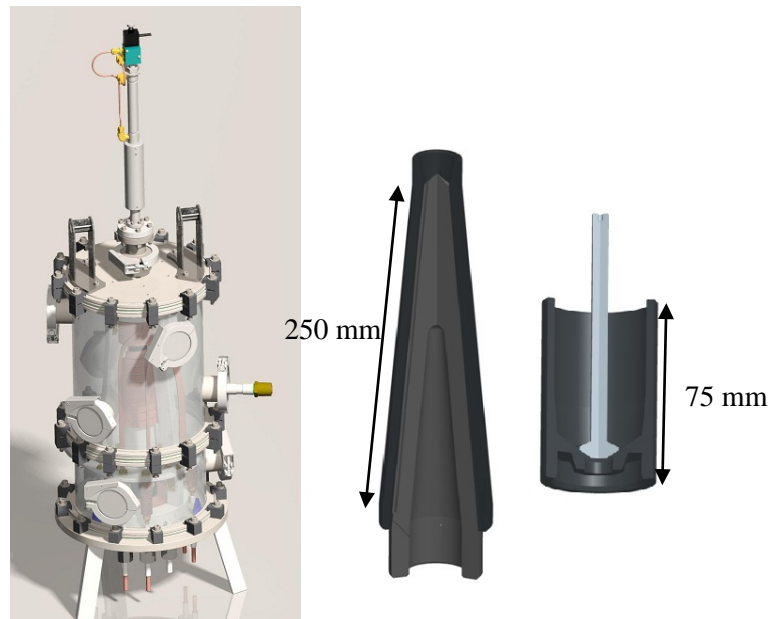
FIG. 3. Left) Schemaic of the IRT fuel casting furnace. Middle) Two piece mold, notice the vent hole at the bottom leading into the inner cone. Right) Crucible and stopper rod, notice the groove to interface with the mold.

Another aspect of the mold and furnace is the possibility of pressure differential assisted gravity casting. To produce a pressure differential a vacuum can be drawn on the mold inner cone. Although the mold is not sealed against the furnace chamber interior a pressure differential will be set up compared to the crucible or furnace chamber. This system has been tested in similar furnaces, however, this led to segmented fuel slugs. However, the capability was incorporated into this furnace to ensure casting flexibility. Another option for pressure differential assisted casting would be to pressurize the crucible. Although this is currently not incorporated into the design adequate feedthroughs have been provided that it could be added at a later date. Because of the high aspect ratio of the pins directional cooling from the bottom to the top is very important to avoid shrinkage voids in the center portion of the slugs. To ensure directional cooling the mold sits on a large copper chill plate which provides an adequate thermal gradient form top to bottom. Also, the copper chill and refractory plate it rests on provide volume for molten material in the event of a crucible or mold failure. There is a high level of confidence in the furance design because furnaces with very similar designs have been tested and performed well.

Settler/Bonder

Settling and bonding is the process of forcing the fuel slug to settle through the molten sodium to rest on the bottom end plug. Following settling the sodium must be bonded to the fuel and cladding. Bonding is done by raising the temperature of the rodlet and holding for adequate time to allow the sodium to wet the surfaces. Bonding is done to improve the thermal conductivity of the fuel/sodium/cladding interface. Throuhghout the settling and bonding process the rodlets are impacted slightly, equivalent to dropping a distance of 12-25 mm. The impacting during settling disrupts the surface tension of the sodium allowing the fuel slug to settle to the bottom endplug. During the bonding process the impacting causes the fuel slug to move slightly which assists in forcing any gas bubbles in the annulus between the fuel and cladding up into the plenum region.

Settler/Bonder Design

A simple and robust settler/bonder system has been designed, shown in Figure 4. The system has four major assemblies 1) Structural stand 2) Rodlet holder 3) Furnace 4) Impact mechanism. The structual stand has been designed to provide structural support for the other subsystems and the chill block which is necessary for ensuring directional cooling from the bottom to the top. The rodlet holder was designed to contain the rodlets in the furnace and provide a solid surface on which impacting can occur. Six rodlets can be processed in a single batch. Provisions have been made to allow for

independent temperaure monitoring at the rodlet holder to ensure a representative temperature is measured. A split furnace was produred to aid in loading and unloading of the rodlet holder. The furance has been modified to ensure temperature control can be maintained at relatively low temperatures, 125°C – 650°C and the total furnace footprint was reduced by removing the outer shell. Impacts are delivered to the rodlet through the roldet holder which rides on a cam that is connected to a electric motor. The cam will raise the holder up to 25.4 mm then allow it to drop. Drop height is controlled by a collar on the holder, this allows the drop height to be fine tuned from 0-25.4 mm. Impact frequency is controlled through a motor speed controller. Settling is a relatively simple process and therefore little automation or instrumentation was needed for the remote system.

Welding System Development

In contrast to the casting furnace and settler/bonder the welding system has not been fully designed however, a large effort was initiated to determine the most efficient welding process and to develop a welding procedure adequate for closure welding of the rodlets and capsules. Two welding processes have been used throughout the fuel fabrication campaigns for EBR-II and the AFC irradiation tests; capacitance discharge (CD) welding and automated orbital gas tungsten arc welding (GTAW). Nearly all of the EBR-II fuel, including both fresh fuel and remotely fabricated, was clsoure welded using the CD welding process. In this process a large electrical discharge melts the entire top surface of the endplug fusing it to the cladding. A similar process was developed and tested for the Integral Fast Reactor program for remote fuel fabrication. Instead of using a bank of capacitors to supply the electrical discharge a standard pulse capable welding power supply was used to create the arc which heats and fuses the endplug and cladding. AFC test fuels have been welded with an orbital GTAW system. A automated tungsten electrode travels around the weld making the closure weld. Orbital welding is a robust process that is used throughout the tube and pipe welding industry. Other closure welding methods such as laser welding are also feasible. A trade study was done which compared GTAW burst welding, laser welding, and resistance butt welding. Each welding process was reviewed against three weighted criteria; cost of welding system, deployability in a hotcell, and in cell system footprint. Deployability was weighted the highest and cost the lowest. Orbital GTAW was not reviewed because it was decided that it required too many fine adjustments and maintaence to warrant inclusion in the study. Table 1 shows the details and results of the study.
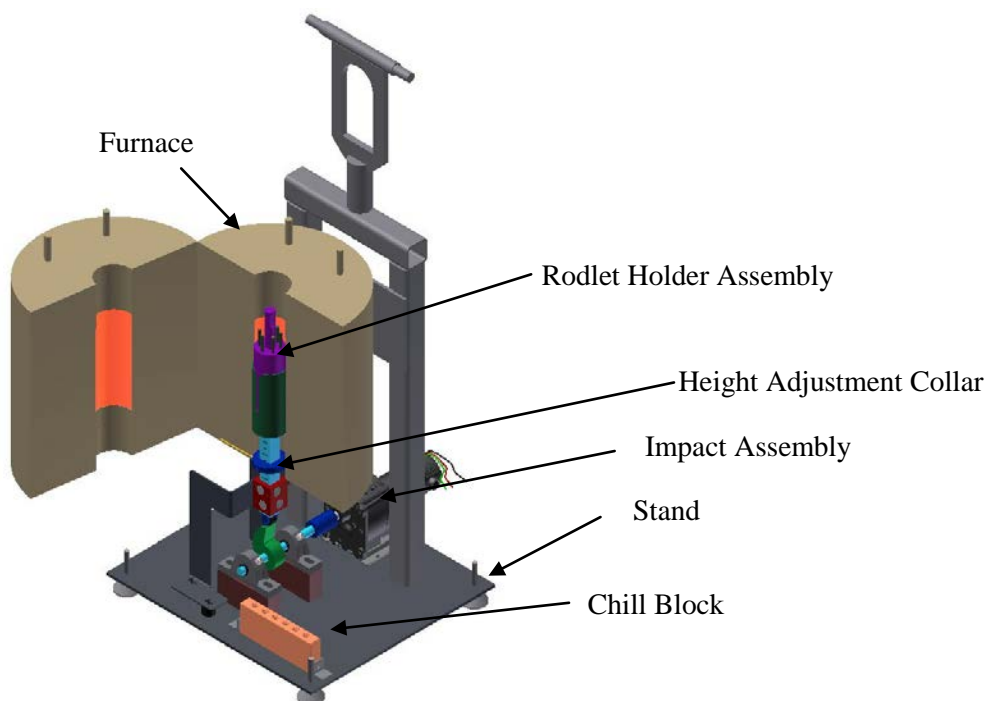

FIG. 4. Schematic of settler/bonder system.

As is shown in Table 1 the most imortant criteria was deployability to a hotcell. This refers to the number of feedthroughs needed to be installed, personnel training required, and overall design risk, development time, and the relative difficulty in installation and operation in a hotcell. Footprint refers to toal hotcell area used by the welding system. Cost refers to the total cost of the welding system and associated tooling. Each criteria was then assigned a weighting factor of 1-7, based on importance as seen by program personel the higher the weight the more important the criteria.A value was also assigned between 1-12, with 12 being the highest. The better a system met a certain criteria the higher the assigned value. Finally a score was tabulated which is the product of the weight and value factor. The score for each system were totalled together and the system having the highest score was selected. Because a simple power feedthrough is all that is needed and the existance of past designs and procedures which lead to shorter development times the final selection was GTAW burst welding, although it should be noted that if a laser feedthrough was not needed in the hot cell this also would have been a very feasible joining method.

After selection a simple protoype was built in order to develop weld procedures and base a remote design on. The prototype system is made up of several parts; 1) programmable welding power supply 2) GTAW torch 3) fixturing stand (includes X-Y-Z translation) and 4) data acquisition system. As with the settler/bonder system because the feedthrough rate is low and fine adjustment are minimal a high level of automation is not needed. Figure 5 shows the fixturing stand and a the resulting weld. Weld development first examined joint configurations going through a number of minor changes on endplug design. These changes affected the final weld profile and weld inspectability by volumetric methods. Because the rodlets must fit within the capsule leaving only a small gap, on the order of 0.05 mm the weld must not increase the diameter of the overall tube. In order to ensure no diametral expansion a groove was placed in the endcap below the weld joint. This groove serves as volume for the molten metal to expand leaving the outside diameter little changed, and also provided an x-ray relief for radiographic inspection to confirm 100% penetration. This groove can be seen in the weld cross section shown in Figure 5. Along with weld procedure development a data acquisition system was also employed. Weld integrity is affected by maintaining a controlled joint configuration, this is done through proper tolerancing of the components, and welding parameters in particular amperage, voltage, and pulse rate. The power supply is a constant current power supply so the current and pulse rate/width are set parameters. The voltage is a function of current, arc length (distance the arc must travel between the tungsten electrode and workpiece), and resistance of work piece. If a small gap is left between the endplug and cladding tube this will affect the overall resistance of the workpiece which will result in a voltage difference. The same is applicable if the arc length is too long or material flaws lead to porosity. The weld data acquisition system will capture these parameters creating a "weld signature" of amperage and voltage v.s. time data. A database will be constructed that will include acceptable signatures, verified through inspection and testing, and signature of flawed welds i.e. improper joint fit-up, increased arc length, weld contamination, etc. Once this data base is constructed as welds are made the signatuures will be compared against the database as an initail quality inspection. If the weld does not fit the accepted weld signature database then it can be rejected. Although the IRT has a very low throughput, <10 welds total for test fabrication, this process is important to give extra assurance of weld integrity because of the potential for data loss should a weld fail. Also, volumetric inspections although commonplace in the fabrication industry are laborius and expensive in the hotcell, and have not been implemented fully. Through a robust weld qualification program the amount of non-destructive testing that is required in cell can be reduced. This is more important when a larger scale of operation is employed. To fully close the fuel cycle production scale remote fabrication and inspection capability must be tested. The weld signature inspection combined with a statistically proven qualification program will be part of the scale-up.

No.	Criteria	Weight (1 to 7 with 7 as best)	Value Ranking	Value (1 to 12 with 12 as best)	1 Gas Tungsten Arc Welding Wt X Value = Score		2 Laser Welding Wt X Value = Score		3 Resistance Butt Welding Wt X Value = Score	
1	Cost of Welding System	3	<$5,000	12	<$5,000	36	>$30,000	3	>$30,000	3
			$5,000 to $10,000	8						
			$20,000 to $30,000	4						
			>$30,000	1						
2	Deployable in Hot Cell	7	Easy	12	Easy	84	Difficult	28	Lots of Effort	7
			Doable	8						
			Difficult	4						
			Lots of Effort	1						
3	In-Cell Foot Print of Welding System	6	<2 ft	12	<2 ft^2	72	2 to 4 ft2	48	>6ft^2	6
			2 to 4ff	8						
			4 to 6ff	4						
			>6ft^2	1						
				Totals	---	130	---	79	--	16

Table 1. Trade study reslts showing GTAW as having the highest total score.

Inspection System Development

As stated earlier because of the potential for data loss should a rodlet fail and the necessity of meeting the intent of the Boiler and Pressure Vessel Code for the capsule a volumetric (below surface) non-destructive technique must be developed. Radiography and ultrasonic inspection both are used throughout industry as inspection techniques, however, neither has been implemented in a hot cell. General difficulties include a high radiation background, difficulty of precise movements and alignments, non-standard geometry, and general system footprint. Experimental development was done on both ultrasonic and radiographic inspection systems to determine if the systems are suitable for hotcell use and can detect incomplete fusion and flaw sizes as small as 75μm.
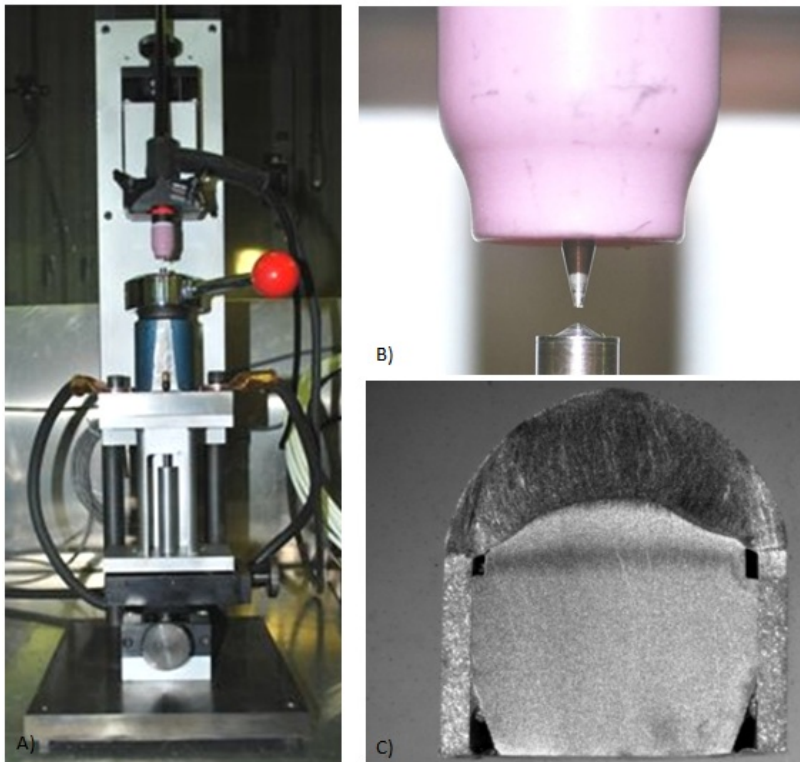
FIG. 5. A) Prototype weld station used for conceptual design and weld procedure development. B) Cladding tube and endplug before welding C) Macrograph of welded endplug.

Ultrasonic System Development

Ultrasonic nondestructive testing is commonly used to inspect welds in industrial settings. It is one of the most cost effective inspection techniques. Ultrasonic testing (UT) relies on short ultrasonic pulses with center frequencies typically ranging from 0.1 MHz up to 100 MHz. The ultrasonic pulses are generated in components to detect internal flaws or to characterize materials. UT is often used to inspect steel, other metals and alloys. It can also be performed on concrete, wood and composites, with less resolution due to higher scattering in these highly inhomogeneous materials. UT has been routinely used for many years in industries including nuclear, aerospace, automotive and other transportation sectors. The basic operational principal of UT is a flaw in the material will change the amount of sound energy either traveling through the workpiece or reflected back to the front. This change in sound energy is then used for flaw detection.

Although how much sound is actually reflected from an interface is a complicated function of acoustic impedances, geometry, and beam size, a general rule of thumb can be used. In general, as long as a defect is at least 1/4 of a wavelength in cross section presented to the ultrasound, there is a high probability that with a suitable test configuration, the defect can be detected. As an example for a 50 MHz center frequency transducer used on a stainless steel part with a speed of sound of 6000m/s (wavelength = 0.12 mm), the minimum detectable size of flaw would be on the order of 30 µm.

Because UT is sensitive to positioning automation will be necessay to obtain consistent results. To automate the imaging of the fuel rodlets, at least six degrees of freedom (X, Y, Z, rotation, pitch, yaw) robotics must be used in an immersion tank to keep the ultrasonic transducer normal to the fuel rodlet. To keep the transducer normal to the specimen being scanned will require a contour following control system. The control system will be based on maximizing the first reflection from the water/part interface. The piezoelectric transducers are sensitive to radiation and will need to be replaced on a regular basis.

Several test pieces were needed to evaluate capabilities to detect defects and lack of fusion conditions within the weld zone with ultrasonic testing. A test piece was developed by drilling small holes within the weld zone and covering them via laser welding. A rodlet (Rodlet 6T) from the historical archive was used to prepare a test piece for ultrasonic evaluation. Several holes approximately 0.5 mm (0.020 in.) in diameter were drilled into the weld zone. The laser welding used to create ligaments over the holes was only partially successful, as two holes remained uncovered.

These test pieces were examined both at INL and at a UT system vendor for flaw detection. Results showed that flaws were detected both at INL and at the vendor site. Vendor results are displayed in Figure 6. The white areas represent the machined flaws while the lighter regions are areas that were slightly out of focus, it is expected that better instrumentation and process development will decrease the amount of these areas. To determine the minimum flaw size detectable a test plate was fabricated with 5 holes ranging from 0.076 mm (0.003 in.) - 0.76 mm (0.03 in.), the holes were drilled to within 0.46 mm (0.018 in.), which is the cladding wall thickness of the rodlets, of the back side of the plate. The plate was examined from the backside, opposite of the drilled holes. The resulting scan is also showed in Figure 6. The four largest diameter holes (0.006 in. (.152 mm), 0.010 in. (.254 mm), 0.026 in. (0.660 mm), and 0.030 in. (.762 mm) were clearly visible. On the undisturbed side, a marker was used to indicate areas of interest for scanning, these faint lines were also visible in the UT results indicating that a very minor height change can be easily detected.The smallest hole was initially not visible however a closer examination of the results suggests that the 0.076 mm (0.003 in.) diameter hole may be observed. This is despite the fact that the scan increment was 0.102 mm (0.004 in.). Important conclusions can be gathered from these data. The observation of both the marker on the surface and holes at a depth of at least 0.46 mm from the surface shows that the depth-of-field for this setup is at least .46 mm for a flat plate. The observation of a hole with a scanning increment of .025 mm greater than the diameter of the hole suggests that small flaws are detectable even without passing directly over them with the transducer. Test were also done to to determine if sodium levels could be detected. The results show that bonded sodium is easily detected but unbonded sodium is not.

This shows that bond defect in the fuel/cladding annulus could potentially be directly detected using UT.
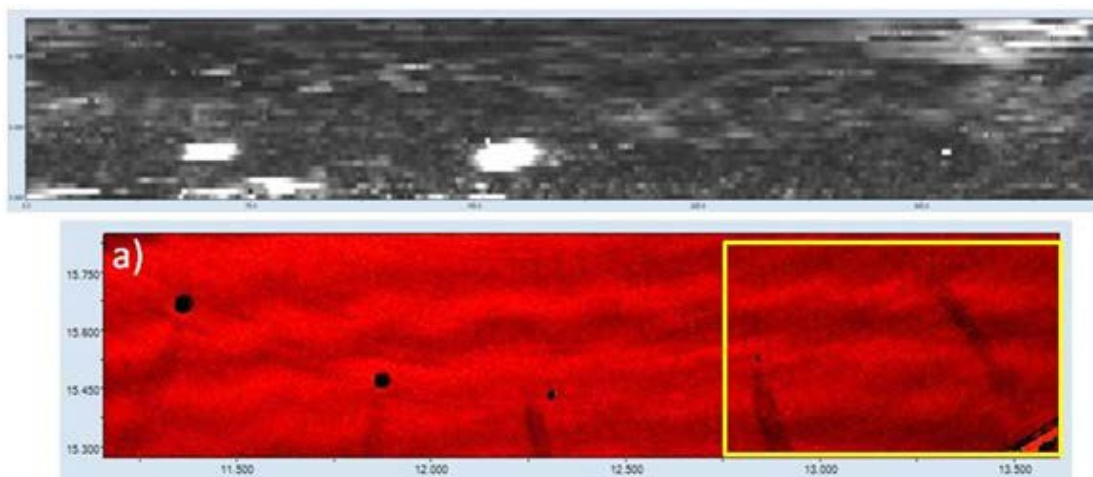

FIG. 6. Top) UT scan rodlet weld with know flaws (white circles) Bottom) UT scan of the undisturbed side of a flat plat with holes drilled into the underside.

Radiography System Design

Radiogaphy was also examined for hot cell feasibility. Although radiography has been a standard inspection method for fast reactor fuel fabrication it has never been implemented in a high background radiation hot cell environment. In order to have the highest resolution and magnification without losing sharpness a digital microfocus radiography system was selected. A maximum magnification of approximately 18X could be obtained in the laboratory, however, because of the hotcell size constaints a magnification of 8X can be expected in cell. Numerous radiographs of the flawed welds fabricated for the UT work, and sodium containing rodlets confirmed that very small details can be easily detected using this radiography system in the lab. However, hotcell background radiation at the proposed work location is estimated to be 100-200R/hr To determine the effects of high background radiation a series of experiments were run using the same laboratory equipment with the exception of lead mats that were placed around the detector to reduce bacground radiation of the detector and a second x-ray source was used to provide a uniform background radiation.

A Line Pair Phantom (LPP) was used to determine relative image quality in both the horizontal and vertical directions with backgrouond radiation. This type of phantom is made of acrylic and has closely spaced 0 .1 mm width and thickness metal strips embedded in it. The phantom is scanned, and the number of strips that are visible are counted. A line pair is *not* a set of two lines, but rather a line and the space between lines. The phantom used during these experiments contained a maximum of 5 lp/mm and could be easily seen with the 212 R/hr background present. Following the LPP images several images of the flawed test piece, flawed welds, and sodium levels were taken. These images were compared to the original without background radiation images. Flaws as small as approximately 40μm (as measured from radiography) could be detected. Examples of the images are shown in Figure 8.
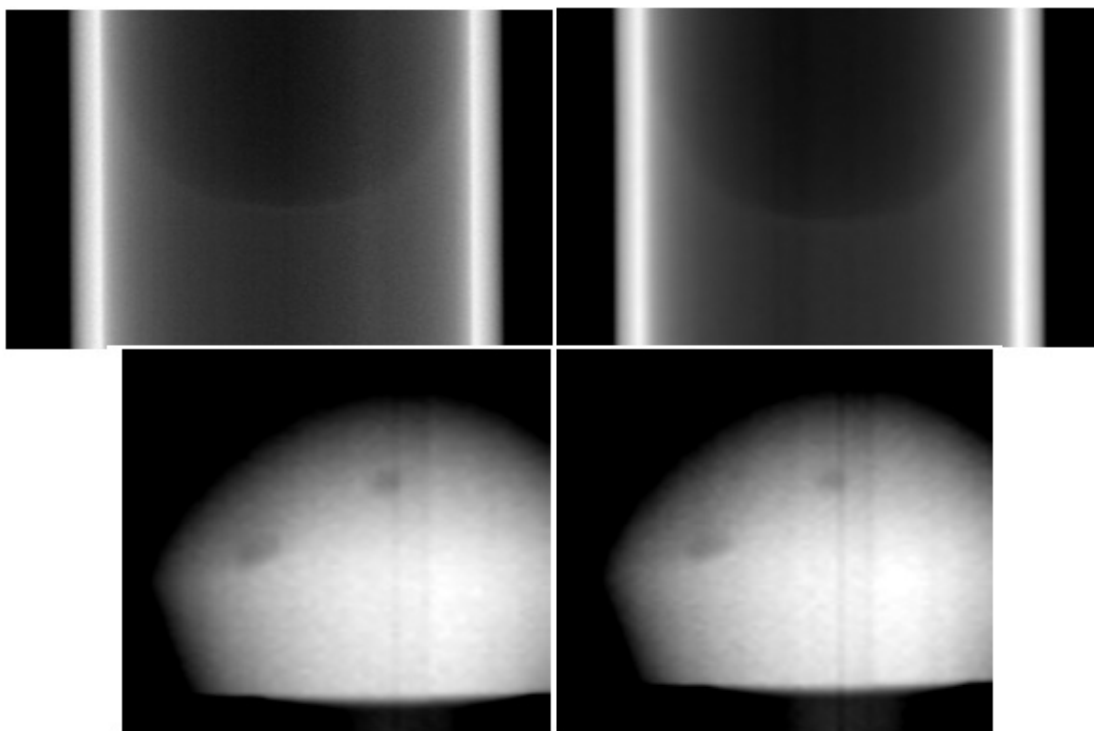
FIG. 7. With and without background radaition image comaprisons, without background radiation is on the left and with is on the right. Top) Sodium miniscus above fuel column Bottom) Machine weld flaws.

Conclusion

The IRT will electrochemcially recycle used LWR fuel into a usable metallic fast reactor type fuel and test these fuel in the ATR. Test configuration will be a double encapsulated rodlet which will run at prototypic sodium cooled fast reactor conditions. Because of possible rare earth fission product carryover from the separation process fabrication was origially planned to occur with a shielded hot cell. The casting furnace and settling bonding equipment has been designed and are ready for fabrication. Welding and inspection techniques have been developed and conceptually designed. Technique development has shown that both radiography and ultrasonic testing is feasible. The GTAW burst welding technique was chosen based on a trade study that compared ease of installation, cost, and equipment size. A protoype welding sytem was fabricated and used to generate many welds for procedure development as well as weld signature capture technology development. It should be noted that although work has been done to develop in-cell fabrication capabilities because of the added expense of operating in the hot cell and the small size of the irradiation test another option is being explored as well. This option will cast the fuel in the hot cell, cut the fuel slug to length and then transfer to a shielded glovebox where the other fabrication activities will occur. Which route will be taken will ultimately depend on radiation levels of the recycled fuel and worker safety.

Acknowledgements

Scenarios for Minor Actinides Transmutation in the Frame of the French Act for Waste Management

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Abstract. In the frame of the French Act for waste management, options of minor actinides (MA) transmutation are studied, based on a scenario of a 60 GWe SFR fleet deployment from 2040 to 2100. The advantages and drawbacks of different transmutation options are evaluated. The transmutation of all MA or only of americium is considered, in homogeneous mode (MA bearing fuel in all the core) or in heterogeneous mode (MA bearing radial blankets). Scenarios have been optimized to limit the impacts of MA transmutation on fuel cycle, with a reduction of the initial MA content in core in homogeneous mode to mitigate the effect on reactivity coefficients and a reduction of the fuel decay heat for transportation in heterogeneous mode. The sensitivity of results to the SFR core design is evaluated by considering a homogeneous core (SFR V2B) or a new heterogeneous core with a significant gain on sodium void effect (CFV).

1. INTRODUCTION

In France, nuclear energy provides the major part of electricity generation: 58 Pressurized Water Reactors (PWR) generate up to 430 TW·he (see *Fig. 1* and [1]) per year. Those reactors are loaded with enriched uranium fuel (UOX containing initially 3 to 4% of ^{235}U). Plutonium from UOX spent fuel is recycled a single time in MOX fuel.
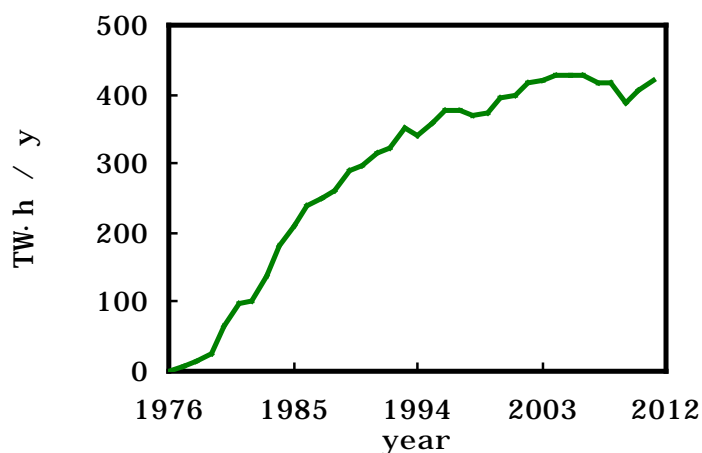

FIG. 1. French PWR fleet electricity production per year (historical data)

In the frame of the French Act for waste management [2], several scenarios consider fuel cycle transition toward a plutonium multirecycling strategy in Sodium cooled Fast Reactor (SFR). Basically, most of these scenarios consider the deployment of a 60 GWe SFR fleet in two steps to renew the French PWR fleet [3]. Transmutation scenarios assess the advantages and drawbacks of different transmutation options: all minor actinides or only americium, heterogeneous or homogeneous, transmutation at the beginning of SFR deployement or only at equilibrium, etc.

The chapter 2 presents the different scenarios and reactors assumptions. Scenarios assumptions are consistent with previous studies [3][4][5]. Optimization of homogeneous transmutation scenarios is described in chapter 3. A delayed SFR deployment (first SFR starts in 2080) with homogeneous transmutation is presented in chapter 4. The scenarios presented in chapters 3 and 4 consider SFR V2B design [6]. The chapter 5 assesses the transmutation in heterogeneous mode or homogeneous mode in CFV (French acronym for Low Void effect Core) [7]. The last chapter deals with the impact of minor actinides transmutation on plutonium inventory. For all the studied transmutation scenarios the plutonium amount evolution is evaluated.

2. REACTORS AND SCENARIOS ASSUMPTIONS

2.1. SFR V2B

The considered SFR core concept (SFR Version V2B [6], see *Fig. 2*) has been developed by the CEA and French partners until 2008. Basically, this core has a breeding gain close to zero with MOX (uranium + plutonium) fuel. Radial blankets with a depleted UO_2 matrix can be added to the core to transmute minor actinides, called Minor Actinides Bearing Blankets – MABB, or americium, called AmBB (heterogeneous transmutation). Minor actinides can also be transmuted by being mixed with uranium and plutonium in the whole core (homogeneous transmutation).
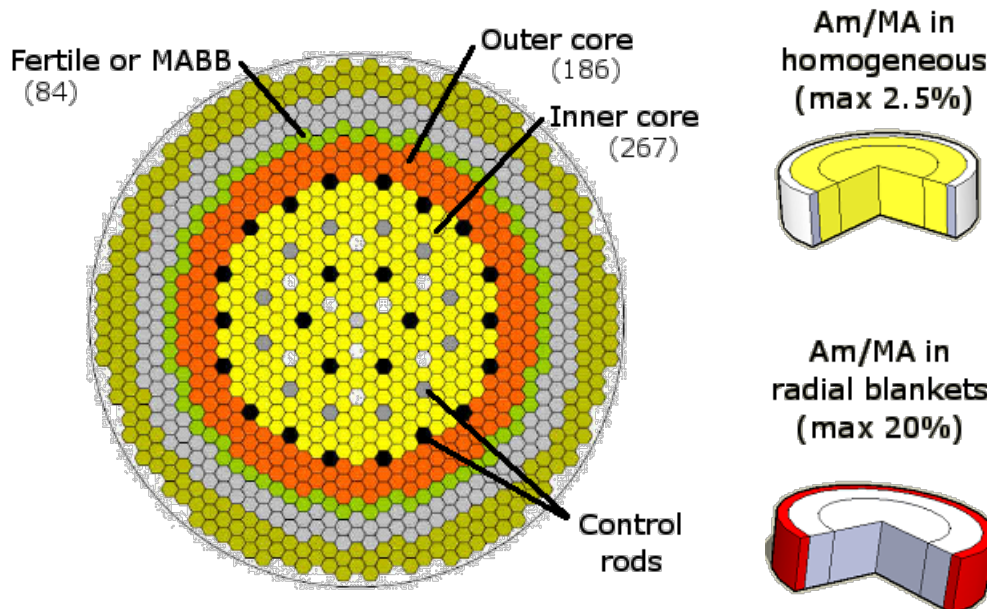

FIG. 2. SFR V2B core concept.

Plutonium net production is + 6 kg / (TW·he) without transmutation options at equilibrium. Plutonium production is increased with transmutation options: + 9 kg / (TW·he) for homogeneous transmutation and + 15 kg / (TW·he) for heterogeneous transmutation in MABB (containing 20% MA and 80% depleted uranium).

2.2. CFV

The innovative heterogeneous core concept called CFV (Low void Effect Core) presents a significant gain on the total sodium void effect [7]. The CFV core results from an optimization of various types of geometrical options combined in a favorable way. The CFV geometry transverse representation is shown in *Fig. 3*. Transmutation options could consist in adding minor actinides in MABB around the core in case of heterogeneous transmutation or diluting minor actinides mode in fissile zones in case of homogeneous transmutation.

The MA transmutation in inner fertile zones is not considered in this study.
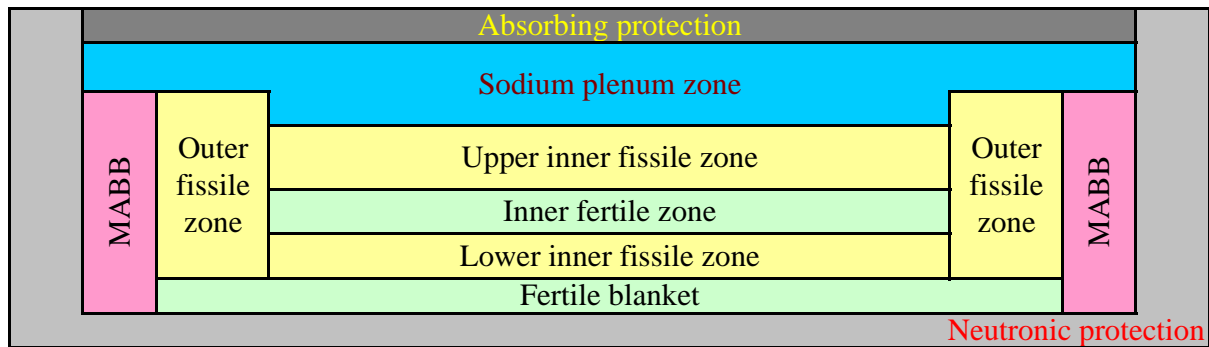
FIG. 3. Core geometry of the CFV design

The design and performances of the concept used in scenario studies are those of an intermediate version of the project called CFV V0. Future scenario studies would take into account the last CFV version.

2.3. Main fast reactors parameters

The fast reactors main features are presented in *Table 1*.

Table 1. Fast reactors main characteristics

	•——— SFR V2B ———•			•——————— CFV ———————•			
	Core	MABB row #1	MABB row #2	Fissile zones	Fertile zones	MABB row #1	MABB row #2
Thermal power (MW)		3,600			3,600		
Electrical power (MW)		1,450			1,450		
Net yield		40.3%			40.3%		
Load factor		81.8%			81.8%		
Mass (tIHM)	74	11.9	12.7	51	37	12.1	13.0
Fuel management (EFPD)	5×410	10×410	10×410	5×400	5×400	10×400	10×400
Initial Eq. ^{239}Pu content	11.0%			16.5%			
Initial Pu content	~ 16%			~ 25%			
Initial MA content	0 to few %	20%	20%	0 to few %	0	20%	20%
Discharge burn-up (GW·d/t)	98	39	12	120	23	60	18

2.4. Scenarios assumptions

The main assumptions and methods are consistent with those of scenarios studied in the frame of the June 2006 French Act for waste management [3][4]. COSI6 software [8] is used to perform the scenarios calculations.

The CESAR software [9] is used to perform the evolution of isotopic content of nuclear fuels and radioactive materials. The core performances (especially plutonium consumption and fissile inventory ratio) are consistent with core design neutronic results (obtained with ERANOS [10] for fast spectrum and APOLLO2 [11] for thermal spectrum).

The scenarios consider the renewal of the current French fleet, which contains 58 PWR loaded with UOX, MOX and enriched reprocessed uranium (ERU) fuels.

Those reactors are replaced by a fleet including first European pressurized reactors (EPR™) then SFR (*Fig. 4*). Their renewal occurs within two steps:

— 2020-2040: deployment of 40 GWe of generation III EPR™ reactors with UOX and MOX[1] fuel;

— 2040-2050: deployment of 20 GWe of generation IV SFR.
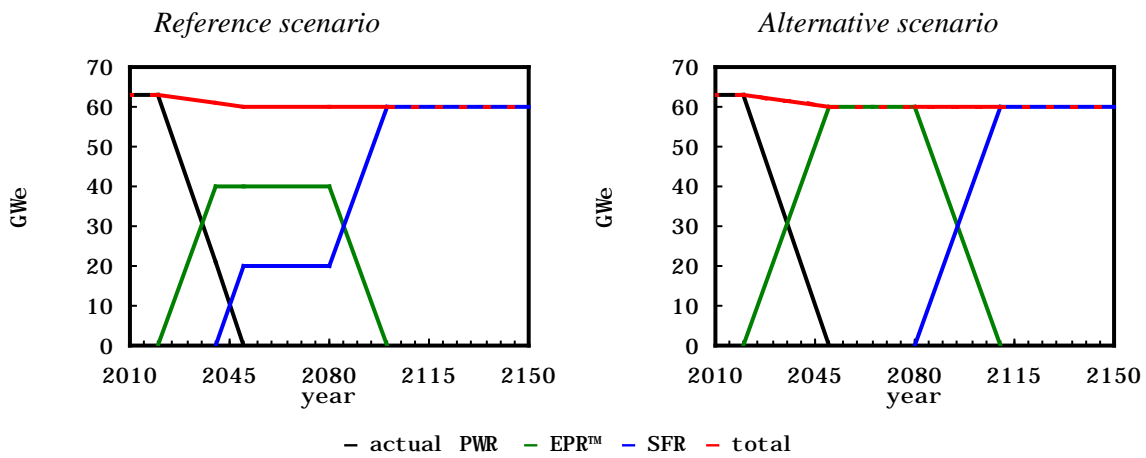
FIG. 4. Evolution of nuclear power share

Assuming that the lifetime of reactors is fixed to 60 years, the fleet is renewed from 2080 with only SFR, leading to a total SFR fleet in 2100.

The alternative scenario presented in chapter 4 considers the transition toward closed SFR cycle during 2080-2110 period.

The load factor for the future reactors (EPR™ & SFR) is 81.8%.

2.4.1. Fuel cycle assumptions

The minimum cooling time for spent fuel before reprocessing is 5 years. If needed, the cooling time for spent fuel before reprocessing can be reduced to 3 years.

The fabrication time is 2 years.

The reprocessing capacity is not limited: the plant capacity may be adapted to meet fissile material requirement.

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[1] plutonium is recycled as MOX in EPR until 2038

3. HOMOGENEOUS TRANSMUTATION SCENARIO OPTIMIZATION

The main results of the reference homogeneous transmutation scenario have been published in [3] and [4]. MOX PWR fuel reprocessing between 2038 and 2055 (as described on *Fig. 5*) leads to a large increase in the minor actinides content in grouped transuranics (see *Fig. 6*). Since minor actinides are not separated from plutonium, the maximal minor actinides mass content (see *Fig. 7*) in fresh fuel is 3.9% (the equilibrium minor actinides content is 1.2%,). In an alternative scenario with only Am recycling, the maximal Am content is 2.9%. The technical feasibility of the homogeneous transmutation remains limited to a content of about 2.5~3.0% minor actinides if one remains on the design of the reference core SFR V2B, with acceptable impacts on reactivity coefficients [12].
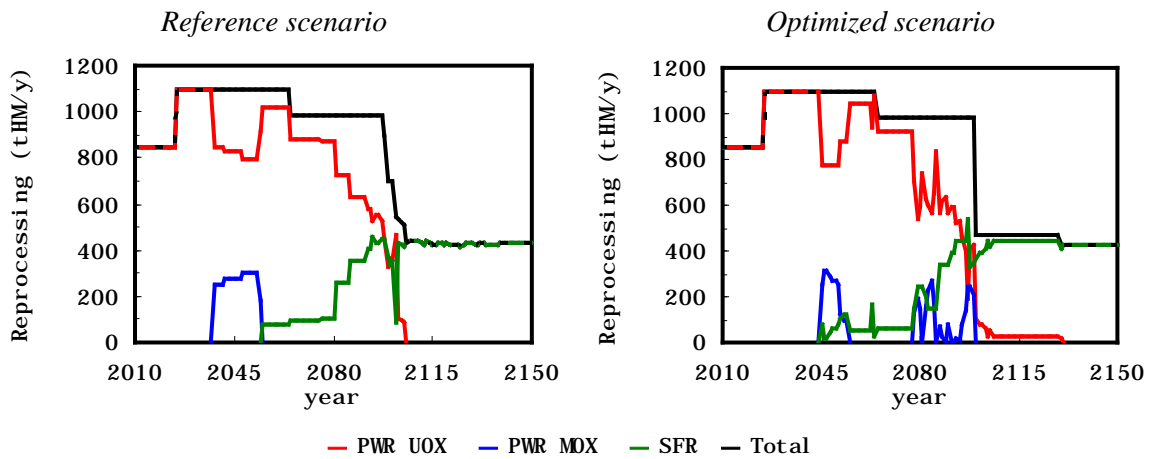
FIG. 5. Optimization of reprocessing strategy

An optimization of the reprocessing strategy (*Fig. 5*) allows to limit the maximal minor actinides content loaded in reactors: PWR MOX fuel assemblies are reprocessed over a longer period thus more diluted, and since all fuels are reprocessed in "last-in-first-out" mode, the MA content in grouped transuranics is limited. Those changes lead to keep the minor actinides content below 2.5% during the transient period of SFR deployment (*Fig. 7*). The same optimization gives a comparable reduction of Am content (maximum is 2.0%) for the scenario with only Am transmutation.
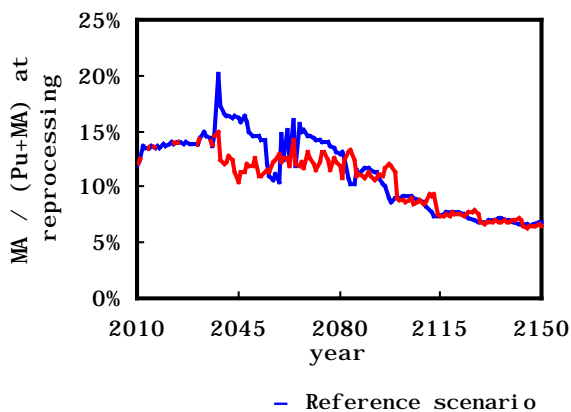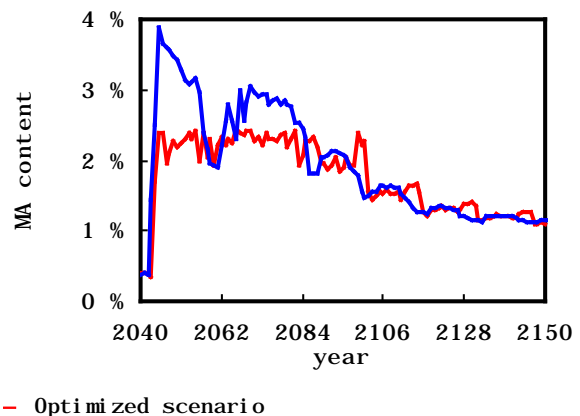

FIG. 6. MA / (Pu+MA) at reprocessing   FIG. 7. MA mass content in fresh fuel

4. SFR V2B DEPLOYEMENT DELAYED TO 2080

4.1. *Main hypotheses*

The scenario envisages SFR introduction between 2080 and 2110 (*Fig. 4*).

Reprocessing and plutonium recycling in PWR (as standard MOX) continue with constant fluxes until 2078: 850 tonnes of UOX fuel are reprocessed each year and provide plutonium to produce 100 tonnes of MOX.

From 2080, both plutonium and minor actinides are multirecycled in homogeneous mode in SFR V2B.

4.2. *Results*

From 2013 to the end of PWR operation, the PWR fleet requires 600,000 tonnes of natural uranium, 140,000 tonnes more than the reference scenario (SFR from 2040).

In order to recover the maximum plutonium amount, all fuel have to be reprocessed between 2078 and 2108. During this period the reprocessing flux is 1,600 tonnes per year (*Fig. 8*).

Since the fraction of MOX fuel at reprocessing is higher and the effective cooling time before reprocessing of all spent fuel is longer, there is more [241]Am in the mixed transuranics (Pu+MA) and in the fresh fuel.

The minor actinides content in the fresh fuel reaches 5% (instead of 3.9% with SFR deployement from 2040, see *Fig. 9)*, which is detrimental for safety parameters such as Doppler feedback, coolant temperature coefficient and effective delayed neutron fraction. This should lead to modifications on the fuel elements design [12].

Since the duration of the transition from PWR to SFR is shorter (30 years instead of 60 years), reprocessing of all PWR MOX fuel over a reduced period (12 years) is necessary to start the SFR fleet. Over such a short period, the inversion of reprocessing order (last-in-first-out instead of first-in-first-out) has very low effect. In the 2080 case choosing between reprocessing PWR MOX or SFR fuel is not possible because of the cooling time constraint.

For these reasons the optimization strategy presented in chapter 3 may be less efficient to reduce the MA maximal content in fresh fuel.
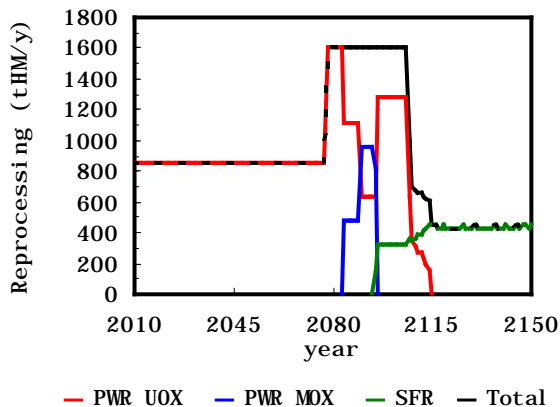

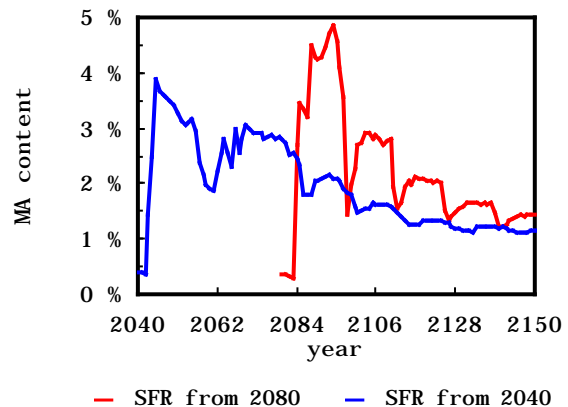*FIG. 8. Reprocessing for SFR deployment in 2080*   *FIG. 9. MA in fresh fuel*

The minor actinides mass in the waste after partitionning and transmutation begininning is stabilized at 126 tonnes, twice as the "SFR from 2040" scenario (see *Fig. 10*). The waste long term radiotoxicity and thermal power are also twice as large when SFR with partitionning and transmutation are delayed to 2080.
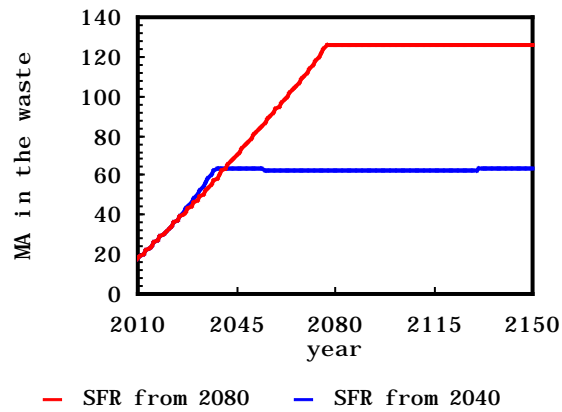

FIG. 10. MA in the waste

5.   TRANSMUTATION IN CFV

5.1.   *Heterogeneous transmutation in MABB from 2040*

The CFV concept with MABB is described in *Fig. 3*.

MABB contain 20% minor actinides and are irradiated during 10 cycles.

The absolute transmutation rate (net consumption of minor actininides divided by energy production) is better in CFV than in SFR V2B (*Table 2*). The minor actinides inventory (*Fig. 11*) reaches 170 tonnes in 2150 with CFV. It is comparable to the SFR V2B scenario [4].

Table 2. Fast reactor with MABB performances

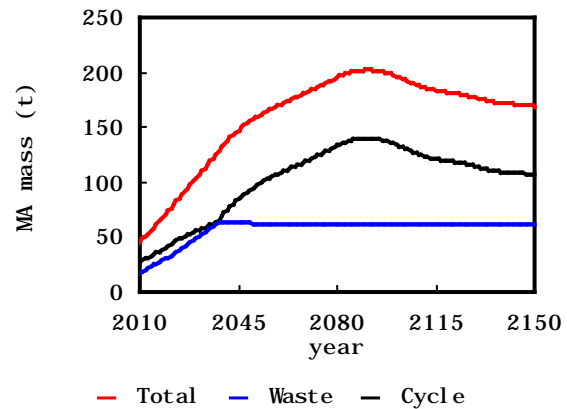|	SFR V2B	CFV V0
MA production in core (kg/(TW·he))	5	5
MA consumption in MABB (kg/(TW·he))	6	7.4
Net MA production (kg/(TW·he))	–1	–2.4
MABB burn-up (GW·d/t)	39	60

FIG. 11. MA inventory evolution

Since the curium content in fresh MABB is increasing during the scenario, thermal power and neutron sources are also increasing (*Fig. 12* and *Fig. 13*). At the end of the scenario (2150) the thermal power of a MABB sub-assembly reaches 10 kW. With such thermal power and neutron emission level, handling and transport of fresh MABB is complex: it could require cooling system and improved biological shielding. An improvement (reduction of minor actinides mass content and irradiation time, as the optimization presented in [5]) of this scenario is necessary to reduce these characteristics and to reach more realistic values.
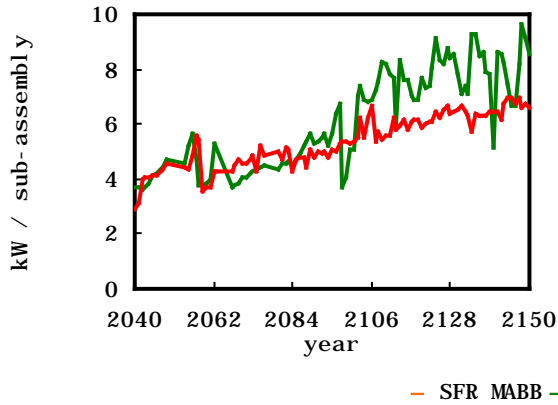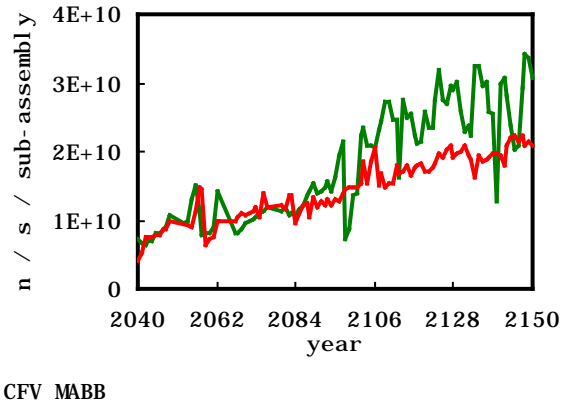

FIG. 12. Fresh MABB thermal power   *FIG. 13. Fresh MABB neutron emission*

5.2. *Homogeneous transmutation in fissile zones from 2040*

In this scenario minor actinides are loaded in fissile zones of CFV (*Fig. 3*). Since homogeneous minor actinides transmutation increases the breeding ratio of the core, it is possible to start 60 GWe of CFV with the nominal 5 years cooling time for all fuel types (without transmutation minimal cooling time have to be reduced to 3 years). At the equilibrium, plutonium inventory increases.

The fissile zone in the CFV mass is 51 tonnes, instead of 74 tonnes in SFR V2B. At the beginning of partitionning the minor actinide mass to be transmuted is provided by the minor actinide content in PWR spent fuel and is independant from the fast reactor design. As a consequence, the minor actinide mass content in the CFV is higher (*Fig. 14*): 5.6% at the maximum. Optimization (strategy presented in [5]) should reduce this value. Studies on fuel and core behaviour are necessary to achieve the technical feasibility of this scenario.
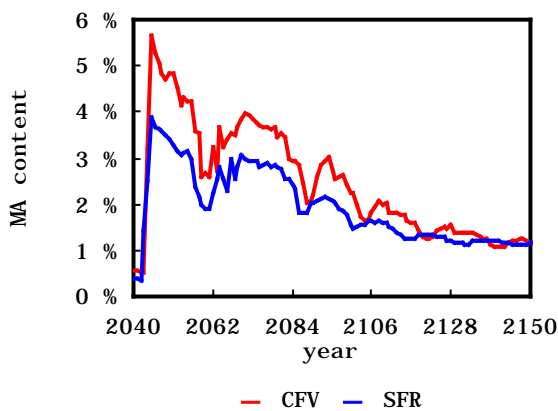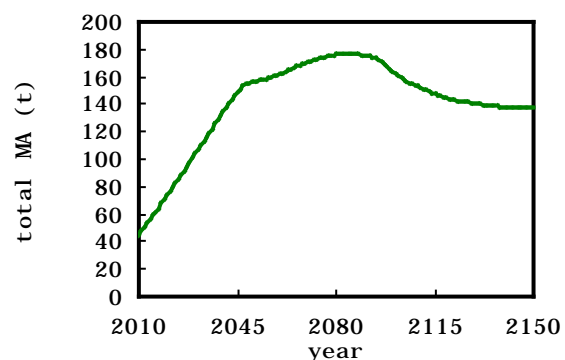

FIG. 14. MA mass content   *FIG. 15. MA total inventory*

The transmutation efficiency is quite the same with CFV as with SFR V2B. The final minor actinides inventory is around 140 tons (*Fig. 15*).

6. PLUTONIUM INVENTORY EVOLUTION

Plutonium makes the principal contribution to the long term radiotoxicity of the spent fuel. The waste management strategy is linked to the strategy adopted for the use of the plutonium.

The SFR core designs (SFR V2B and CFV) are breakeven with U-Pu fuel and become breeders when minor actinides are transmuted. As a consequence, the plutonium inventory is increasing in all the studied transmutation scenarios. (*Fig. 16*).
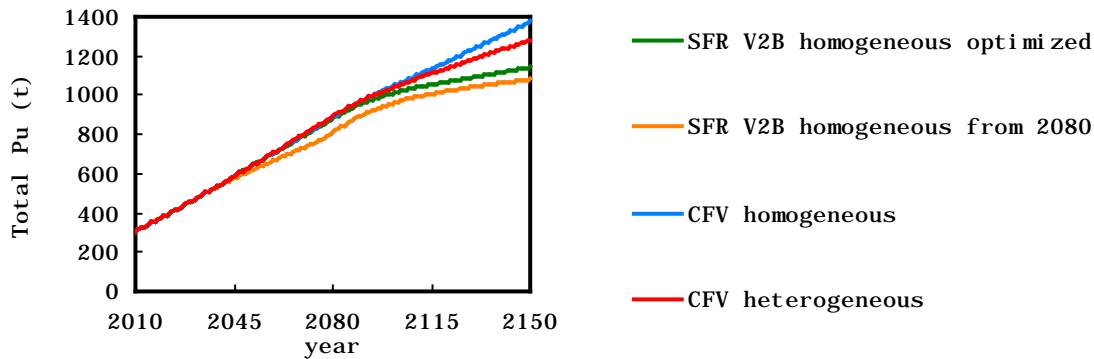

FIG. 16. Plutonium inventory

An alternative SFR concept could be specially designed to reach isogeneration while burning minor actinides. It would stabilize both minor actinides and plutonium inventories at equilibrium.

7. CONCLUSION

In the frame of the French Act for waste management, several scenarios have been studied, taking into acount a deployement of SFR, generally from 2040. Different transmutation options have been evaluated; this paper presents sensitivity and optimization of the transmutation scenarios.

Optimization of the reprocessing strategy may reduce the maximal minor actinide content in the fresh fuel (homogeneous transmutation case): with an appropriate reprocessing strategy the minor actinides mass content in the fresh fuel remains under 2.5% during the whole scenario.

The sensitivity to the SFR core design is also evaluated: the scenarios including CFV core design, with a significant gain on sodium void effect, have similar results as scenarios involving SFR V2B. The fuel cycle impacts are higher in heterogeneous transmutation case, the maximal minor actinides content in reactor is higher in homogeneous transmutation case.

A different date for the beginning of the SFR depoyment is investigated: the transmutation scenario which considers SFR deployment from 2080 has the same final steady state but the amount of minor actinides in the waste is doubled. The reduction of transition period to 30 years results in higher minor actinides content in fresh fuel; optimization of reprocessing strategy may be less efficient.

8.   PERSPECTIVES

The future studies may apply optimized reprocesing strategy to the CFV transmutation scenarios and take into account the last CFV design.

The possibility to transmute minor actinides both in fissile zones and fertile zones of the CFV should also be investigated.

SFR future designs without plutonium production when minor actinides are transmuted may provide scenarios with a stabilization of both plutonium and minor actinide inventories

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Feedback on FBR fuel fabrication process at the ATPu facility

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Abstract. Initial productions of mixed oxide fuel for the RAPSODIE and PHENIX French reactors, in the early 60s enabled CEA and AREVA to develop a specialized and robust process for the manufacturing of SUPERPHENIX fuel. It involved a thorough co-milling and granulation of powders prior to pelletizing and sintering operations. Pins, filled with these sintered pellets, were subsequently bundled together to produce the assemblies. In order to accommodate changes in fuel designs, materials and technologies, as well as improvements in quality and production efficiency, CEA and AREVA developed the process not only by adapting the powder preparation operations, but also by continuously improving the cladding and bundle assembly steps.

The purpose of this paper is to present the know-how of AREVA and CEA relative to mixed-oxide fuel fabrication for FBRs (e.g., SUPERPHENIX fuel fabrication at ATPu). This know-how will be employed in the design of the new Fuel Fabrication Facility (AFC).

I – Background and production data

The plutonium technology workshop (ATPu) was built to produce plutonium-based fuel elements within the scope of programs conducted by the French Atomic Energy Commission (CEA). Between 1962 and 2005, the workshop recycled 25 tons of plutonium which was used to produce 450,000 fuel pins, corresponding to more than 110 tons of oxides. The technology imposed when manipulating plutonium (a high α emitter) can also be used to manufacture fuel elements containing other transuranium elements such as neptunium, americium and curium within the limits imposed by the radiological characteristics of each of these elements.

These facilities were used to manufacture fuels for the Rapsodie, Rapsodie-Fortissimo, Phenix and Superphenix reactors under the French fast reactor program, as well as a fuel reload for the Prototype Fast Reactor (PFR) and various experimental fuels. From 1988, the ATPu workshop was also making MOX fuels for LWRs at the same time, which required re-organising the process and the hot cells.

In manufacturing these fuels, the ATPu workshop covered a broad range of products and designs:
- PuO$_2$ contents ranging between 13% and 30%
- Depleted uranium to highly enriched uranium
- Pellet diameter between 4.2 mm and 7.2 mm, with or without a central hole
- Pellet masses ranging between 1 g and 4.5 g with a density of 95% d_{th}
- Sub-assemblies from 1,600 mm to 5,400 mm and from 15 kg to 600 kg.
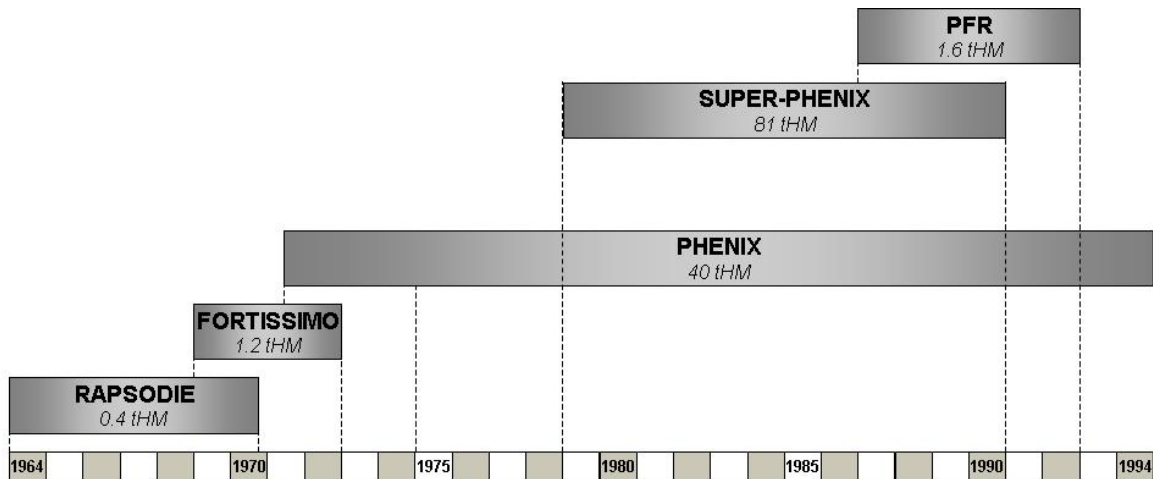
Chronology of FBR fuel production

II – Fuel fabrication process

a – General description

In the fuel fabrication process for fast reactors, all the UO_2, PuO_2 and chamotte (up to 30%) powders were finely ground to make an intimate mixture. This operation was performed in a uranium ball mill. This equipment was designed to grind up the initial powder agglomerates to increase their specific surface area and reactivity so as to enhance the homogenisation of Pu during sintering. This grinding technology included the formation of UO_2 and PuO_2 oxide agglomerates. This resulted in a mixture of generally poor flowability properties. Grinding was therefore followed up with a granulation operation which first and foremost aimed to improve the flowability properties. The granulation process was based on the compacting of powder under low pressure and the crushing of the resulting compacts. A sieving stage was then performed to select the grain size range and to remove fines so as to increase flowability and limit segregation phenomena. These operations were performed to manufacture all or part of the Phénix and Superphénix cores. After shaping by uniaxial pressing, sintering was performed in a continuous furnace (except for Rapsodie) in a reducing atmosphere.
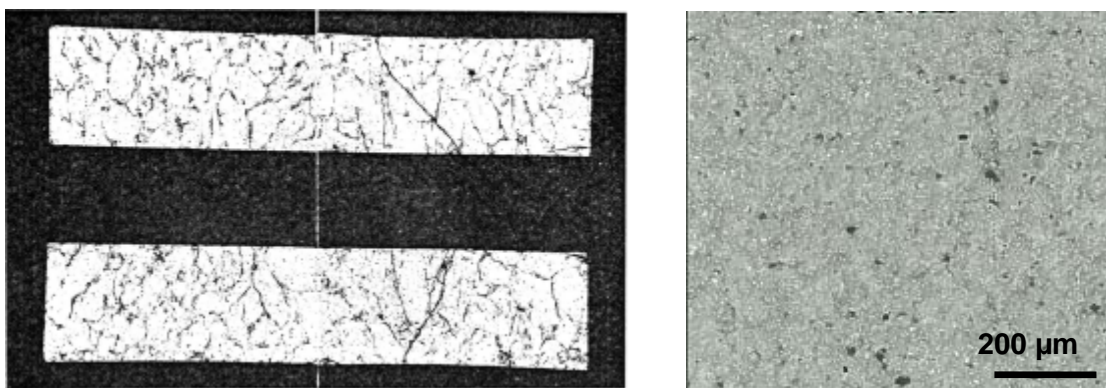
Left: Optical observation of a Superphénix pellet in a cross section

Right: X-Ray ($Pu_{M\beta}$) observation of a pellet with 25% PuO_2 (Pu appears in black)

Once sintered, the dense pellets were aligned on a tray and then inserted into the stainless steel cladding in a helium atmosphere using a pusher. The ends of the cladding were plugged and welded using a tungsten inert gas (TIG), and then a spacer wire was wrapped around the pins. Lastly, the pins were grouped together to form a hexagonal bundle which was inserted into a stainless steel hexagonal tube. TIG welding of the base and the top neutron shielding finished the fabrication process of the sub-assembly.

Checks were performed during the entire process. From checking the raw materials up to inspecting the sub-assemblies, about 60 different checks were performed.

b – Superphénix fuel fabrication line

The Superphénix fuel fabrication line offered a greater capacity. It was used to manufacture more than 80 tons of oxides for a nominal capacity of 18 tons of heavy metal per year. This fuel fabrication line was set up horizontally between a series of hot cells grouping the basic functions of the process over a total surface of about 2,500 m^2. The functions were grouped as follows:

- UO_2 procurement
- Dosing of powder jars
- Ball milling, granulation and lubrication
- Pressing
- Sintering
- Cladding
- Rod inspection and winding of spacer wire
- Forming of bundles and assembly of the fuel sub-assembly.

The connecting modules ensured communication between the process glove boxes located in the specific hot cells. The modules were used to store and transfer the powder jars. The sintering boats and pellet trays were transferred between the process glove boxes via an overhead transfer system. The entire process was blanketed by nitrogen, excepting the cladding station which used helium.

The pellet fabrication production yield rose as high as 99.3% for the first reload of Superphénix. This yield took into account a scrap recycling rate of about 9%. The overall yield for this fabrication process was 98.7%.

III – Process developments and changes

The fuel fabrication process was the subject of numerous tests and adaptations that made it possible to increase the above-mentioned yields.

Ball milling is a key stage in the pellet fabrication process since it directly determines the reactivity during sintering and the final homogeneity of the fuel. Special attention was paid to the milling cycle by alternating the milling tank filling and discharge operations on the one hand, and by optimising the milling angles on the other hand. Furthermore, tests were performed on milling tanks coated with a layer of polymer to limit wear of the surface and to reduce the incorporation of impurities in the powder. As the results proved unsatisfactory, the milling tanks have since been made of stainless steel.

Powder granulation is a proliferating stage that can have an impact on the staff dosimetry levels and on the quality of the products. This stage is nevertheless essential because it makes the powder flowable so it can be sent to the presses. The pre-compacting and crushing technique was the most frequently used method. Nonetheless, fabrication operations were also successfully performed with a roll-compactor. This equipment performed compacting and crushing in a single stage. It nonetheless made the compacting process more complex to control and put the manufacturer at the risk of double-cycle inverse. Tests also involved the successful implementation of a sieving-forcing system that made it possible to eliminate the pre-compacting stage.

A number of uniaxial presses were tested during the service life of the ATPu workshop. It is worth mentioning the single-punch mechanical pressure, the multi-punch hydraulic press and the rotating press. The single-punch presses had a very short cycle of about 2 seconds, leaving very little time to fill the matrix hole. This made granulation an essential stage. The onset of rotating presses made it possible to increase the filling time and tests were even conducted with non-granulated powder. Forming the central hole was also an important issue. Improvements also made it possible to reduce the number of central punch breakages and thereby increase productivity on the Superphenix line. Nevertheless, pellets with a small central hole remain difficult to manufacture and require reducing the rate of the presses, as was the case for the PFR fabrication operations.

The use of plutonium oxides of varying origins and isotope contents implied the variableness of the thermal and radiolytic characteristics of the powder mixtures. The variableness was taken into account by adapting the lubricants used. Initially used for Rapsodie fuel fabrication, calcium behenate was used. Calcium stearate was preferred for harder spectrums. However, the resulting calcium residues led to using zinc stearate whenever possible.

The specifications of fast breeder reactor fuel generally defined a stoichiometry ranging between 1.96 and 2.00 to avoid the formation of a secondary phase on the one hand, and to limit pellet-cladding interactions on the other hand. The sintering conditions required an atmosphere of argon and hydrogen. Sintering gas humidification tests nonetheless proved successful. These tests aimed to improve the homogenisation of plutonium while meeting the stoichiometric criterion.

Structural elements from the Phenix and Superphenix sub-assemblies have always been made from stainless steel. However, these alloys evolved during the service life of the ATPu facility so fuel elements with increasingly higher burn-ups could be used. The cladding materials were mainly composed of 15-15 Ti steel and then cold-drawn 15-15 Ti steel. The spacer wire was made from the same material. Depending on the period, it was either welded or crimped onto the pin plug. The materials used for the sub-assembly were first made from a simple stainless 316 steel grade to 316 Ti and then the EM10 alloy. The sub-assembly structure was first fixed to the other structural elements by means of TIG butt welding without filler metal. Tests were performed by press-fitting and crimping before using TIG welding with filler metal.

IV - Conclusion

The variety of fuels produced and the range of developments made to the different stages of the process showcase the wealth of experience accumulated by Areva and the CEA in the field of oxide fuel fabrication for fast reactors. This expertise is now fully exploited and guarantees the success of the future fuel fabrication workshops for the ASTRID reactor core.

The ASGARD project, an introduction

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Abstract. The ASGARD project (Advanced for Generation IV reactors: Reprocessing and Dissolution) started in January 2012. Its main goal is to understand and bridge the gap between the fuel reprocessing/separation community currently represented by the ACSEPT project and the fuel manufacturing and irradiation community currently represented by the FAIRFUELS project. The main goal is to investigate the technical challenges posed by nuclear fuels for GEN IV fast reactors, namely: oxide and inert matrix fuels, nitride fuels, and carbide fuels. These three fuel groups also constitute the three scientific domains. In each domain similar issues are addressed concerning the fabrication and recyclability of these novel fuels. Thus different production routes are investigated and these routes are in parallel reviewed by our industrial partners to assess the feasibility of large scale manufacturing. The manufactured fuels are also investigated with respect to chemical and physical characterisation. When a suitable route for uniform production on lab scale has been settled, the possibilities for recycling is addressed by investigating possible dissolution routes. Different fuels have different issues, e.g. in the nitride case the isotopically enriched nitrogen (15N) must be recycled and for the carbides the formation of different organic species produced upon dissolution needs to be addressed.
In parallel to this conversion issues for the possible recycling and separation processes are addressed in collaboration with the separation community. The final aim is to find a convenient route to convert the separated product solutions (U, Pu, MAs) from reprocessing and convert them into materials suitable for fuel production.
Since the ASGARD project deals with considerable amounts of nuclear material, training and education is a vital part of the project. During the course of the project several campaigns will be launched to educate younger scientists in the art of handing radioactive material in a safe and secure way. This will be carried out in collaboration with other relevant EU framework projects such as ACSEPT, SACSESS, FAIRFUELS and CINCH.

1. Introduction

Nuclear power is considered by many to be the solution to the global warming issues we debate today due to its extemely low carbon emission potential. However, there are evident drawbacks in both the effect of accidents and the handling of the nuclear waste.
In 2011, 435 nuclear reactors were in operation in the world producing about 12.3% of the electric power. Although nuclear power has seen a slight recession in political interest since the Fukushima accident in March 2011 there were still 65 reactors being built at the end of 2011[1]. As a result of the Fukushima accident countries like Germany, have decided to phase out nuclear power. But at the end of 2012, the pro nuclear agenda by the elected government in Japan signalled that they may continue their nuclear power production according to or close to their original plans. Thus it is reasonable to assume that nuclear power will be part of the energy mix in the world for many years to come.
Throughout the development of nuclear power there are attempts to clasify the different reactor types as "generations" with the first experimental reactors being "Generation 1" and the majority of todays

fleet built in the seventies and eighties being "Generation 2". New improved concepts called "Generation 3" and "Generation 3+" are now considered and in some cases built. However, all these generations typically use the nuclear fuel only once (with the exception of countries like France which reuse the plutonium in the fuel one time as Mixed Oxide fuel (MOX)) leading to a very low usage of the inherent energy. Seen in this context of "sustainability", it is not unreasonabe to suggest that the used nuclear fuel should be recycled to use a considerably greater part of the energy in the fuel. In addition, the uranium waste piles from the enrichment process would then also be available as fuel. In addition it has been pointed out that by totally recycling all the actinides the remaining highly radioactive waste could reach the radiotoxicity of natural uranium after about 1000 years,.

In order to achive the greater energy usage and shorten the storage time a new generation of nuclear power systems have to be applied since fast neutrons are required to fission most of the actinides without out irradiating the lanthanides or other fission and corrosion products. Thus we are now not discussing a new generation or reactors. Fast neutrone spectrum reactors have been operational since 1951 when EBR1 in the US was the first electricity power producing reactor in the world. Rather we have to utilise a "Generation 4 *system*" comprising spent fuel dissolution and separation, novel fuel production and fast neutron spectrum reactors (maybe in combination with thermal reactors).

When reviewing the different activities being done in relation to novel nuclear power generation in Europe, it was clear that significant reasearch was made in many of the necessary areas but some parts were missing to bind it all together. With this in mind the ASGARD project was created and lauched in January 2012.

2. The ASGARD project

As was pointed out earlier, Generation 4 reactors are planned to have a breeding ratio of plutonium equal to unity, while also functioning as burners of minor actinides. The use of novel coolant technologies and advanced fuels in combination with stringent safety objectives of Generation 4 systems requires significant R&D to be carried out in the immediate future, in order for demonstration on industrial scale to become possible in the next decade. Relevant research is performed in national programmes as well as in FP7 projects such as ESFR, LEADER, GOFASTR, ACSEPT, SACSESS, GETMAT, FAIRFUELS, FREYA and F-BRIDGE. Unfortunately, today, integration between reactor, fuel and recycling communities is lacking. There are discrepancies between the reactor design on one hand, and the technological feasibility of fabricating, dissolving and reprocessing the selected fuel on the other hand. This is reasonably true for MOX fuel, but even more evident for advanced nuclear fuels. Such future nuclear fuels comprise e.g. inert matrix fuels, nitride fuels and carbide fuels. In all these areas, there are still large gaps in knowledge before any process for the manufacturing, operation and recycling of these fuels can take place. The orientation of ASGARD to two highly relevant FP 7 projects ACSEPT and FAIRFUELS is given in Fig 2.

FIG. 1. The sustainability circle for nuclear fuel where ASGARD fills the gap between the main focus of FP 7 ACSEPT and FP7 FAIRFUELS

Consistently with the above mentioned future nuclear research, the ASGARD project's main objective is to provide a structured R&D framework bridging the research on fuel fabrication and reprocessing issues. The main problem today is to tie the recycling of the nuclear fuel to the fabrication of new fuels. Seen in this context the outline of the work on each of the fuel types

will be: dissolution, conversion and fabrication. These processes will be applied to the different fuel types that have been identified as possible alternatived for the Generation 4 systems: Oxides and CerCer / CerMet inert matrix fuels, Nitride fuels and Carbide fuels. Based on these building blocks the structure of ASGARD was created. For continous updates on the progress of the project please visit the official project website at: www.asgardproject.eu**.**

2.1. *Participants*

The wide range of personal skills and abilities together with facility needs in the ASGARD project is well reflected by its participants. In ASGARD we have respresentatives from universities, national laboratories, research intritutes and industry from nine different coutries in Europe.

2.2. *Project structure and content*

In order to reach the goals set up for the project, there is a need to find an optimal structure of the project. It seems natural to focus the technical domains around the different fuels identified as the important ones and then to have the different activities relating to the selected fuels as work packages within each fuel domain, as seen in Fig 3.
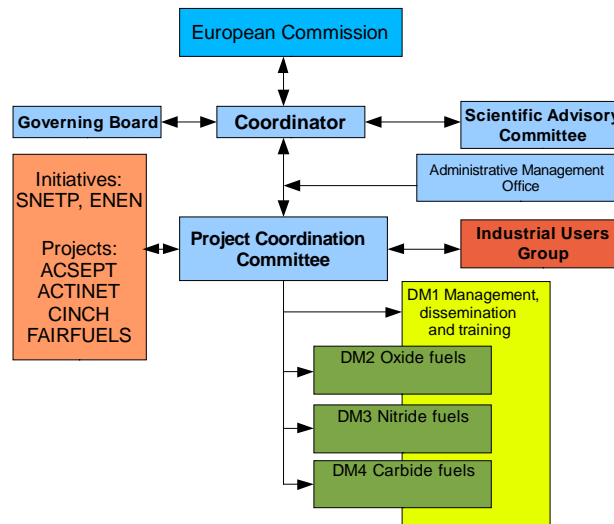

FIG. 2. General structure of ASGARD

Each Domain will be described in more detail below. However, it is important to point out that a large emhasis is put on education and training since working with highly radioactive material is a skill that very few people have and can be only in fewer places. Therefore one important goal of a project like ASGARD is to ensure good possibilities for mainly younger scientists and PhD students to get "hands on" training on working with these materials and get a deep understanding of the risks involved and how to handle them in a safe and secure way.

2.2.1. *Domain 1 - Management, Education and Training, Dissemination*

The management of the project, sustainable education, training and dissemination of the knowledge achieved within ASGARD will be addressed in Domain 1, in three integrated work packages (WPs).

2.2.1.1. WP 1.1 Project Management

The objectives of WP1.1 is to assure efficient co-ordination of technical activities of ASGARD project, quality assurance of the project's deliverables and the processes leading to them. Effective management is applied to overall legal, contractual, ethical, financial and administrative management

of the project and management of the project's decision-making processes to respect relevant standards. Internal communication within the partners . Management and logistics for transportation of different unirradiated fissile material and irradiated material between partners is also included.

2.2.1.2. WP 1.2 Education, Training and Mobility

The main objective of WP1.2 is to stimulate exchange of knowledge and practical experience among the community and future researchers. Students (MSc and PhDs) represent the primary target group, but also teachers and other members of the community will benefit from ASGARD activities and measures in area of education/training and mobility. Dedicated courses based on the outputs of the domains and previous experience will be developed. A special Winter School in nuclear fuel manufacturing was given jointly between ASGARD and the FP-7 projects FAIRFUELS and CINCH in January 2013. A special course in industrial manufacturing techniques will be given by one of our industrial partners, Westinghouse. Special emphasis will be put on safety aspects related to dissolution, conversion, reprocessing and fuel fabrication under normal and accident conditions. Even more is a continuous feed-back and eventual improvements with regard to safety and handling of materials will be set-up. This will continue all along the project and collected in a document and presented at the end of the project. Joint presentations with the ACSEPT project was made during the ATALANTE conference in September 2012 where ACSEPT handled a session on separations and ASGARD one session on actinide materials chemistry.

Also, scientific outputs from one of the DM2, DM3 or DM4 will be used for development of an e-learning module for an already existing e-learning platform. This action is seen as a complement to previous and parallel efforts of other EURATOM projects and will act as a dissemination measure of one of the projects outcomes.

2.2.1.3. Dissemination, Exploittion and Networking

The main objectives of WP 1.3 are to guarantee dissemination of knowledge of the project and results from the project to the nuclear community.

In order to reach the nuclear community and the interested stakeholders, a careful identification, approach and management of key target groups represented mainly by nuclear industries, key research organizations and the nuclear technical community as a whole will be conducted within WP1.3. A database comprising the stakeholders will be made available on ASGARD website. Two International Workshops will be organized during the project, the first one two years into the project and the second one at the end of the project.

A sustained networking effort will be conducted towards synergy with other European networks and organizations (ENEN, SNETP, TSO, etc). The networking, especially with ENEN representatives will be ensured by analogy with already well established relations between ENEN and other FP7 Education and training projects, e.g. CINCH. There natural links between ASGARD and these projects through partner participations.

2.2.2. Domain 2 - Oxide Fuels

The main objectives of Domain 2 are addressed in three separate work packages. Work Package WP2.1 looks at Inert Matrix Fuels (IMF), whereas work package WP2.2 is concerned with basic studies on oxide fuels for Generation 4 systems. Finally, work package WP2.3 covers the conversion issues for IMF and Generation 4 oxide fuel, coming from dissolved spent fuel to suitable precursors for fuel fabrication. In this way, ASGARD builds an essential bridge, complementing the re-processing studies in ACSEPT on one hand, and the fabrication studies in FAIRFUELS on the other hand. The tasks in WP2.1 and WP2.3 are basically independent. WP2.3 represents the conversion theme in Domain 2 and is the cross-cutting theme across the technical Domains.

2.2.2.1. WP 2.1 Inert Matrix Fuels

The main objective of WP2.1 is to gain a comprehensive knowledge of the reprocessibility of MgO and Mo-based actinide bearing CerCer and CerMet targets. The two types of fuel designed for a transmutation cycle involving multi-recycling are (minor) actinide oxide based CerCers (with MgO matrix) and the CerMets (with Mo metal matrix). As IMF contains significant amount of inert matrix (e.g. MgO, Mo) special head end treatments after dissolution are necessary. On the other hand, it is necessary to remove the inert material to simplify the separation of the actinides and to improve the final conditioningof the remaining fission products before vitrification. The main objectives of WP2.1 are to assess the head-end step of both MgO-based CerCer and Mo-based CerMet fuels. Specifically for Mo, the recovery of isotopically tailored molybdenum is also studied.

For Mo-based CerMets, aqueous reprocessing routes are applied to investigate the dissolution of the CerMet targets. Mo-based inert matrix fuels with UO_2 and PuO_2 as actinide compound will be fabricated and used in pre-treatment and dissolution studies. The recovery and recycling of dissolved depleted Mo, which is isotopically tailored to improve its neutronic properties, is also extensively pursued.

In MgO-based CerCer fuels, Mg(II) must be separated prior to vitrification. Specific head-end steps and methods will be studied to separate Mg(II) from surrogate solutions containing nitric acid of relevant concentrations. The studies aim at: minimising the MgO ending up in the vitrified glass, assessing how Mg(II) separation can be implemented in separation schemes and screening new and/or other extracting agents for Mg(II) separation not used in actinide separation schemes.

2.2.2.2. WP 2.2 Basic Studies on Oxide Fuels for Generation 4 Systems

Work Package 2.2 addresses the solubility of plutonium from (Pu,Am)oxide with various concentrations of plutonium and minor actinides. Within ASGARD the minor actinides will be represented by Am. Dissolution and reprocessing of this system has never been fully studied. But it represents a key scientific issue for process development, as, in a multi-recycling scenario, ultimately fuels with various plutonium and minor actinides conventration need to be reprocessed.

In the first part of this work package, the composition of actinides in spent fuel for various P&T scenarios will be determined. The outcome of this modelling yields a series of realistic compositions of actinides (U, Pu and Minor Actinides) to be envisaged in spent transmutation fuels. These compositions and, specifically, the ratios between U, Pu and Americium form the basis for the fabrication and dissolution studies.

Based on that, series of $(Pu,Am)O_2$ targets will be made with varying Am content for dissolution and reprocessing test. Envisaged targets for transmutation can obtain up to 50 wt% of minor actinides; however the adverse effect of the MA-content (specifically Am) on the dissolution capability is unknown. It will be a key objective to assess generally the issue of solubility of high Am-content targets and to establish a relationship between Am-content and dissolution capability. Small samples (disks) of $(Pu,Am)O_2$ will be manufactured and then dissolved in two different labs. The fact that two institutes are involved in the fabrication allows a comparison between the different samples.

Final objective of WP 2.2 in establishing a relationship between Am-content and dissolution capability will address open key questions concerning the maximum achievable Minor Actinide content in fuels and targets for transmutation purposes in future Fast Reactor systems.

2.2.2.3. WP 2.3 Conversion from Solution to Oxide Precursors

In order to foster and strengthen the links between partitioning and transmutation, WP2.3 carries out studies for the conversion of separated elements to solid precursors prior to fuel fabrication with focus on inclusion of minor actinides in rather high amounts in U,Pu oxides.

After partitioning, the actinides it is planned to reconvert them into fuel for further transmutation by ADS or Generation 4 reactors. For this purpose, a suitable material is required to contain minor actinides retrieved from partitioning. The objectives of the research are related to the development of methods for the co-conversion of separated actinides for fuel preparation. ASGARD focuses the work on sol-gel routes such as the well-known internal gelation route and the new Complex Sol-Gel Process

(CSGP) developed at ICTHJ in Poland. Additionally, the impregnation of actinides into selected inorganic/organic matrices will be studied.

The first option will use the experience gained in earlier studies using composite inorganic-organic materials with polyacrylonitrile binding matrix. The second option is based on the exchange of metal ions with the acid form of a weak-acid resin. In the past it was developed in US for the preparation of uranium based microspheres for HTR application At ForschungsZentrum Jülich in Germany studies for the preparation of minor actinide loaded resins for subsequent fabrication of MA loaded oxide based spheres will be undertaken.

A new and innovative method based on the photo- and radiation induced co-conversion of selected actinides will be assessed. Solutions containing various necessary precursors, scavengers and/or stabilizers will be irradiated to obtain the solid phases; both direct irradiation route and its combination with a radiation/high temperature thermal treatment will be studied.

Before studying the technological aspects of the co-conversion process, many fundamental data such as the thermodynamics and kinetics of the conversion are needed. In the sol-gel processes, ammonia will be the hydrolyzing agent for the formation of the actinides hydroxides. Hydrolysis of Am and Cm (oxidation state III) is not so easy as that for Th, U, Pu (oxidation state IV, or VI). Complexing agents will be tested for the adjustment of the reactivity of different actinides.

The determination of the performances of the co-conversion methods, including the kinetics of the hydrolysis reaction, the yields of co-conversion in dependence of the composition of the aqueous solution will be studied. The elaboration of the solid pre-cursors (i.e. microspheres by sol-gel) will be investigated in process oriented research. The solid precursor products formed after sol- gel or impregnation will be characterised and the further fabrication steps including calcinations and sintering to the final oxide product will be investigated.

2.2.3. *Domain 3 - Nitride Fuels*

In ASGARD, the dissolution performance of mixed actinide nitrides as well as ZrN stabilized compounds will be assessed based on tests with irradiated and fresh fuel. Processes for recovery of N-15 enriched nitrogen will be developed. Alternative methods for dissolution, such as hot water processing, shall be investigated in this context.

The dissolution tests will be performed on both fresh and irradiated fuel samples, the latter deriving from the CONFIRM irradiation. Fresh fuel samples will be fabricated in order to carefully investigate the influence of carbon and oxygen impurities.

2.2.3.1. WP 3.1 Dissolution of Fresh and Irradiated Nitride Fuel

Pure uranium nitride is known to be readily soluble in HNO_3. Conflicting data on the dissolution rate of ZrN in hot HNO_3 exist, possibly being due to the presence of oxygen impurities in the nitride. Data on the solubility of (U,Zr)N is lacking, but very low dissolution rates have been observed in the analogous (Pu,Zr)N system at high zirconium contents. It needs to be established at what Zr content and at what levels of oxygen impurity the conventional reprocessing methods become inapplicable for (U,Zr)N (Pu,Zr)N and (U,Pu,Zr)N fuels. The dissolution of ZrN and mixed zirconium nitrides in HNO_3 is however strongly accelerated by the addition of a small amount of HF (hydrofluoric acid), which is known to attack ZrO_2. The exact amount needed can be established for any particular material composition and dissolution temperature.

Pure UN reacts rapidly with water at temperatures above 200°C. This does not result in a true dissolution, but a decomposition of the pellet and formation of uranium oxide sediment. The exact composition of the formed oxide will depend on pH, oxygenation and other environmental conditions, but will have an oxidation state of approximately +4 unless oxidative agents are present. There are conflicting reports of the rate of this decomposition, which can be expected to vary strongly depending on what form the UN is in (powder, porous sintered pellet, dense sintered pellet etc). The rate increases with temperature and is the most rapid in hot steam. We speculate that reprocessing of pure UN fuels in aqueous solution or dilute non-oxidising acid, rather than the standard HNO_3 solution, may be feasible. It should not be necessary to oxidise the uranium to +6 state (uranyl ions) as in conventional reprocessing. In the presence of a chelating agent, the formation of UO_2 sediment could

be completely avoided, and the result would instead be true dissolution of uranium as a metal-organic complex amenable to extractive separation methods.

The conversion cross cutting activity in ASGARD will have significant relevance also in the nitride domain. Assuming that voloxidation methods will be used for recovery of N-15 from irradiated nitride fuels the following separations can be made using state of the art separation techniques developed in e.g. FP7 project ACSEPT. Then, depending on manufacturing method selected for the nitrides the conversion has two routes. Either follows the methods developed in DM2 to produce oxides or there is a need to develop a novel process resulting in actinide metal compounds.

2.2.3.2. WP 3.2 Fabrication of Nitride Fuels

Previous work on the production of nitride fuels has typically utilised actinide oxide powders as starting material. The perceived advantage is that oxides are more readily available. However, this path of synthesis introduces several difficulties. Firstly, the oxygen needs to be eliminated, which commonly is done by carbothermic reduction, in which the oxide powders are mixed with carbon dust and allowed to react at very high temperature. Near quantitative elimination of oxygen (as CO) is practically feasible only in the presence of a certain excess of carbon. However, the excess carbon also tends to form stable carbide with uranium. The carbothermic reduction is performed in parallel with the nitridation reaction to avoid formation of liquid metallic uranium; this is achieved by streaming nitrogen gas through the reaction vessel. Unreacted carbon is then removed by reaction with a nitrogen-hydrogen mixture.

While elegant in principle, the product will in reality tend to contain considerable residues of oxygen and carbon as substitutional solution in the nitride, or rather, the carboxynitride. Tweaking reaction parameters can ameliorate but not completely eliminate this problem.The presence of oxygen and carbon is likely to affect dissolution performance.

In ASGARD, high purity (U,Zr)N and (Pu,Zr)N will be manufactured by first producing hydride powders from metallic uranium, plutonium and zirconium, all of which are available in Sweden. The hydrides are readily formed at modest temperatures, relaxing the requirements on equipment and (in principle) totally excluding oxygen and carbon from the process. The hydride powders are then immediately reacted with nitrogen in a second step to form the corresponding nitrides. The stoichiometry of UN can be controlled in a final step of heating in argon, while PuN only exists as a mono-nitride. The UN and ZrN powders are mixed, with the option of additional co-milling, and then cold pressed and sintered for densification and the formation of solid solution. Sintering may be done by conventional furnace heating. An alternative route is hot pressing and sintering by SPS (Spark-Plasma Sintering) technology which will be investigated.

The produced pellets are characterised by SEM (grain size, overall homogeneity), XRD (atomic-scale homogeneity, i.e. verification of solid solution) and densitometry. Elemental analysis is performed to verify oxygen and carbon impurity levels in the end product.

2.2.3.3. WP 3.3 Enrichment of Nitrogen in N-15

A disadvantage of the standard dissolution route is the dilution of expensive N-15 likely being necessary for fabrication of industrial nitride fuels. A possible method of recovering N-15 may be hot water processing.

A new technology for nitrogen enrichment up 99 atomic percent of N-15 suitable for nitride fuel production on industrial scale will be elaborated by INCDTIM. The method is based on separation by isotope exchange method in a Nitrox system under pressure. Sulphuric acid waste production will be avoided by reduction to SO_2, which then can be used in the N-15 production cycle for conversion of nitric acid into nitrogen oxides in the product refluxers of the isotope separation plant. The reuse of sulphur dioxide results in an important cost reduction for the production of N-15, taking into account that, at present, more than 50% of the costs are due to the feed of sulphur dioxide.

2.2.4. Domain 4 - Carbide Fuels

Despite their excellent thermal properties carbides can show considerable swelling upon irradiation leading to fuel cladding mechanical interactions (FCMI). Fuel swelling can be greater than for oxide pellets leading to early fuel/cladding gap closure.

Carbide fuels can be pyrophoric and direct dissolution can result in flammable gases and organic complexants that interfere with actinide extraction and enhance the formation of unwanted emulsions. The overall goal of Domain 4 is to address the key technical issues associated with carbide fuels to a level of understanding approaching that of oxide fuels.

2.2.4.1. WP 4.1 Design and Manufacture of Carbide Fuels for Generation 4 Systems

The objectives of this work package are to establish a production route to a carbide material that will provide better thermal properties than oxides while at the same time minimises the FCMI. As part of this work package there will be a review of global experience to date relating to irradiation of carbide fuel and define the operating conditions for a Generation 4 system with particular focus on the recent experience gained at the Indian FBTR at Kalpakkam. Modelling work will establish an optimum density/porosity for the fuel while experimental work will establish a range of production routes. Methods will be developed on uranium carbide fuel incorporating appropriate lanthanides as a surrogate for the minor actinides.

The study will examine a number of options such as the effect of varying the amount of open and closed porosity across the pellet radius, the selective use of additives which increase the creep rate of the outer region of the pellet adjacent to the cladding. The selective use of additives which increase the diffusion rate of fission gas ions in the central regions of the pellet can also be examined and, if realised, can be expected to contribute to a reduced swelling rate. This initial modelling study will also help to define the manufacturing requirements of uranium carbide fuel. Two fabrication approaches will be pursued 1) Gradient pellet pressing; 2) Novel carbide production and sphere-pac technology. The modelling will examine the main factors that can be influenced to strike a balance between good thermal properties and capacity for reduced fuel swelling.

Advanced pellet forming techniques using radial gradient pellet pressing, pore former additives and additives to increase the compressive steady state creep rate will be employed for traditional pellet formation and post carbothermic reduction. Sphere-pac techniques with advanced internal gelation and microsphere formation for the production of carbides will also be studied. This technique is particularly well suited for the incorporation of minor actinides by infiltration or direct inclusion methods. Lanthanides will be used as a surrogate for minor actinides and the effect of the % w/w loading will be established.

As part of the cross cutting theme of actinide conversion from liquor to fuel material novel carbide production routes will be explored that are compatible with MA incorporation and have the advantage of fewer powder handling operations reducing the overall dose to operators during the production process.

       Weak Acid Resin Process It is based on the WAR process which was originally developed at Oak Ridge National Laboratory, and consists of loading cation exchange beads with an actinide cation followed by mineralizing the loaded resin in an inert atmosphere to make microspheres of metal oxide intimately mixed with carbon, which provides precursor for the carburisation step.

       Synthesis of uranium carbide derived from colloidal precursors and sugar.

The proposal concerns the study of new synthesis routes of uranium carbide from colloidal precursors and sugar. Various precursors of uranium (oxide, hydroxide, oxalate) will be combined with a carbon source derived from the pyrolysis of sucrose. This route has been successfully used to at temperatures as low as 1300°C for silicon, zirconium and hafnium carbides.

       Polish Complex Sol-Gel Process . Synthesis of Uranium carbides by the following steps: preparation of ascorbate uranium sols; dispersion of carbon black in those sols; gelation of the dispersion by water evaporation to microspheres (diameter <100µm) using a patented ICHTJ; thermal decomposition of carbon containing gels in all shapes to a homogeneous mixture of $UO_{2.x}$-C and in-situ carbothermic reduction in a vacuum to UC or UC_2.

PAN bead process Making use of the experience gained in the ACSEPT project, conditions will be defined for the application of highly porous polyacrylonitrile (PAN) beads (infiltration technique) or solid extractants with extraction agents incorporated in PAN matrix (extraction method) for the preparation of actinide oxides (U and Eu as a model for Am) in a carbide matrix. The preparation of uranium and europium carbides will be demonstrated on laboratory scale

The final task is to study the high-temperature chemical interaction between the different gas cooled reactor fuel materials in order to direct the choice of these materials. The reference fuel is the mixed carbide (U, Pu)C_{1+x}. The reference case material is the SiC / SiC$_f$ composite. In the "classical" configuration, a metallic liner (W, W-5Re, Ta, Nb, Nb-Zr) is placed between the fuel and the SiC/SiC$_f$ case to insure the integrity of the fuel towards the emerging gaseous fission products. Experiments will be led to study the interaction UC/liner, (U, Pu) C/liner and liner/SiC. Information from Task 4.2.4 will be an input to this task. Specialist computer modelling codes will determine the most appropriate type of cladding material for a particular fast reactor type.

2.2.4.2. WP 4.2 Reprocessing of Carbide Fuel

To achieve a closed fuel cycle the reprocessing of carbide fuels must be achievable on an industrial scale with full (> 99%) recovery of the actinides. Carbides are viewed as more hazardous than oxides from a reprocessing point of view. They are thermodynamically less stable than oxides and can react with air and water to release potentially explosive gas mixtures under certain conditions. Any decision to designate carbides as the fast reactor fuel of choice must consider their specific reprocessing needs. To help achieve this objective the following tasks will be delivered.

Work to be undertaken here involves the formulation of appropriate dissolution rate equations. In particular, emphasis would focus on (U, Pu)C fuel pellets, either pre-treated by controlled oxidation in a furnace to a range of particle sizes or direct dissolution of the carbide. Additionally, this study will also consider the use of catalysts for the enhancement of dissolution rates (e.g. silver II). Published ignition temperatures and oxidation mechanisms for carbides vary widely depending essentially on: the powder processing, the powder specific surface area and the processing atmosphere partial pressures. An important output from this work will be a definition of the safe operating envelopes for reprocessing carbide fuels in a nuclear environment. The information will be of great benefit in establishing the safety case for experimental work within ASGARD and for nuclear reprocessing plants.

With guidance from Task 4.2.1 the oxidation of (U,Pu)carbides as a pre-treatment step using CO_2 or air as the oxidant will be assessed. The evolution of CO/CO_2 gases with time will be monitored to establish reaction rates and validate the model in Task 4.2.1. A vast body of knowledge from India, France, Japan, USA, Russia and the UK archives will be reviewed and previous experience used to establish the most appropriate way to pre-condition carbide fuel in a safe way that is acceptable to the nuclear industry. PSI has installed an inductive heating device (InVAP) in combination with a mass spectrometric detector to investigate the release kinetics of volatile fission products from fuel material as a function of temperature (PSI contribution to the FP7 ACSEPT program). This equipment will be used for the ASGARD program to study possible advantages of a thermal pre-treatment on sphere-pac fuel. The direct dissolution of (U,Pu)carbides in nitric acid including the destruction of any organic residues detrimental to the chemical separation stage will be explored. Previously components such as mellitic and oxalic acid have been identified in addition to acetylene and other flammable gases. One aim of this task is to study the impact of these potential complexants on the extraction and backwashing of uranium(VI) and plutonium(IV) by TBP (diluted at 30% in TPH). The mechanism of organics formation will be examined and their effects on solvent extraction processes established together with strategies for avoiding/dealing with them. The output will be a recommendation as to whether the benefits of direct dissolution can be made to outweigh the potential hazards. Conventional PUREX reprocessing of nuclear fuel from 2nd generation reactors involves the shearing of fuel assemblies containing both the fuel and the fuel cladding. The actinides are leached from the relatively insoluble metal cladding and sent to waste for encapsulation. The final part of WP 4.2 looks at how the cladding material will impact on the head end fuel pre-treatment and/or dissolution steps. Simple tests on candidate cladding materials will be performed under the optimised conditions found in Tasks 4.2.2 and 4.2.3.

2.2.4.3. WP 4.3 Molten Salt Processing of Carbide Fuels

Chemical oxidation or chlorination of carbides within molten salts will be explored in processes that can be made compatible with a hydro or pyrometallurgical process to recover the actinides from fission products. This will include examination of cladding materials e.g. SiC/SiC_f and uranium carbide pellet processing methods compatible with state-of-the-art molten salt reprocessing methods. Electrolytic methods to be explored for the treatment of carbide fuels (direct, or after *ex situ* or *in situ* chemical pre-treatment) will include direct electrochemical dissolution methods, anodic dissolution and selective electroplating of actinides. Anodic dissolution experiments will exploit the established electronic conductivity of uranium oxycarbide solid solutions (possibly formed by *ex situ* or *in situ* treatment in MS) with electrodes being fabricated from these materials,or precursors thereof. The results will be considered within the context of state-of-the-art molten salt reprocessing of fast reactor fuel and comment on the potential benefits of this method over hydrometallurgical reprocessing methods.

3. Conclusions

It is expected that through its structure, content and participants that the ASGARD project will advance the knowledge of production and handling of novel nuclear fuels far beyond the current state of the art. At the same time it is expecteed that the different research communities needed to bring the next generation of nuclear reactor systems from the laboratories to the actual implementation will be integrated and working towards a common goal.

ACKNOWLEDGEMENTS

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A new transport packaging for fresh ASTRID fuel transportation

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Abstract. AREVA through its subsidiary TN International has a huge experience in terms of design, licensing, manufacturing of packaging and finally the transport of nuclear material and especially fresh and used fuel (UO_2, MOX, etc.,) .

During the 70's, AREVA developed a transport solution for transportation of fresh fuel for French fast reactors PHENIX and SUPERPHENIX: the so called FS41.

In the frame of the ASTRID program, CEA and AREVA are working on the development of a new generation of packaging for fresh fuel based on latest developments of the MX fleet of packages developed for French, European and Japanese MOX needs. This packaging and its transport solution will include an improved payload compared to the previous FS41 development, higher levels of safety, security and physical protection due to the evolutions of regulatory requirements. This packaging will be able to transport either fuel pins or a full sub-assembly.

1 Introduction

TN International (known in the past as COGEMA LOGISTICS or TRANSNUCLEAIRE) is the AREVA subsidiary dedicated to logistic regarding nuclear material. TN International has 50 years experience in term of Design, Licensing , Manufacturing of nuclear casks and transportation through the world of nuclear material in the all the recycling cycle as raw nuclear materials, fresh or spent fuels for nuclear power plants, research reactors and wastes and a huge experience in intermediate storage of spent fuels through the world.

2.Transport cask fast reactor experience

AREVA developed in the 70's a dedicated transport solution for the transport of fresh for the fast reactors PHENIX and SUPERPHENIX: the so called FS41.

This package was able to transport either rods in canister or completely assembled fuel.
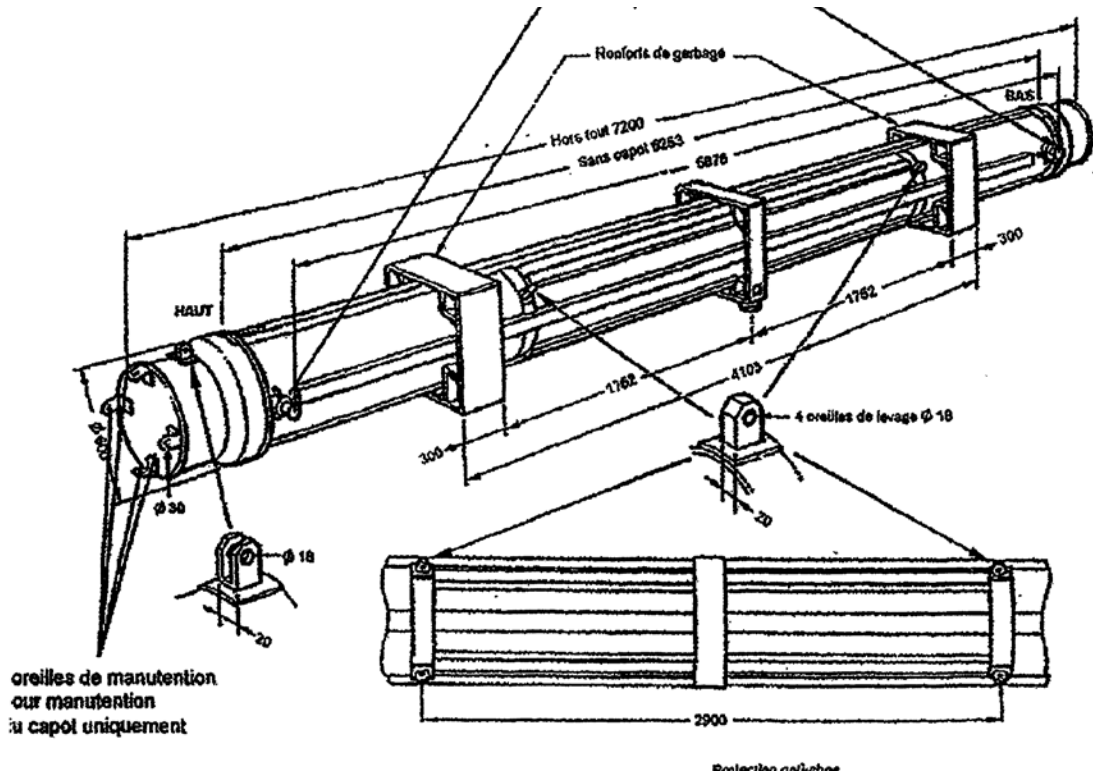
The main charactistics of this package are the following:

Performances

- 1 fresh fuel assembly classic or experimental hexagonal section with 271 rods. Pu content up to 30% of heavy metal
- Rods in canister
- Maximal thermal power : **363 W**

Main features

	LOADED	EMPTY
WEIGHT (kg)	3 600	2 630
SIZE	LENGTH	DIAMETER
CAVITY (mm)	5645	257
OVERALL (mm)	7 200	600

General description

The body of the FS41 package was made out of two coaxial steel cylinders separate by neutron and thermal protection. The cavity was closed at each side by a closure equipped with an internal shock absorber so that the packaging stays leak-tight under normal and accidental condition.

Two shock absorbers at each side protected package regarding NCT and ACT drop conditions and assumed also protection regarding dose rate and thermal insulation of the elastomer gaskets of the closure

Fuel assembly was protected during transport, loading and unloading operation by mean of a non leak tight canister introduced in the cavity of the package.

The packages were loaded per 4 units in a dedicated security caisson the CBTO8 (that mean 4 assemblies per transport). The CBTO8 caisson assumed the main part of physical protection of the nuclear material.

Licensing

This package was licensed in France regarding 1973 IAEA regulation till 2010, and could not be licensed according 1996 IAEA regulation (no double containment regarding criticality issue for such a content) . Last transports to move the last half core manufactured in the CADARACHE AREVA FACILITY to SUPERPHENIX Reactor plant were performed in 2007.

This package is no more licensed .

3. New development in progress

In the frame of ASTRID program managed by CEA for the development of a new generation of fast reactors, CEA and AREVA launched in the middle of 2012, preliminary studies for development of transport solution for both rods and assembled fuel assemblies.

Assumptions regarding fuels

Hexagonal section

Overall length around 14 feet (4500mm)

Pu content up to 35% of heavy metal. Possibility of use of reprocessed Uranium

Maximal thermal power around 900W per FA

Request for transport solution

Maximum payload in order to reduce the number of transport (four fuel assembly in previous FS41 solution)

Licensing according last version of IAEA regulation applicable

Gross weight package + fuels assemblies + security caisson (physical protection) +truck compliant with road regulation

Dry loading and unloading

Vertical loading for fuels assemblies

Horizontal loading for rods

Preliminary study

In a first approach we considered among the existing packages (proven solutions) which ones could be compliant with the requirements.

Two families or cask were preselected for this study:

- MX casks families for fuel assemblies or rods
- FS65 cask families for rods

Preliminary study is currently in progress and expected results are to confirm the choice of preselected package or give an orientation on need of development of new package (to merge safety issues or need of increase payload).

4. MX casks families for fuel assemblies

MX family is the last generation of MOX fresh fuel package developed and operated since beginning of 2000's for transport of PWR 17X17 MOX fresh fuel for EDF (MX8) or BWR and PWR MOX fresh fuel for German, Belgium, Swiss and Japanese customers (MX6).

MX6 is the only one compliant with a fuel assembly around 14 feet length, high payload (6 PWR 16x16 or 18X18, 16 BWR 10x10), and thermal payload up to 6600W. MX6 and MX8 could be compliant in length for rods transportation.

Performances

- 6 MOX PWR 16X16 or18x18
- 16 BWR 10X10
- Maximal thermal power: **6600 W**
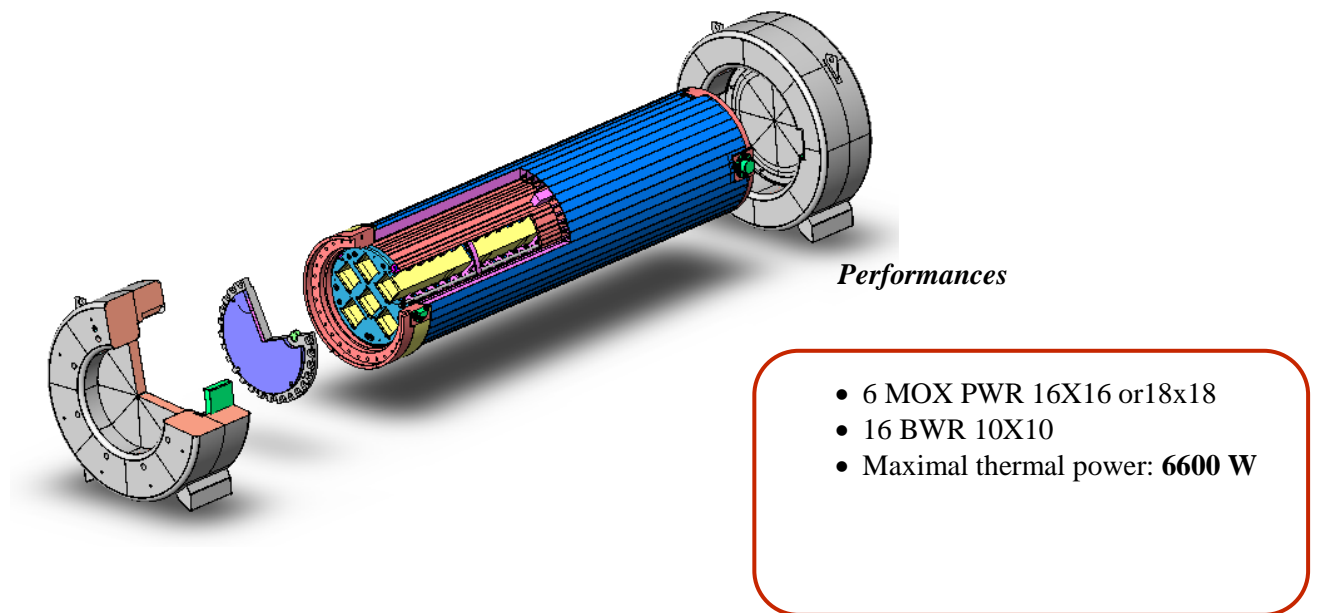
Main features

	LOADED	EMPTY
WEIGHT (kg)	19400	11110
SIZE	**LENGTH**	**DIAMETER**
CAVITY (mm)	5020	1072
OVERALL (mm)	5974	2125

General description

The body of the MX6 package is made out of two coaxial stainless steel thin cylinders linked with copper fins to improve thermal exchange and separate by resin for neutron and shielding protection. The body is equipped with a closure system equipped with EPDM gaskets so that the packaging stays leak-tight under normal and accidental condition. For ASTRID application it may be assumed at this state of the preliminary study that an additional lid creating a double containment in order to provide water exclusion for criticality studies might be added

Two shock absorbers at each side protected package regarding NCT and ACT drop conditions and assumed also protection regarding dose rate and thermal insulation of the elastomer gaskets of the closure

A new basket will be developed to be adapted to the hexagonal design of the fuel assemblies made with boronated (for criticality control) stainless steel for lodgement and aluminium plate for structural, thermal exchange and shielding protection. Aluminium is also required regarding constraint of weight.

The package will be loaded in a dedicated security caisson new generation with improved thermal exchange by natural convection the so called: CBTO11.

At the state of the preliminary study the pay load is assumed to be at **7 fuel assemblies** that means quite twice the ability of the former FS41 transport solution.

Licensing

MX6 is currently licensed in France, Belgium, Germany and Japan under IAEA 96 regulations and more than 70 transports have already been performed since the starting of operation.

5. FS65 cask families for rods

FS65 cask families was developed in 80's for inland transports for the MOX Japanese PWR 900MW and BWR fuel assemblies (FS65) and for 1300 MW MOX fuel assemblies (FS651300).

Either FS65 or FS65 1300 Package regarding length of the rods to be transported could be adapted for the ASTRID application.

FS65 Performances

- 1 PWR MOX fuel assembly
- 2 BWR MOX fuel assembly
- Maximal thermal power : **900 W**
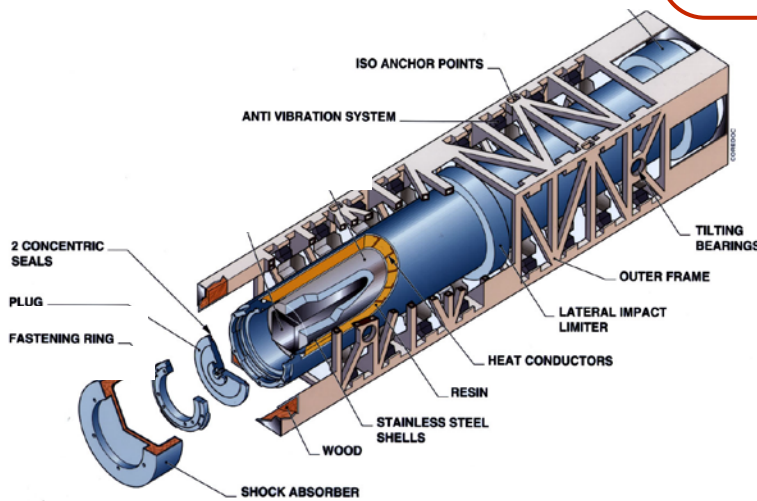
FS65 Main features

	LOADED	EMPTY
WEIGHT (kg)	5800	3946
SIZE	LENGTH	DIAMETER/WIDTH
CAVITY (mm)	4670	502
OVERALL (mm)	5323	1031

General description

The body of the FS65 family package is made out of two coaxial stainless steel thin cylinders linked with copper fins to improve thermal exchange and separate by resin for neutron and shielding protection. The body is equipped with a closure system type bayonet equipped with elastomer gaskets so that the packaging stays leak-tight under normal and accidental condition. Two shock absorbers at each side and a central one protected package regarding NCT and ACT drop conditions and assumed also protection regarding dose rate and thermal insulation of the elastomer gaskets of the closure.

The body is linked to a handling cage made of aluminium profile by means of elastic pads whose function is to guarantee fuel integrity in routine conditions.

A new basket will be developed adapted to the rod design of the fuel assemblies with a leak tight lid to create a double containment for water exclusion (criticality).

Rods will be place in a box that will be loaded in horizontal position in the cask.

Such of design of basket for FS65 package has already been developed and licensed in the past for transport rod box in the frame of EUROFAB project to transport Mox fuel rods between France and United States of America.

Such as FS41 up to 4 units were loaded in a dedicated security caisson .The caisson will assumed the main part of physical protection of the nuclear material.

At the state of the preliminary study the pay load is assumed to be about at least one box per package with a number of rods equivalent to one fuel assembly.

FS65 Licensing

FS65 is currently licensed according IAEA 1985 transport regulation but licensing according IAEA 1996 edition has already been delivered in the past at least for EUROFAB application.

6. Conclusions

AREVA has experience in transport solution for fuel for fast reactors and has already transported in the last few years such fuels for SUPERPHENIX and PHENIX. In the frame of ASTRID new development of current fleet or new designs is under progress for this new generation of fast reactors.

Fluidic Analysis in an Annular Centrifugal Contactor for Fuel Reprocessing

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Abstract. An annular centrifugal contactor (ACC) is a promising device for fuel reprocessing process, because it offers several advantages—a smaller size, a smaller holdup volume, and a higher separation performance—over conventional contactors such as a mixer-settler and a pulse column. Fluid dynamics and dispersion in an ACC, which has a combined mixer/centrifuge structure, are closely related to its separation performance and capacity, and this information is useful in improving equipment design. In this paper, experimental and computational fluid dynamics (CFD) studies were conducted to analyze fluidic and dispersion behavior in ACCs. Multiphase mixing (water/TBP-dodecane/air) in the annular zone was observed by Particle Imaging Velocimetry, and the change in the fluidic and dispersion behavior was ascertained under several operational conditions. The results of the CFD studies, which considered multiphase turbulent flow in the annular and rotor interior zones, were in a good agreement with the experimental data.

1. INTRODUCTION

Annular centrifugal contactors (ACCs), first developed for nuclear fuel reprocessing in the United States and now being considered in many countries [1], offer some attractive advantages for solvent extraction, such as increasing throughput and reducing solvent radiolysis in the process. The Japan Atomic Energy Agency (JAEA) has been also developing ACCs for solvent extraction in the advanced aqueous reprocessing process and has investigated fluidic and mass-transfer performances for different sizes and types of ACCs [2]-[4]. Figure 1 shows a schematic diagram of a typical ACC. The aqueous and organic phases are separately supplied into the housing and mixed in the annular zone. High-mass-transfer performance between both phases is achieved by rotor rotation, which causes efficient liquid-liquid dispersion in the annular zone. The mixed phases flow inward below the rotor and enter the central opening of the rotor. The dispersion entering the rotor is forcibly separated by high centrifugal power as it moves upward. The separated phases are discharged from the upper part of the rotor into the aqueous and organic collectors in the housing.

As suggested from Fig 1 and our previous studies [2]-[4], the phase separation and mass-transfer performances of an ACC are closely related to the fluid dynamics and dispersion in it. Therefore, to improve these performances and equipment design, it is important to investigate and characterize such phenomena. Several studies on the fluid mechanism in ACCs have been carried out using experimental methods and computational fluid dynamics (CFD), and these studies are summarized in Reference [5]. However, despite these studies, experimental and CFD techniques have not yet reached a stage at which the flow characteristic in an ACC can be sufficiently analyzed—especially in a multiphase (aqueous phase/organic phase/air) mixing system. In this study, we conducted some experiments using particle imaging velocimetry (PIV) and CFD analysis by considering multiphase turbulent flow to gain an understanding of the fluidic and dispersion behavior in the JAEA ACC under several operational conditions.
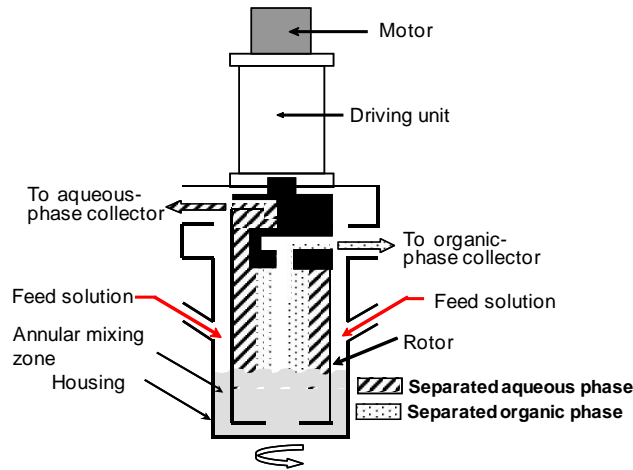
FIG. 1. Schematic diagram of a typical ACC

2. EXPERIMENTAL METHODS

The experimental setup is shown in Fig. 2. Two ACCs with different rotor diameter (D_r)—28mm and 59mm—were used in this study. For analyzing the flow characteristic in the annular zone, an aqueous phase (distilled water) was supplied from the inlets into the housing. The flow behavior in the annular zone was observed from a side view by a digital video camera at various rotor speeds and flow rates after reaching the steady state. The liquid horizontal velocity vectors in the annular zone were measured by PIV under typical conditions. The annular zone was irradiated using a YAG laser sheet (λ: 532 nm) at heights of 1, 3, and 5 mm above the bottom of the housing. Fluorescent particles 15μm in diameter (Em: 580 nm) were used as tracers. The motion of the tracer particles was captured by a high-speed video camera (Photron, Inc.) for 5 s at a frame rate of 2000 fps and a shutter speed of 1/3000 s. To obtain information about the dispersion in the multiphase mixing system, an aqueous phase (water colored with Rhodamine B) and an organic phase (30 vol% TBP–n-dodecane) were supplied from the inlets into the housing of the ACC with D_r = 59 mm. Under the condition of the YAG laser sheet 2 mm above the bottom, a 1.6 mm × 1.4 mm area of the mixing phase in the annular zone was captured by a high-speed video camera at various rotor speeds and O/A (the flow rate of the organic phase/that of the aqueous phase) ratios, at which the continuous phase was always the organic phase. The droplet size distribution of the dispersed phase (aqueous phase) and its change according to the operational conditions were evaluated by analyzing the captured images.
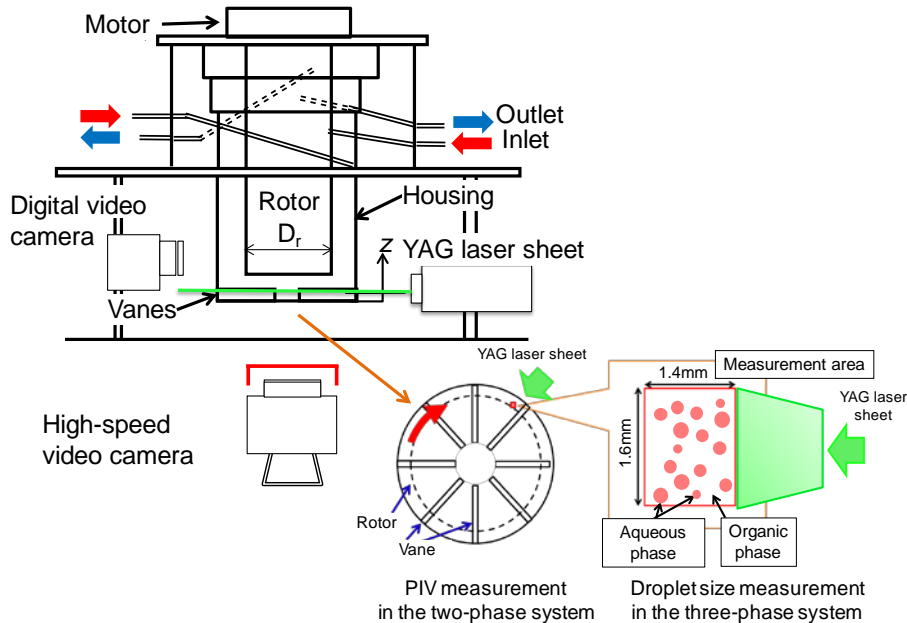

FIG. 2. Experimental setup for analyzing the fluidic and dispersion behavior in an ACC

3. COMPUTATIONAL METHODS

For the CFD analysis, the rotor and housing parts of an ACC were considered under a periodic boundary condition. Figure 3 shows the geometries of these parts, which were a one-quarter symmetric section of those used in the experiment. In the simulation, the polyhedral meshes were used for the bottom of the housing and the rotor, and the hexahedral meshes were used for the other parts. The total number of meshes was approximately 70,000. These geometries and meshes were constructed using ANSYS GAMBIT. After these preparations, unsteady calculations using ANSYS FLUENT 13 were carried out using the standard k-ε turbulence model. In these calculations, the Eulerian multi-fluid model was used for the two-phase [aqueous phase (continuous-phase)/air (dispersed-phase)] system and the three-phase [aqueous phase (dispersed-phase)/organic-phase (continuous-phase)/air (dispersed-phase)] system. The drag coefficient between each phase was estimated by the Schiller–Naumann drag model. To calculate the droplet size of the dispersed phase in the three-phase system, a user-defined function (UDF) containing Equation (1) below was created.

$$D_d = \frac{\sigma (We_d)_{crit.}}{\rho_c u_c^2}, \qquad (1)$$

where D_d is the droplet size of dispersed phase, σ is the surface tension, $(We_d)_{crit.}$ is the critical Weber number, ρ_c is the density of continuous phase and u_c is the slip velocity between the continuous and dispersed phases. The time-step size for the unsteady calculation was 0.002 s. Several calculations with different operational conditions (various rotor speeds and flow rates) were carried out for comparison with the experimental results.
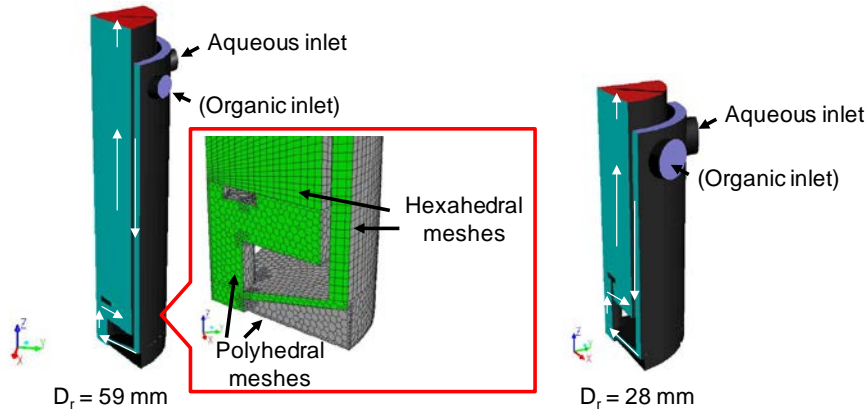

FIG. 3. Geometry of rotor and housing parts of an ACC

4. RESULTS AND DISCUSSION

4.1. *Flow behavior and velocity vectors of the aqeous phase in the two-phase system*

Figure 4 shows the flow behavior in the annular zone of an ACC with $D_r = 59$ mm, which was captured under different operational conditions. Through the experiments, two characteristic flow behaviors were observed with the change in rotor speed. At a low rotor speed, the annular zone was filled with the supplied water from the housing bottom up to the lower edge of the rotor (see the left side of Fig. 4). This flow behavior was named Type A. At a high rotor speed, the water in the annular zone was divided into two liquid regions vertically; one of them was near the housing bottom and the other was around the lower edge of the rotor (see the right side of Fig. 4). This behavior was named Type B. The change in flow behavior in the annular zone of both rotor diameters in ACCs according to the experimental conditions is summarized in Fig. 5. In both ACCs, two flow behaviors— Type A and Type B—and an intermediate region were observed, but the ACC with $D_r = 28$ mm had a larger intermediate region. The boundary operational conditions of these phases are related to the pumping capacity of the rotor and the water flow rate [6]. Figure 6 shows the mean horizontal velocity vectors of the water in the annular zone of the ACC with $D_r = 59$ mm, which were measured by PIV under different flow conditions. In both Type A and Type B, the water surrounded by two vanes and the housing wall flowed in the direction of rotor rotation along the wall near the water–air interface, and then the flow was bent by a vane and moved toward the center of the housing bottom. In Type A, the mean velocities around the housing bottom are approximately directly proportional to the rotor speeds, and they became higher as the flow rate increased. In Type B, the mean velocities around the housing bottom also increased with the flow rate, but they were not

dependant on the rotor speed. This might be due to the lower transfer of the momentum of rotor rotation to the liquid flow in Type B in which the water in the annular zone was divided into two liquid regions. Such changes in mean velocities under operational conditions in Type A and Type B were observed in the annular zone of an ACC with D_r = 28 mm.
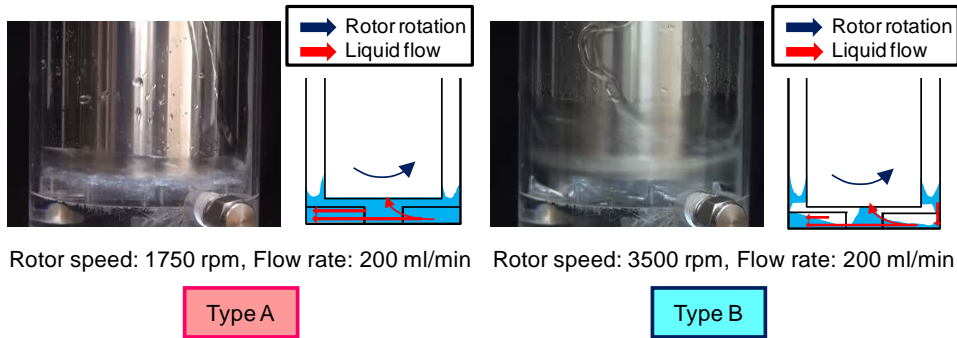

Rotor speed: 1750 rpm, Flow rate: 200 ml/min   Rotor speed: 3500 rpm, Flow rate: 200 ml/min

Type A   Type B

FIG. 4. Flow behavior in the annular zone of an ACC with D_r = 59 mm (experimental results)
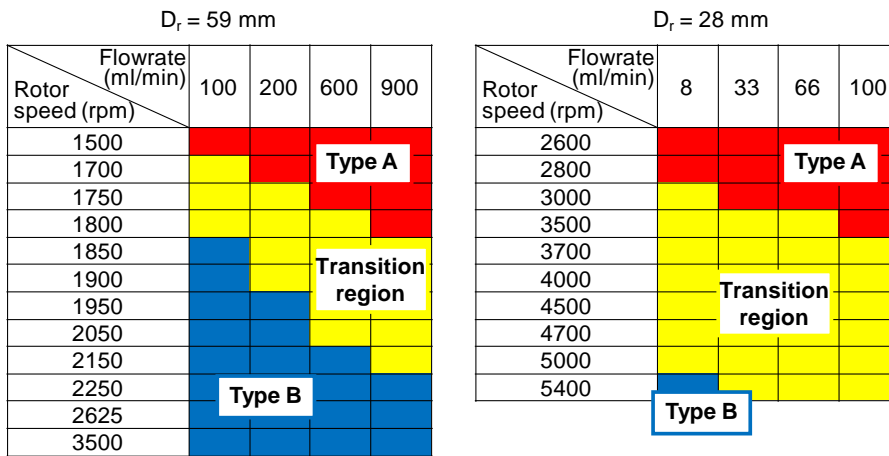
FIG. 5. Types of flow behavior in the annular zone (experimental results)
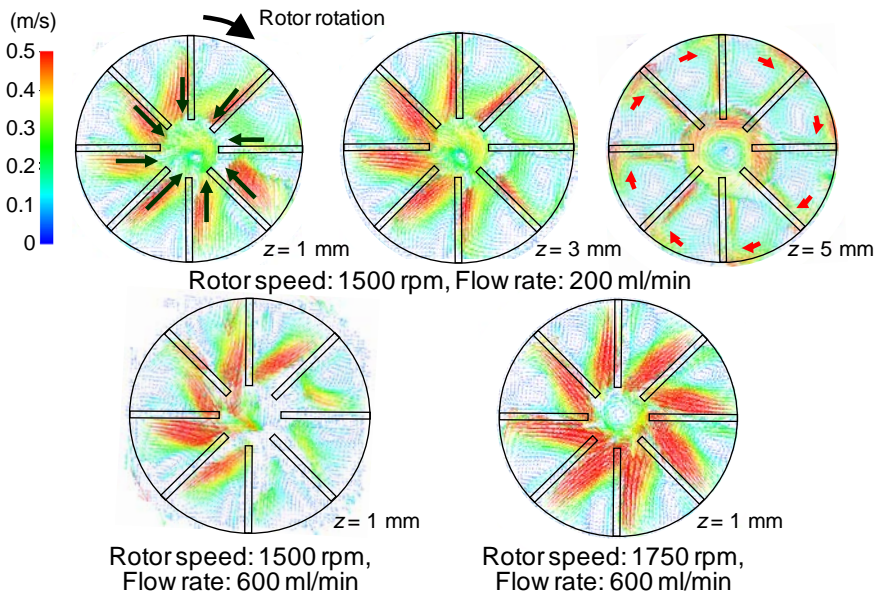
FIG. 6. Mean horizontal velocity vectors of water in the annular zone of an ACC with D_r = 59 mm (experimental results)

Figure 7 shows a calculation results using FLUENT, which shows the time dependency of the water volume fraction in the annular zone of an ACC with $D_r = 28$ mm under the operational condition of a rotor speed of 4500 rpm and a water flow rate of 100 ml/min. In the calculation, the interface between water and air was settled at a height of 5 mm above the housing bottom as the initial condition. The water volume fraction in the annular zone appeared to be in the steady state after approximately 1 s of feeding the water. Similar results were obtained in other calculations; therefore, the results after at least 1 s after the start of the calculation are used in this study. Figure 8 shows the water volume fraction in the annular zone for both rotor size ACCs under different operational conditions. For each ACC, at a higher flow rate and lower rotor speed in which the flow behavior was assigned to Type A, the calculation results showed an almost constant water volume fraction from the housing bottom up to the edge of the rotor. At a lower flow rate and higher rotor speed in which the flow behavior was assigned to Type B, the zone having a high water volume fraction tended to be divided into two regions vertically—the housing bottom and the lower edge of the rotor. These calculation results have the same tendencies as the experimental ones. Figure 9 shows the mean horizontal velocity vectors of the water in the annular zone of an ACC with $D_r = 59$ mm, which was obtained from calculations under the different operational conditions. As observed in the experiment, the calculation indicated that the water surrounded by two vanes and the housing wall flowed in the direction of rotor rotation along the wall near the water–air interface, and then the flow was bent by a vane and moved toward the center of the housing bottom. The mean velocities increased with the flow rate at all rotor speeds, and with the rotor speed under a high-flow-rate condition. These changes in mean velocities also agree with the experimental results.

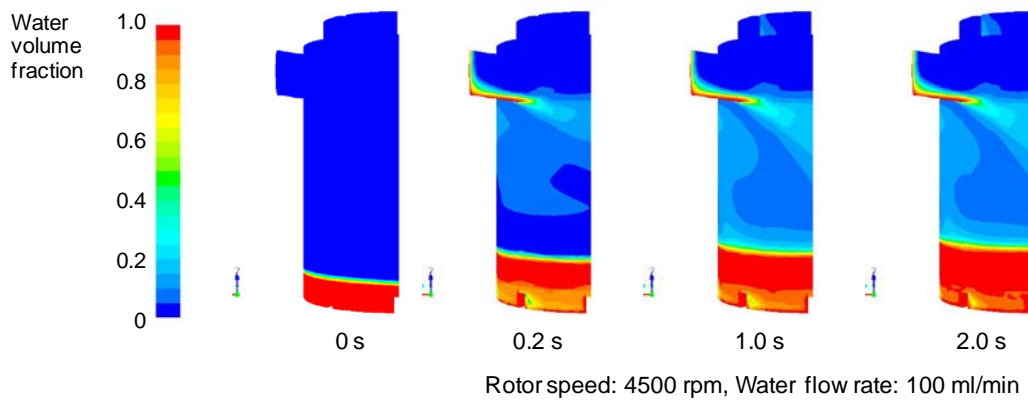Rotor speed: 4500 rpm, Water flow rate: 100 ml/min

FIG. 7. Time dependency of water volume fraction in the annular zone of an ACC with $D_r = 28$ mm (calculation results)
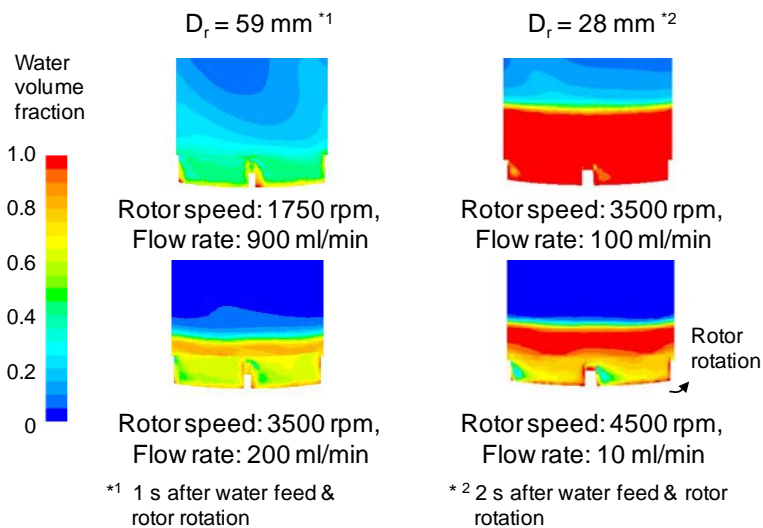

FIG. 8. Water volume fraction in the annular zone of an ACC (calculation results)
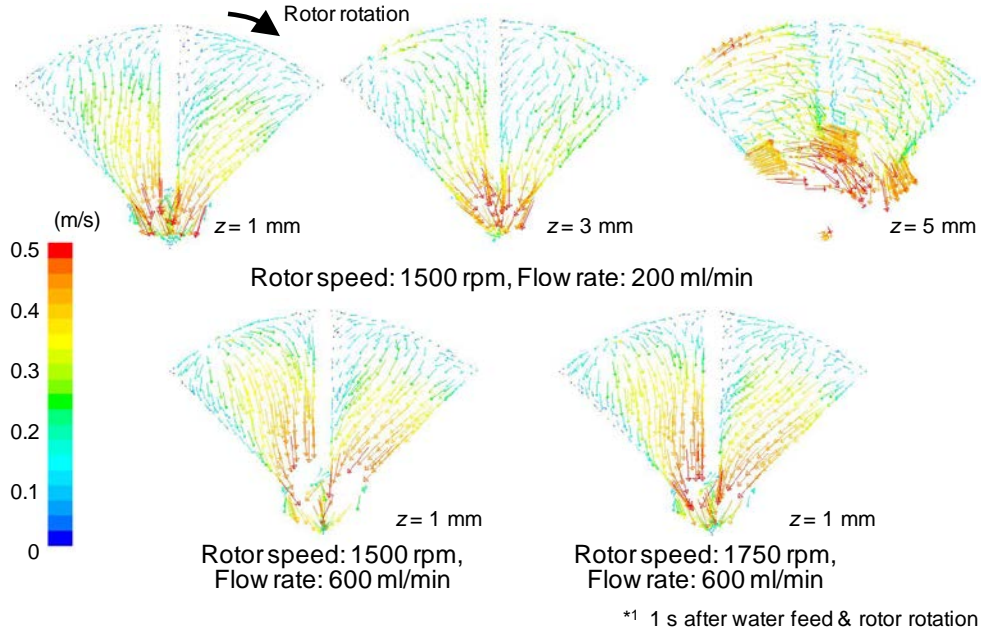
FIG. 9. Mean horizontal velocity vectors of water in the annular zone of an ACC with D_r = 59 mm (calculation results)

4.2. Droplet size of dispersed phase in the three-phase system

Figure 10 shows the distribution of the droplet size of the dispersed phase (aqueous phase) in the three-phase system, which was obtained in the annular zone of an ACC with D_r = 59 mm under several operational conditions. The Lower rotor speed and the O/A ratio caused the distribution of the droplet size to shift toward larger diameters. This was clarified by the change of the mean droplet size (d_{32}) according to operational conditions as shown in Fig. 11. Figure 12 shows a contour map of a droplet size of 2 mm above the housing bottom of the ACC with D_r = 59 mm, which was estimated by calculation using FLUENT with a UDF under different rotor speeds and O/A ratios. The calculation was conducted under the condition where $(We_d)_{crit.}$ = 0.1, $\sigma = 1.1 \times 10^{-3}$ N/m, and ρ_c = 0.85 g/cm^3. Although the mean droplet size was larger than the experimental one, the calculation results suggested that the droplet size of the aqueous phase changed with the rotor speed and the O/A ratio similar to that observed in the experiment, that is, a low rotor speed and the O/A ratio increased the droplet size. To improve calculation accuracy, the application of an appropriate value to $(We_d)_{crit.}$ is required.
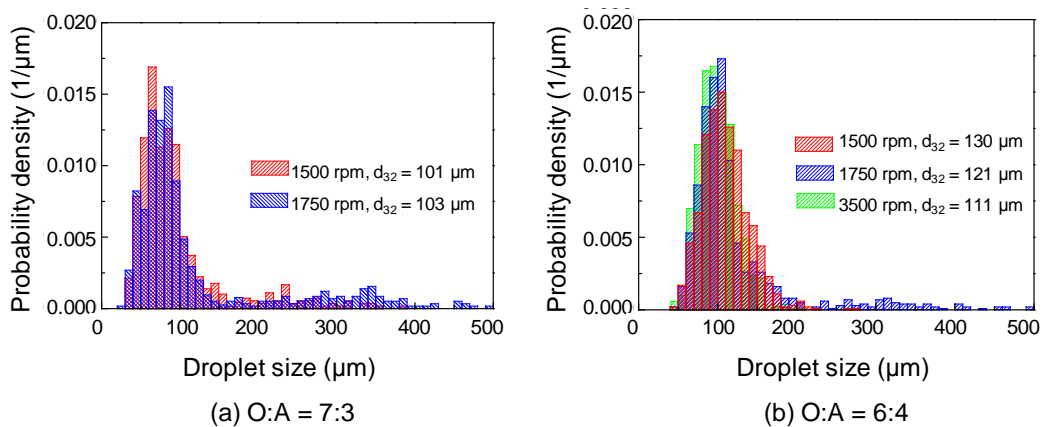

(a) O:A = 7:3   (b) O:A = 6:4

FIG. 10. Distribution of droplet size in the aqueous phase in the annular zone of an ACC with D_r = 59 mm (experimental results)
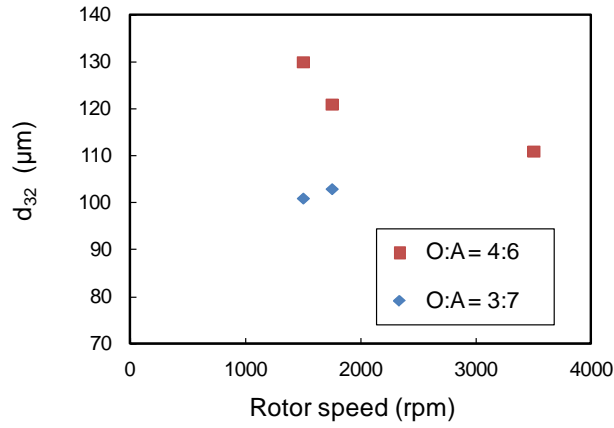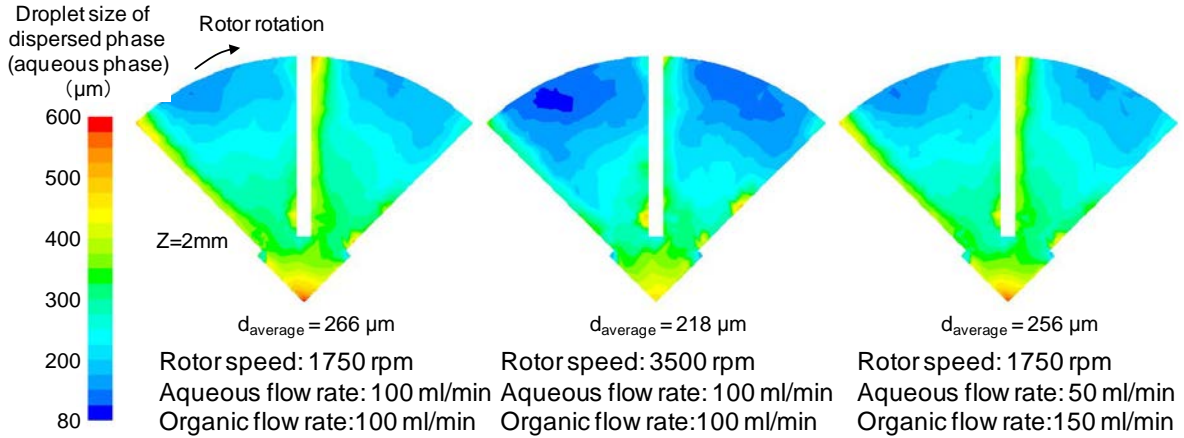
FIG. 11. Change in mean droplet size (d_{32}) with rotor speed and O/A ratio (experimental results)

*[*1]* 1.5 s after feeding aqueous/organic phases & rotor rotation

FIG. 12. Contour map of droplet size 2 mm above the housing bottom of an ACC with $D_r = 59$ mm (calculation results)

5. CONCLUSION

Fluid dynamic and dispersion in two ACCs with two different rotor sizes were analyzed by experimental and CFD studies. In the two-phase (water/air) system under different rotor speed and flow rate conditions, the experimental observation showed that the flow behavior in the annular zone of both ACCs was classified into two characteristic types: Type A in which the annular zone was fully filled with water from the housing bottom up to the lower edge of the rotor, and Type B in which the water in the annular zone was divided into two liquid regions vertically. The liquid horizontal velocity vectors measured by PIV indicated that the water surrounded by two vanes and the housing wall flowed in the direction of the rotor rotation along the wall near the water–air interface, and then the flow was bent by a vane and moved toward the center of the housing bottom in both Type A and Type B. The mean velocities increased with the flow rate at all rotor speeds (in Type A and Type B), and with the rotor speed under a high-flow-rate condition (Type A). In the three-phase (water/30 vol% TBP–n-dodecane/air) system, the experimental analysis clarified that the droplet size of the dispersed phase (water) in the annular zone increased with the decrease in the rotor speed and the O/A ratio. The CFD results based on the unsteady calculation using ANSYS FLUENT 13 in the multiphase turbulent flow showed a good agreement with these changes of fluidic and dispersion behavior in the annular zone with the operational condition.

We will continue to analyze the fluidic and dispersion behavior in the upper part of the rotor as well as in the annular zone, which is essential in evaluation of the separation performance of aqueous and organic phases. In addition, a quantitative assessment of the effect of fluidic and dispersion behavior on the mass transfer will be

carried out to establish a computational method that considers the mass transfer between the aqueous and organic phases.

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An Indian Perspective of the Development of Fast Reactor Fuel Reprocessing Technology

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Presented by A.Ravisankar

Abstract. Structured development of Fast Reactor Fuel Reprocessing technology (FRFR) is being undertaken in India. With the experience of two decades R&D on process, equipment and safety, the pilot plant, COmpact Reprocessing of Advanced fuel in Lead cells (CORAL) was commissioned in 2003 for reprocessing Plutonium rich carbide fuel of Fast Breeder Test Reactor (FBTR) at Indira Gandhi Centre for Atomic Research (IGCAR). Several campaigns with different burnups and cooling periods have been carried out in this facility. In CORAL, highly pyrophoric Plutonium rich fuel with as high as 155 GWd/t burnup has been reprocessed successfully which bears testimony to the capability of plant designers to meet the safety requirements and also alpha tightness as is required for Plutonium rich fuel reprocessing. From the results of these campaigns, it was possible to establish the technical feasibility of adopting the modified PUREX process for short cooled high burn up Plutonium rich spent fuel. This facility has provided unique opportunity of not only validating the process flowsheet but also in identifying many future activities to improve the performance. The operating experience from CORAL enabled fine tuning of the design of various equipment and processes for the upcoming plants, namely Demonstration Fast reactor fuel Reprocessing Plant (DFRP) and Fast reactor fuel Reprocessing Plant (FRP). The primary objectives of DFRP are the establishment of plant throughputs for reprocessing both carbide and oxide Plutonium rich fuel of FBTR to close the fuel cycle, high recoveries and reduced waste volumes. This facility which is under construction will also demonstrate the reprocessing of Prototype Fast Breeder Reactor (PFBR) spent fuel. Concurrently many R&D activities are being pursued on the development of various technologies for solvent cleanup, optimization of process flowsheet to reduce the number of solvent extraction cycles, red oil explosion, etc., as well as for identifying prospective alternate solvents and diluents. FRP, aimed at closing the fuel cycle of PFBR, will be the technology demonstrator.

A comprehensive account of various developmental activities on this technology is given in this paper.

1. Introduction

Fast Reactor Fuel Reprocessing (FRFR) is more complex due to handling of high burn up, short cooled, Pu rich fuel in a high acidic environment. Based on four decades of operating experience of reprocessing plants for thermal reactor spent fuel and the R&D programme to address the typical issues of Plutonium rich Fast Breeder Test Reactor (FBTR) spent fuel, a pilot plant, COmpact facility for Reprocessing of Advanced fuel in Lead cells (CORAL) is designed and commissioned in Indira Gandhi Centre for Atomic Research (IGCAR)[1]. The objective of CORAL is validation of PUREX based process flowsheet and the equipments that are typical to the FRFR. Single pin chopper, dissolver, centrifuge, centrifugal extractors and sampling systems are a few vital equipments that are being evaluated in this facility. Also, various conceptual designs of hot-cell system and equipments, which are important for the safety of the operators, are also validated. Several campaigns of reprocessing with the spent mixed carbide fuel from FBTR containing up to 70% Pu and having burnups as high as 155 GWd/t and cooling period as low as two years have been carried out since the commissioning of the facility which has demonstrated the feasibility of meeting the product

specification requirements. The recovered product has been reconstructed as fuel subassembly and put back in FBTR.

The operating experience led to the designing of equipment and systems for the Demonstration Fast reactor fuel Reprocessing Plant (DFRP). The primary design objectives of this plant are the establishment of high plant throughputs, high recoveries and reduced waste volumes. In this plant, not only mixed carbide but also mixed oxide fuel of FBTR will be reprocessed. The reprocessing of spent fuel from the Prototype Fast Breeder Reactor (PFBR), which is currently under construction at Kalpakkam, will also be demonstrated in this plant. DFRP is in advanced stage of construction and vital equipments, such as single pin chopper, dissolver and Centrifugal Extractors have been designed and fabricated based on the CORAL operational feedbacks are under installation.

The regular reprocessing of spent fuel from PFBR will be carried out in Fuel Reprocessing Plant (FRP) of Fast Reactor Fuel Cycle Facility(FRFCF), the detailed design of which has been completed and construction is awaiting financial approval. This facility is designed for reprocessing PFBR fuel with high availability factors to meet the refuelling requirements of PFBR to sustain the fuel cycle. This paper highlights the structured R&D activities taken up concurrently for the speedy implementation of the technology.

2. HOT CELL EQUIPMENT
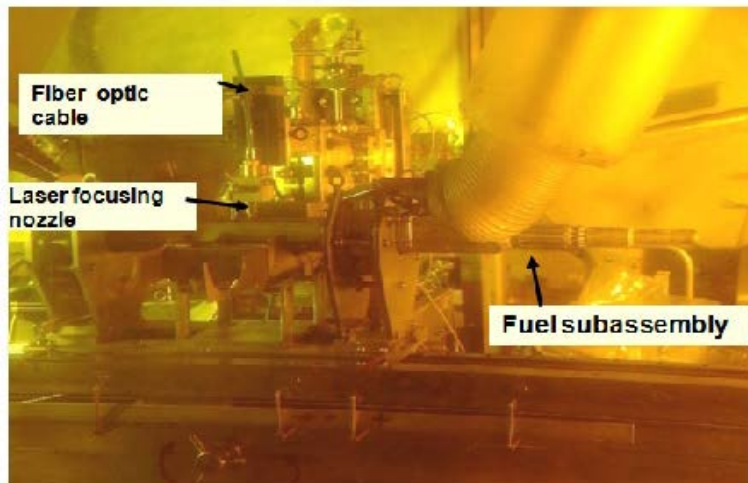
2.1. *Fuel Sub Assembly Dismantling Machine*

FIG. 1. Laser dismantling

A typical Laser dismantling machine (Fig.1) has been developed, deployed in the hot cells of Post Irradiation Examination and dismantling of many FBTR spent Fuel SubAssemblies (FSA) have been successfully carried out. Laser dismantling of irradiated FSA from FBTR and PFBR is also proposed to be carried out in Head End Facility of DFRP. It has the advantages like high capacity, less powder/chip generation, less solid waste generation, and modular in design amenable for remote maintenance.

2.2. *Development of chopper*

Because of the slender nature of the FRFR fuel pins, to avoid crimping, single pin chopper are being developed. The single pin chopping machine designed and developed for CORAL has, fuel pin feeding cum rotation, gripping and shearing steps. A microprocessor-based controller controls all the operation and sequence. This equipment is amenable for remote operation and maintenance. Based on CORAL experience, the pin feeding mechanism has been modified for increasing the reliability and throughputs. Improved designs of choppers are being implemented for DFRP (Fig.2) for chopping

three types of fuel pins of FBTR with different dimensions. To meet the capacity requirements of FRP, a multi pin chopper has been designed which will chop ten pins in a single cut.
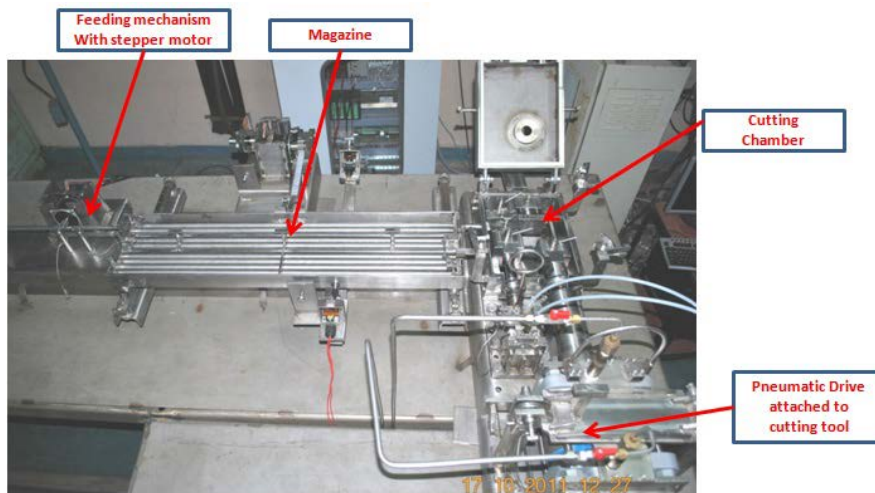

FIG. 2. Single pin chopper for DFRP

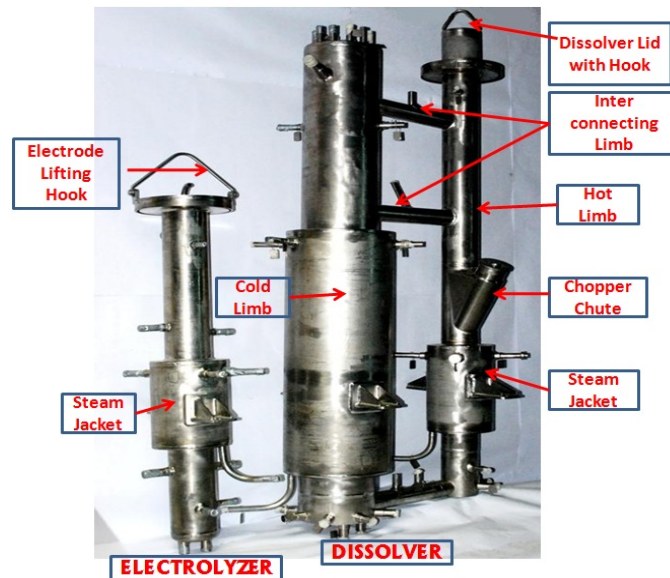## 2.3. Design and development of Ti Dissolver

FIG. 3. Dissolver for DFRP

The dissolution of mixed carbide spent fuel of FBTR has proved that refluxing under boiling conditions is sufficient for complete dissolution. But the Plutonium rich MOX fuel are expected to throw surprises which may require electrolytic conditions. To implement ceric mediated dissolution, an electrolyzer is designed and coupled with dissolver of DFRP (Fig.3) which would take the MOX test assemblies of FBTR. The electrolyzer can be operated as and when required. It is planned to use electrolytic conditioning of Pu. Based on extensive corrosion studies, titanium is selected as the material of construction for dissolver. The dissolver has additional features of a mechanical agitator for Hull rinsing to reduce hull losses.

2.4. Development of High Speed Centrifuges

High Pu bearing dissolver solutions are known to contain finely suspended particles which are mainly inter-metallic noble metal alloys. To avoid difficulties in downstream processing, the dissolver

solution is required to be clarified. The centrifuge (Fig.4b) is intended for efficient separation of very fine solids from liquids. An air turbine driven centrifuge which can be operated and maintained remotely is deployed in CORAL whose performance is satisfactory. Since the centrifuge rotates at super critical speeds developing high centrifugal acceleration, detailed vibration analysis for evaluation of the critical speeds was carried out in order to address the various maintenance problems encountered at CORAL [2]. Improvement in the design of bearings and speed sensor are identified as issues for resolution. The feed clarification of MOX dissolver solution is expected to be vital.

2.5. *Development of manufacturing technology for thin wall centrifugal extractors*
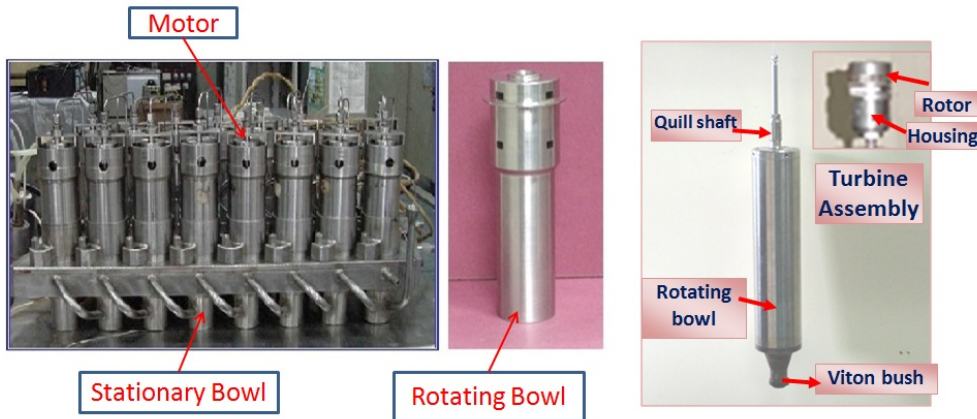

FIG. 4. *a) Centrifugal Extractor*   *b) Centrifuge Rotating Bowl*

Centrifugal extractors(CE) (Fig.4a) are considered vital for the success of deployment of PUREX process for shorter cooled Pu rich fast reactor fuels. They have very low residence time to minimize solvent damage compared to the pulse column type extractors used in thermal reactor fuel reprocessing plants. The internals of centrifugal Extractors are very intricate and for getting required process performance, it is divided into six individual components which have been machined and fabricated with less than 20 microns tolerance and later these components are welded together by Pulse TIG welding technique. The satisfactory performance of centrifugal extractors in CORAL has given confidence for scaling up to the required capacity units for DFRP and FRP[3].

3.   PROCESS DEVELOPMENT

3.1. *Dissolution Process*

The dissolver installed in CORAL has features for evaluating the Electro Oxidative Dissolution Technique (EODT) process developed at IGCAR. Since the choice of dissolution process has to be finalised so that the dissolver solution is compatible with the downstream steps, experimental studies were carried out using the CORAL dissolver solution obtained by dissolving the chopped fuel pins in nitric acid under refluxing conditions. The MOX fuel containing high Pu content as encountered in PFBR may require more aggressive conditions. Since no plant scale experience is available, it is decided to adopt ceric mediated dissolution process for DFRP.

Plutonium content being higher in fast reactor spent fuel, ensuring nuclear criticality safety issue is of utmost importance. Addition of soluble neutron poison is one such option. Gadolinium is found to be the best possible choice as soluble neutron poison due to its high neutron cross section, adequately high solubility in nitric acid concentrations prevalent in the processing of fast reactor spent fuel and chemical compatibility in the PUREX solvent extraction process conditions[4]. As the decontamination factors required are very high, studies were carried out to investigate its extraction behavior under typical PUREX process conditions[5].

3.2. Solvent extraction process

The standard PUREX process is adopted for the deployment for fast reactor spent fuel reprocessing after addressing some specific challenges. As fast reactor spent fuel has higher plutonium content and high radioactivity, though the basic flowsheet for solvent extraction is similar to that of the thermal reactor spent fuel reprocessing, it needs to be modified to meet the challenges of plutonium recovery, limitations in the loading of plutonium due to Limiting Organic Concentration and increased decontamination factors required for specific fission products.

Increased plutonium content necessitates higher acid profile because of its comparatively lower distribution with respect to uranium in PUREX solvent. This calls for an analysis of the challenges that would be encountered in the solvent extraction to achieve a product with the desired purity, as zirconium extraction is favoured with increase in acidity. Considering the difficulty in removing the fission products especially zirconium and ruthenium, whose extraction behaviour are quite opposite to each other, removing them in a single extraction cycle is a difficult proposition. A flowsheet with dual scrub, one for removing ruthenium which requires higher acidity and another for removing zirconium (with a lower acidity) is required to be formulated. Because of the dual scrub, there is a challenge of refluxing of plutonium which might lead to third phase formation due to the lower solubility of the plutonium complex in the organic phase. As this would lead to safety issues such as criticality apart from operational difficulties, this is to be avoided. The concept of dual scrub is unique which has not been followed in the conventional PUREX flow sheets.

FIG. 5. A proto type 20-stage ejector mixer settler

At the Reprocessing Development Laboratory (RDL) of IGCAR, extraction behaviour of Zr and Ru is studied from the plant solutions and relevant mathematical models are developed. A Computer code PUSEP (ver-2) has been developed at IGCAR for high plutonium bearing flowsheets[6]. The distribution coefficients relations for U(VI), U(IV), Pu(IV), Pu(III) and the models developed for Ru and Zr are incorporated in the programme. Also included are the redox reaction rates of the species involved for the separation of U and Pu from each other (partitioning cycle). The model equations are solved numerically to obtain concentration profiles of all the components. The validity of the model equations and associated computer program is tested by carrying out experiments in a proto type 20-stage ejector mixer-settler (Fig.5) with simulated solutions. The stage-wise experimental concentration profiles of uranium, plutonium, nitric acid, Ru and Zr compare well with the theoretical predictions. The optimum extraction flowsheet for FBR fuel reprocessing has been proposed using the developed computer code. [7]

4. Design of hot cells

Hot cell equipments and necessary remote handling gadgets have to be robust withstanding high radiation and acidic environment. Hot cells(Fig.6) usually have either thick reinforced concrete or lead walls and Radiation Shielding Windows (RSW).
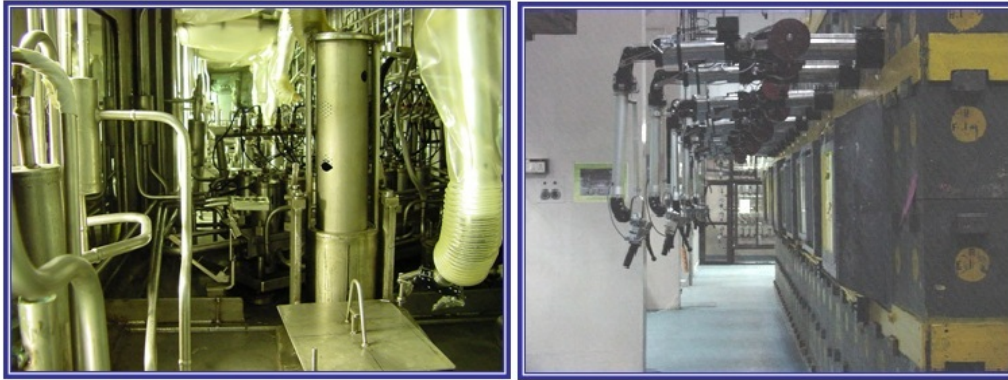
FIG. 6 .a)Equipments inside CORAL   b)Operating area

Operation and maintenance inside the hot cell is accomplished with the aid of Master Slave Manipulators (MSM), in-cell crane and special gadgets amenable for the operation and maintenance equipments. The inability to perform contact maintenance in FRFR hot cell with high alpha contamination requires special design consideration such as simple in design, modular construction, high precision with interchangeable interfaces, amenability for providing access to remote handling equipments and maintenance systems, operational interfaces, etc. Due to alpha tightness requirement of the hot cell, the design of equipments & remote gadgets is more challenging. A decade of CORAL operation with several FBTR spent fuel reprocessing campaigns, under regulatory supervision, without alpha contamination validated the hotcell design adopted.

5.   Remote handling systems

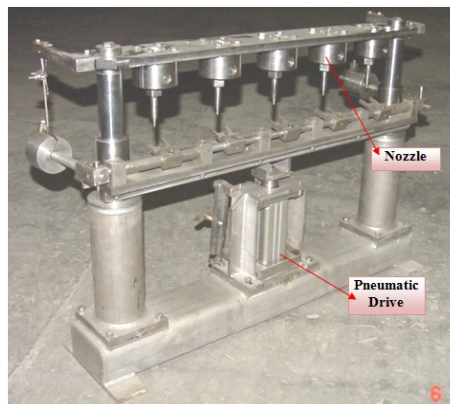### 5.1. *Automated Remote sampling system*

FIG. 7.Sampling Station

Automated Remote sampling system consist of a novel sampling station(Fig.7) with five different sampling points and operated by a pneumatic actuator, capper decapper unit and pneumatic conveying system. All the operations are carried out remotely by manipulator and in cell crane. The total sampling system is commissioned at CORAL facility and is successfully operating for past ten years aiding the analysis and accounting of Special Nuclear Material, a mandatory requirement for Reprocessing. In order to reduce the load of MSM , robotic sampling system is designed and developed for DFRP[8].

5.2. *Development of Robotic Sampling System for the analytical cell in DFRP*

The robotic sampling system(Fig.8) of DFRP consists of modules namely, Sample Handling Robot(SHR) Capping/Decapping Robot(CDR) and Pipette Robot(PPR). A Cartesian configuration has

been chosen for SHR with X, Y and Z axes to cover 6000 x 700 x 400 mm. Additionally, a rotational axis (about Z axis) with two redundant Y-axes, which gives extended reach along Y- axis as well as precise motion to reach the target position with two grippers. The function of SHR is to collect sample bottle from the user defined location and transport to the pre-defined sampling station and collect samples and place in the user defined storage location. The sample is collected by piercing the bottle to the sampling nozzle and retrieval after sampling.

SHR plays a major role since it has to cover 60 sampling stations in a cluttered environment. Similarly analytical operations such as collecting sample and dispensing it in analytical station, cleaning and disposing of waste are carried out by CDR and PPR with the assistance of MSM.
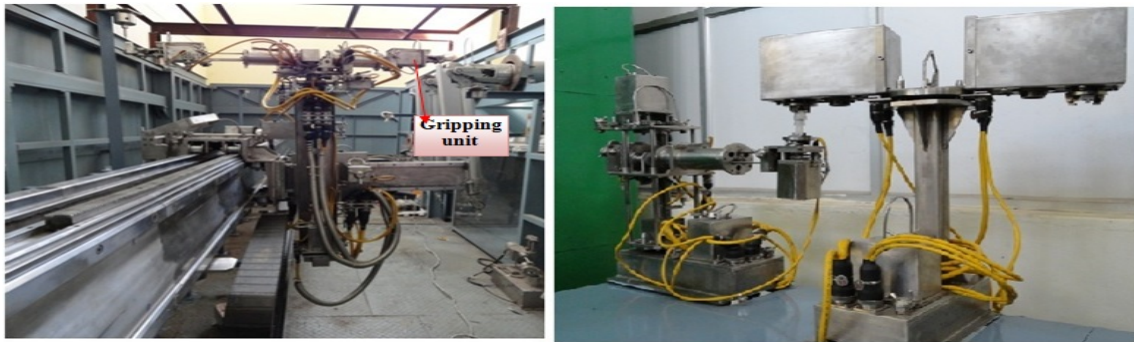

FIG. 8. a)Sample Handling robot   b)Capping & De-capping robot

The complete sampling system is controlled by PLC based system. Dedicated application software has been developed with complete security features having three layer administrative privilege and system operation/configuration rights and safety interlocks. Status monitoring and control screen has been provided to monitor the erroneous operations/operator violations which are simultaneously logged in the database for review. The sampling operations can be executed through human machine interface. The operation has lead-through teaching facility as well as auto mode execution, where provision is made to ensure execution of instruction only on receiving operator's acknowledgement. This feature facilitates the operators to correct any over shoot or under shoot during sampling. Each operation and sampling movements are logged on to the back-end database which can be used later for analysis, report generation, etc. Salient feature of all the robots is that remote assembly and disassembly is possible for maintenance using in cell crane and MSM.

5.3. Stainless steel mini crane for CORAL

FIG. 9. Incell Crane at CORAL

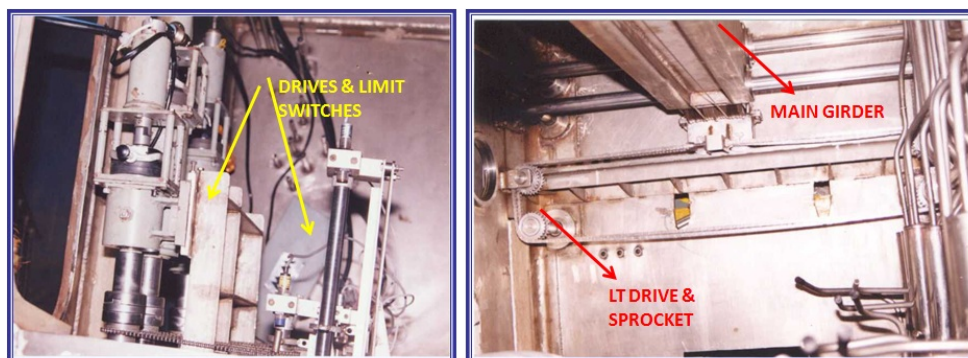A special stainless steel mini crane of 50 Kg capacity is developed and erected inside the α-tight containment box (Fig 9). The hook of crane can receive different types of gadgets and can be fixed to the required system with the aid of manipulator to carry out the operation remotely. This crane substitutes the power manipulator, which has to be imported. The special features of this crane are all

the drives including limit switches have been brought out of the hot cells with novel mechanisms[9]. With the feedback and experience gained from CORAL, a typical 250 kg capacity stainless steel in cell crane(Fig.10) for DFRP has been designed with improved features such as single failure proof to hoist and anti fall system for trolley. A prototype has been manufactured and tested successfully.
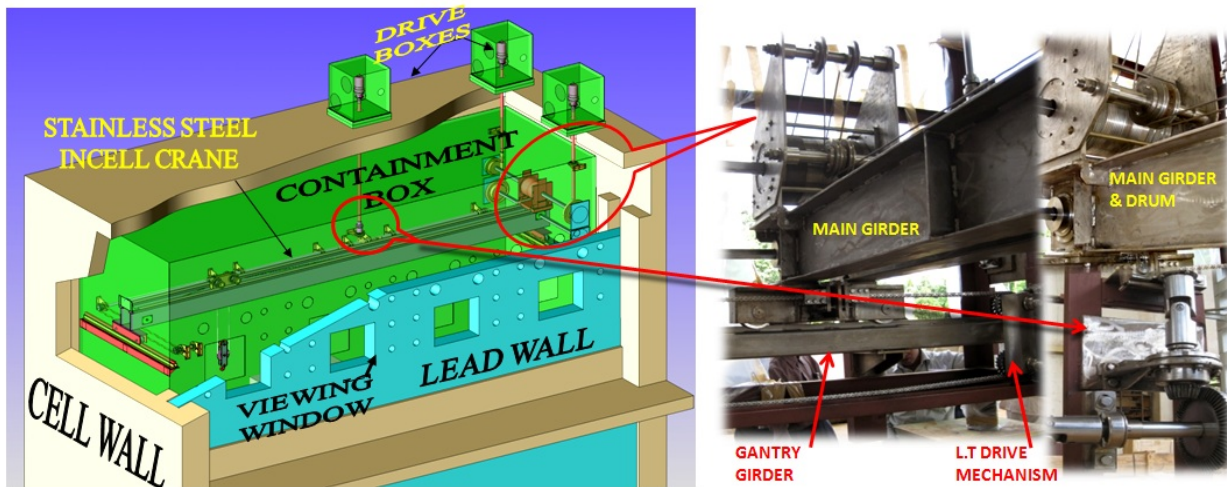

FIG. 10. Incell Crane at DFRP

5.4. *Development of remote handling gadgets*

The development of remote handling devices is of paramount importance in FRFR plants, as it is extremely difficult to carryout direct maintenance, because of the high radiation and contamination.

5.4.1. *Remote maintenance of Centrifugal Extractors*
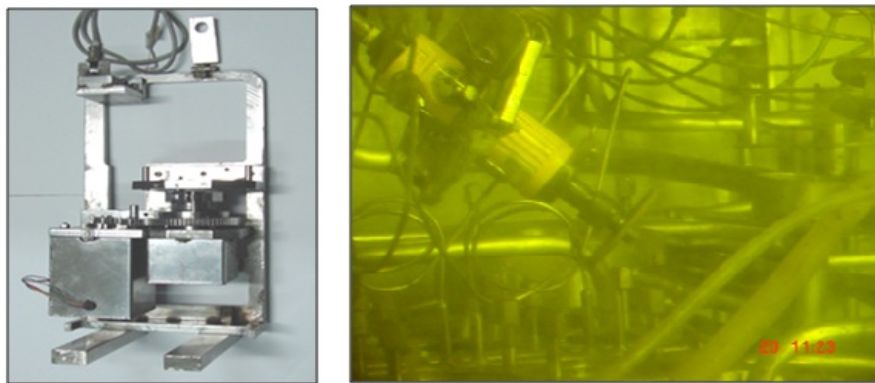

FIG. 11. a)CE Dismantling Equipment   b) CE-Bank Interphase Airline Cutting

During the operational phase of CORAL, it was decided to replace one set of CE bank with another. This was done remotely without any safety issues with the aid of master slave manipulators and incell crane. An automated equipment (Fig.11) was successfully developed for assembling/disassembling of CE motor with rotating bowl remotely since the motors required modifications. By adopting this system at CORAL contact maintenance could be avoided.

5.4.2. *Development of gadgets for In Service Inspection (ISI)*

A comprehensive ISI program using Non Destructive Examination techniques has been formulated and initiated in IGCAR for the fast reactor fuel reprocessing facilities. Critical components & areas such as dissolver vessel, evaporator, process tanks and waste tanks in the waste vault have been identified for periodic inspection in addition to continuous on-line monitoring. Addressing the above

needs, various devices have been developed and used for remote inspection in the pilot fast reactor fuel reprocessing plant (CORAL).

A remote inspection device using a camera was developed and the visual inspection of the dissolver vessel limb in CORAL was successfully carried out. Visual inspection of the CORAL dissolver vessel didn't reveal any significant degradation of the inner surfaces or weld joints. No unwanted material or debris are trapped or blocked inside the vessel or various openings of the vessel. Fig.12a shows the remote inspection device with the inspection results obtained from the dissolver vessel limb.

FIG. 12. a) Remote Visual inspection of CORAL Dissolver Vessel b)2-axis telescopic scanner for dissolver wall thickness measurement using UT

A 2-axis scanner (Fig.12 b) has been developed to remotely carry out the wall thickness measurements of the dissolver vessel during the service period. The inspection technique is by immersion ultrasonic testing with water as the coupling medium filled in the dissolver vessel. The device is basically a 2-Axis Scanner having one rotation (θ) and one translation (Z) motions. The scanner has been tested and validated in a mock-up vessel.

FIG. 13. Mobile Vehicle Inspection

A mobile robotic device (Fig.13) with a camera was conceptualized for carrying out a global visual examination of the waste vault. A working model of four-wheeled robotic device has been tested with a camera having pan/tilt in the waste vault. Special stainless steel guide rails on which the mobile vehicle will move were laid along one of the walls of the CORAL waste vault. Trials of the vehicle were carried out in the CORAL waste vault and images of the waste farm tanks were acquired using the on-board camera.

6. Conclusion

The CORAL campaigns have demonstrated the deployability of PUREX process for Pu rich FBTR fuel, which enabled the design of DFRP and FRP to be taken up confidently. The operation and maintenance experience vindicated the hot cell systems. R&D issues have been taken up to improve the availability and capacity factors. Also the thrust is on reducing the waste volumes and manrem expenditures.

ACKNOWLEDGEMENTS

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Overview of the French R&D program for the development of minor actinides separation processes

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Abstract. After the scientific and technical feasibility demonstration on 15kg of spent fuel of the Am+Cm separation by DIAMEX-SANEX process, CEA has launched in the framework of the law 2006 R&D program aimed to improve and optimize the minor actinides separation processes for the different recycling modes:

- GANEX process for recycling the MA (Np, Am et Cm) with plutonium in the fast reactor core in an homogeneous recycling route;

- SANEX-TODGA process for the separation of americium and curium for the heterogeneous transmutation route in the fast reactor blankets;

- EXAm process for the separation of the sole americium for the transmutation in heterogeneous concept in dilution on uranium support ($UAmO_2$).

Furthermore, additional studies were performed to enlarge the results towards the by-process for the management of the effluents and the development of piloting tool. The demonstration on the genuine solutions of the feasibility of these various separation processes were carried out in the Atalante CBP hot cell between 2008 and 2010 and the main results will be presented.

1. INTRODUCTION

Nuclear power has the worldwide potential to curtail the dependence on fossil fuels and thereby to reduce the amount of greenhouse gas emissions while promoting energy independence of the different countries. Therefore, retaining nuclear power as a key piece of the nation's energy portfolio strengthens French energy security and environmental quality.

After use, PWR fuel contains approximately 95% uranium, 1% plutonium, and 4% fission products. In France, this spent fuel is reprocessed and the recovered uranium and plutonium are partially recycled in LWRs, while the fission products including minor actinides are vitrified in ultimate waste, to be stored in a geological formation. The purpose of separation procedures is mainly to isolate the minor actinides that have a very long half-life and high radioactivity, so that they are no more part of the ultimate waste whose radio toxicity, heat and volume are so drastically reduced (see fig 1). Then these separated products have to be transmuted in a reactor or a dedicated tool.

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Fig. 1: Relative radiotoxicity versus time, depending of the waste management strategy

As mentioned, the recycling of the plutonium is essential to reduce the potential long term radiotoxicity of the ultimate wastes, but we can look to further reduce it by an additional recycling of

minor actinides. During the first Waste Management Act voted in 1991, major progress has been achieved on MA partitioning thanks to the studies performed in the CEA Atalante at Marcoule [1, 2] and the scientific demonstration of the DIAMEX-SANEX process for Am and Cm selective extraction has been demonstrated in 2005 on ~15 kg of spent nuclear fuel in Atalante hot cells [3, 4]. High efficiency rates better than 99% have been obtained for Np, Am and Cm recycling. In the framework of the 28th June 2006 waste management Act [5], R&D aims now to assess by 2012 the industrial potentials of the different P&T options and related separation processes, with a particular emphasis on the following issues:

- defining the several options of interest, which could be successively deployed (all-actinide, americium only, heterogeneous or homogeneous recycling…);
- assessing benefits/costs ratio for the several recycling options, considering different criteria and "densification" of the final storage;
- designing and optimizing the separation processes, transmutation fuels and their fabrication process;
- gathering technical elements for industrial operation evaluation.

This paper gives an overview of the major results obtained since 2006 on the new partitioning processes which could be implemented for recycling MA, respectively named the DIAMEX-SANEX, GANEX or EXAm processes.

2. GENERAL APPROACH

For these complex separations, hydrometallurgical processes were considered as the reference option as they could be easily added to the PUREX process, industrially implemented in the La Hague plant for several years. Furthermore, with such processes, achievable performances in terms of recovery and decontamination are very high and amount of technological wastes is limited.

For actinide separation, specific processes have been conceived. Thus, the two groups of elements, lanthanides (Ln = 4f elements) and actinides (An = 5f elements) are present in the PUEX raffinate at the oxidation state +III, and their physico-chemical properties are very similar. They are strongly hydrated and their ionic radii are close. Considered as *hard* acids in Pearson's *Hard and Soft Acids and Bases* theory, they react preferentially with hard bases, such as ligands bearing oxygen atoms (electron donors), via electrostatic interactions. Their coordination numbers vary from 6 to 12 depending on the chemical systems considered, and their discrimination is therefore governed by size effects (fit of the geometry of the coordinating sites of the oxygen ligand with the radius of the metallic cation). The two series of elements, consequently, can only be partially separated from one another, though fairly well separated from other fission, corrosion, or activation elements present in the PUREX (or COEX^{TM}) raffinates.

Given the acidity and the element inventory of these raffinates, selective extraction of minority An(III) would appear to be logical. However, this strategy is complicated by the fact that the organic extracting agents to develop have to be :

- very efficient (as the « H$^+$/An^{3+} » competition is very strong);
- highly selective, especially vis-à-vis the transition metals (Fe, Pd, Mo, Zr) and the Ln(III).

Thus actinide/lanthanide separation is very difficult. To get viable processes, specific extracting systems fulfilling following criteria have been conceived:

- Ability to extract targeted elements with enough selectivity;
- Reversibility to be able to back extract these elements;
- Stability versus radiolysis and hydrolysis;
- Possible implementation in counter-current apparatuses, with diluents compatible with industrial use.

Then once an extracting system seems promising, it is necessary to develop a dedicated process. For that, many distribution data of cations were acquired in process conditions, depending on different operating parameters. Thanks to these data, preponderant chemical equilibria can be identified and modeled. Then they are introduced in the PAREX code, initially developped for the PUREX process and the extended to other process simulation. Thanks to this code, a flowsheet can be elaborated and then tested. Genrally the first test is implemented with representative simulated elements. And if the

corresponding results are satisfying, a test using of a few kilograms of real solution (generally a raffinate issued from a PUREX run) is performed. If the performances are in agreement with the targets, the scientific feasability is considered to be obtained.

This progressive approach was lead to developp successively various processes corresponding to the possible transmutation options.

3. MAIN RESULTS RELATED TO PARTITIONING PROCESSES

Three main options are considered in the current research: (i) the DIAMEX-SANEX process which aims to recover Am+Cm which correspond to an heterogenous recycling strategy, (ii) the GANEX process which aims to recover in a single flux all the actinides Pu+Am+Cm which correspond to an homogeneous recycling strategy, (iii) the new EXAm process which aims to specifically recover the sole Am in a dedicated flux. This last and recent option would allow specifically recovering and recycling Am, which is the main MA contributor to the final waste thermal power, contributing therefore to a potential surface and subsequent cost decrease of the final repository.

3.1. SANEX-TODGA process: an improvement for MA recovery

Minor actinide recycling has been investigated at the CEA for the two last decades. The technological feasibility of the Am and Cm recovery was demonstrated in 2005 through the treatment of 13 kg of genuine spent nuclear fuel in the ATALANTE facility with actinide high yield recovery (>99.9%). For that, two cycles were successively implemented (see figure 2): (i) DIAMEX to coextract trivalent 4f and 5f elements (respectively Ln(III) and An(III)) and (ii) SANEX to selectively strip An(III) thanks to polyaminocarboxylate compound used in a buffered medium around pH = 3 (citrate buffer for example).
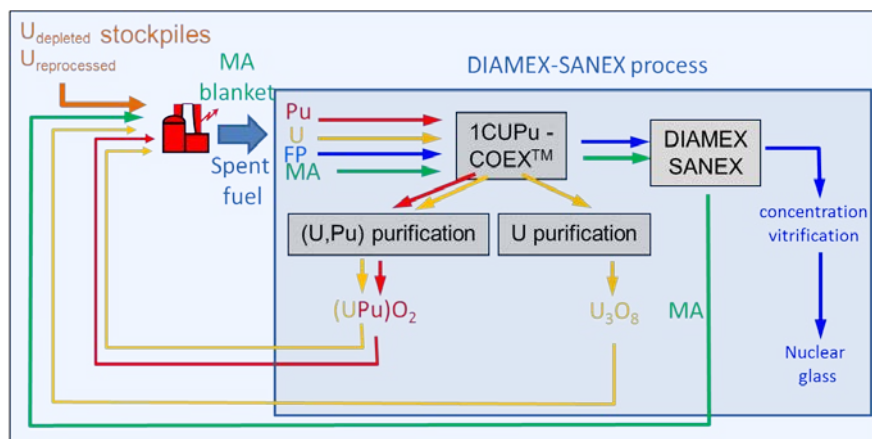

Fig. 2: Heterogeneous MA recycling by implementing a DIAMEX-SANEX separation process.

In order to develop a simpler single-cycle An (III) partitioning process, new extracting molecules have been investigated at CEA. The TetraOctyl-DiGlycolAmide (TODGA) which presents a very high extraction affinity towards trivalent actinides and lanthanides appeared very promising. A simplified flowsheet was designed; it consists of three main steps:

- First trivalent actinides and lanthanides are coextracted by TODGA/TBP solvent;
- Then the selective stripping of the An(III) is feasible by a hydrophilic polyaminocarboxylate complexing agent (diethylenetriamine-pentaacetic acid DTPA) in a buffered solution (malonic acid at pH 2), while the Ln(III) remain complexed by TODGA in the organic solvent thanks to a salting-out agent in the aqueous phase;
- Finally, the lanthanides are stripped thanks to diluted nitric acid.

A progressive approach was developed between 2007 and 2009 in order to validate this concept including [6]:

- Distribution coefficients measurements under various conditions to achieve solvent composition and aqueous solution formulation for the trivalent actinide stripping key step;

- Cold counter-current test performed in November 2007 in the MARCEL loop of the CEA Marcoule to assess the hydrodynamic behaviour of the SANEX-TODGA separation system, to determine the decontamination factors of the fission products and to (in)validate the model and code calculations;
- Spiked counter-current test performed in March 2008 in the glove boxes of the ATALANTE facility on a surrogate feed spiked with Eu-152, Am-241 and Cm-244. They aimed to assess the An(III)/Ln(III) separation efficiency on a reduced number of stages in the An(III) stripping section and to determine the influence of pH variation on the process performances. The flowsheet sensitivity towards pH could thus be evaluated, integrated in the model and validated through code calculations;
- Finally a hot test using a genuine PUREX raffinate performed in 2009 in the Atalante facility. Very good results were obtained during this counter-current hot test: recovery yields of An(III) larger than 99.9% with high decontamination factors towards lanthanides(III) (less than 5%mass of Ln in the An product).

3.2. GANEX process for actinide grouped separation

The GANEX process (Group ActiNide EXtraction) aims at the recovery of all transuranium elements from the HA spent fuel dissolution solution. It consists of two steps (see. Fig. 4): selective extraction of uranium, and then partitioning of actinides from fission products and lanthanides.
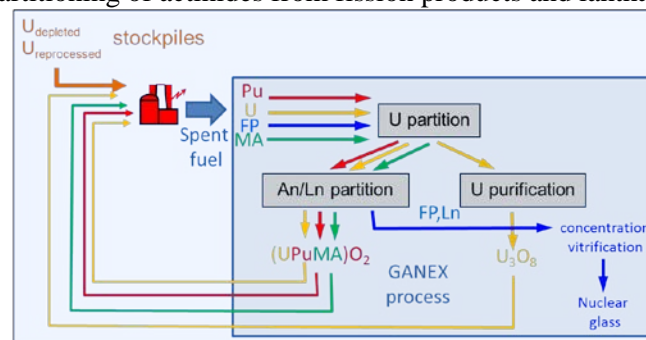

Fig. 4: the GANEX concept.

The selective separation of uranium(VI) is operated by a hydrometallurgical process using a monoamide extractant DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide) diluted in an industrial aliphatic solvent HTP. Based on batch experimental results, a physicochemical model was developed to describe the extraction of U, Np, Pu, and Tc by DEHiBA. With the help of this model, a flowsheet was designed and tested in 28 mixer-settlers (laboratory scale) on a genuine High Liquid Waste (HLW) in the CBP hot cell (Atalante facility) in June 2008. After running 60 hours, more than 99.99% of the initial uranium was recovered with a good purity versus transuranium elements and fission products [7].

The GANEX 2nd step process consists of a group separation of transuranium elements (Np, Pu, Am, and Cm) by solvent extraction. The DIAMEX-SANEX process, initially developed for the partitioning of trivalent minor actinides (Am and Cm), was optimized to handle neptunium and plutonium along with americium and curium. Based on the experimental distribution ratios of actinides and major fission products, the initial DIAMEX-SANEX process was modified to allow the grouped actinide extraction GANEX by adjusting experimental conditions (selection of complexing agents, optimization of reagent concentrations) [8]. This GANEX 2nd step process was progressively checked on dedicated experiments:
Several cold tests have been carried out on lanthanide and major fission products in order to check the hydrodynamic behavior and the extraction performances of lanthanides, Mo, Pd, Zr, and Fe.
the actinide group separation was performed using the high active raffinate issued from the GANEX 1st step test. The flowsheet consists of four sections of laboratory scale mixer-settlers corresponding to the extraction-scrubbing, the Mo-Tc stripping, the actinide stripping (including 8 stages for lanthanide scrubbing) and the lanthanide-zirconium-iron stripping steps.

In terms of results, Np, Pu, Am and Cm were recovered altogether in a single flux (actinide product) and the losses of transuranium in the different outputs and in the solvent were estimated at a value lower than 0.5% (essentially neptunium) at the end of the test, corresponding to a recovery yield of actinides higher than 99.5%. Nevertheless, the decontamination factors versus some lanthanides (especially Nd, Sm, and Eu) were much lower than expected and the mass of lanthanides in the actinide product was around 5% at the end of the test.,This was explained by an accumulation of lanthanides in the actinide stripping section which could not be resorbed during the test. The decontamination factors versus some lanthanides were not as high as expected but could be well simulated by the model.

3.3. EXAm process for the sole americium recovery

The last route investigated in the frame of the 2006 Act is the recycling of the sole americium since its recycling (without curium) could be more easily implemented (mainly for fuel manufacturing) while allowing a subsequent potential benefit for the geological repository (see fig. 5).
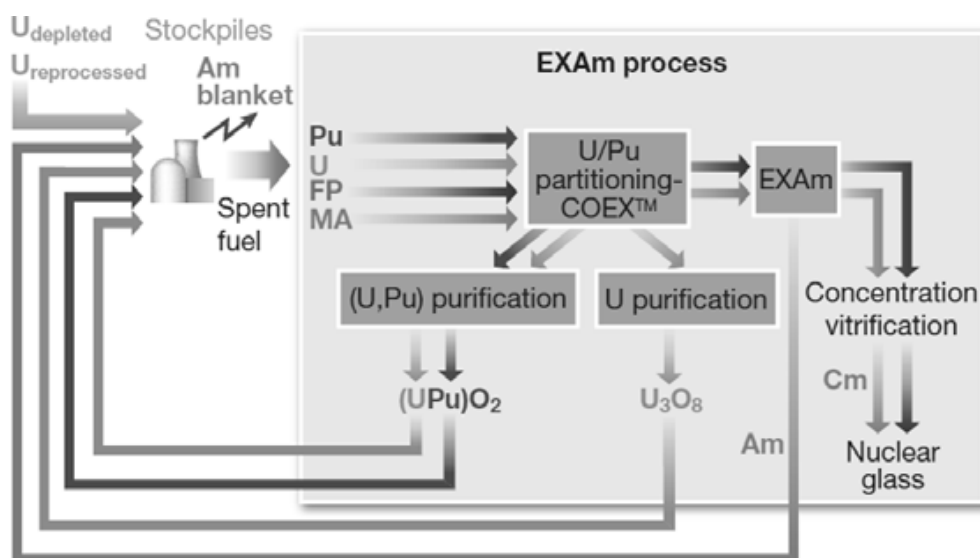

Fig. 5: Potential future fuel cycle in which would be implemented the EXAm concept

The principle of the ExAm process is based on the extraction of americium together with some light lanthanides having close values of distribution coefficients in high nitric acidity, while curium and other lanthanides remain in the aqueous phase. The TEDGA amide molecule is added in the aqueous phase, in order to increase the selectivities Am/Cm and Am/heavy Lns, because of the preferential complexation of curium and heavy lanthanides by this amide: global efficiency of the process is largely improved, with a corresponding decrease of the number of the necessary separation stages. Then Am is selectively stripped from light lanthanides like in the GANEX 2 step (see figure 6).

Between 2008 and 2009, numerous experimental data has been acquired mainly for the key step (Am+light Lns extraction and scrubbing): distribution coefficients versus $[HNO_3]$, $[TEDGA]$, $[cations]_{org}$, identification and stoechiometry of complexes both in the organic and aqueous phases, determination of stability constants between Ln and TEDGA. The data was used to implement a phenomenological model in the PAREX process code [9].

Spiked counter-current test involving mainly the innovative extraction-scrubbing step was performed in December 2009 in the glove boxes of the ATALANTE facility on a surrogate feed spiked with lanthanides, Am-241 and Cm-244, to assess the Am/Cm and Am/heavy Lns separation efficiency in comparison with the modelling. Satisfactory results were obtained: more than 97% of americium was recovered, with decontamination factor higher than 1000. The concentrations of the radioelements measured during the test were in good agreement with the values calculated using the PAREX code.

Finally, a complete hot test, using a genuine PUREX raffinate was then carried out in April 2010, in order to confirm these promising results. This counter-current hot test lasted about 60 hours. It consisted of 68 mixer-settler stages to insure americium only extraction-scrubbing-stripping. According to preliminary results, good agreement between experimental and simulated performances

was obtained: more than 99% of americium initially in the raffinate was extracted and the decontamination factor of americium versus curium is more than 500. Exhaustive analysis of the samples at the end of the test is in progress and should confirm the first promising results.

4. STUDIES TOWARDS POTENTIAL IMPLEMENTATION

Another important part of the program related to partitioning and transmutation in the frame of the 2006 Act is related to the potential industrialisation of these 3 processes [10].

The advanced processes based on liquid-liquid extraction benefit from the experience gained by operating the PUREX process at the La Hague plant. Great experience is available in the field of extracting apparatus. However, these processes have specificities which have to be considered more in detail. These specificities have been classified according to the following thematics:

- evolution of the simulation codes, including phenomenological representations: with such a simulation tool, it will be possible to assess operating tolerances, lead sensitivity studies and calculate transient states;
- definition of the implementation conditions in continuous contactors (such as pulse columns), according to the extractant physico-chemical characteristics;
- scale-up of new extractants, such as malonamides used in the DIAMEX process, facing purity specifications and costs estimation;
- solvent clean-up studies to assess long term behaviour of the separation systems towards radiolysis and hydrolysis: the first question is to assess basic scrubbing efficiency to remove acidic degradation products (coming from radiolysis and hydrolysis). The irradiation loop settled in Marcoule since 2004 will be helpful for that. In addition, the need for complementary treatments such as soft or flash distillations will be considered;
- liquid waste management: the question is to assess the impact of organic reagents introduced in the various steps of the flowsheet (especially downstream steps). If necessary, complementary treatments will be developed;
- transitional operations: the recovered actinide flow must be compatible with downstream co-conversion processes.

4.1. Extractant stability and clean up

For industrial implementation solvent has to be recycled as long as possible. Thus degradation products issued from hydrolysis and radiolysis have to be removed continuously.

Theses degradation products are generated after the rupture of a liaison; these ruptures can occur at several places and lead to the formation of various degradation products, more or less disturbing for the process implementation.

The approach consists in a first time in identifying the various degradation products and assessing their potential disturbing power. These products will be removed thanks to a dedicated first level treatment: basic compounds such as amines can be removed by acidic washes, whiles acidic compounds (if they are not too lipohilic) can be removed by basic washes [11].

Efficiency of such treatments was assessed during long time runs (lasting several weeks) performed in a dedicated loop called MARCEL: degradation is obtained both via hydrolysis at 40°C and γ radiolysis (via circulation of the flow through a Cs irradiator). A run in the MARCEL loop is able to simulate between one to three years in a plant; it gives significant results on potential accumulation of degradation products in a process.

Even after this first level treatment, at long term, it is possible that some degradation products are not completely removed and their accumulation could become too disturbing.

It is the reason why a second level treatment was conceived. The choice is rather limited because extracting molecules are thermo sensible. Preliminary studies were achieved to assess potentialities of CO_2 supercritical extraction, as this technique is able to preferentially solubilize some compounds. Results showed separation could be possible but difficult.

4.2. Aqueous effluent management

Several organic reagents are used in the various flows of the MA separation processes. They are complexing agents such as HEDTA, DTPA, TEDGA, buffer reagents (carboxylic acid associated with

a base) such as malonic or citric acid and even reductive agents. These reagents, their degradation products and those issued from solvent degradation will be collected in the various aqueous effluents. Dedicated treatment flowsheets were conceived with the objective of an optimized management of reagents and liquid waste, while end product quality is insured. Impact of organic compounds on functioning and safety was assessed while exit flows are compatible with downstream steps, especially outlets.

Thus it seems that the aqueous effluents, even if they contain high concentrations of organic compounds should not lead to major problems. In some cases, it could be necessary to add complementary treatments able to destroy residual organic compounds.

4.3. Technologies for process implementation

For industrial implementation of these innovative processes, it does not seem necessary to develop specific contactors. Pulse columns should be convenient for setting up extraction steps, even if in such apparatuses, interfacial surface is lower than in mixer-settlers.

Complementary experiments are necessary to insure industrial implementation. The approach will be different from that performed for the La Hague plant where full scale tests were performed. The extrapolating approach will include both calculations and limited experimental experiments.

4.4. Process simulation

Solvent extraction modelling was initiated by the CEA thirty years ago for the description of the PUREX process reactions. Thanks to the code named PAREX, it was possible new processes from the laboratory scale up to the industrial scale.

The description of innovative systems, especially those developed to MA separation processes, was performed and integrated in the PAREX code. Due to the variety and complexity of phenomena taking place, only preponderant reactions have been included.

For each process, the main following phenomena have been taken into account:

- Specie distribution;
- Chemical reactions in homogeneous phase;
- Transfer kinetics between the phases;
- Hydrodynamics in the extraction apparatuses;
- Thermal release: chemical reactions enthalpy, thermal exchanges.

GANEX 1, SANEX-TODGA and EXAm are now implemented in the PAREX code. Each key step of these processes was validated via comparison between experimental and calculated results [12, 13].

Process modelling is an important tool which helps phenomena understanding, selecting and thus minimizing experiments, especially for processes very sensitive to operatory parameters [14].

Future developments will consist in consolidating modelling but also progressively in substituting experimental data by numerical simulations relying on theoretical chemistry.

4.5. Process piloting

Process piloting is crucial to define an operating range in which safety, performances and specifications are guaranteed. The definition of the piloting procedure includes first the identification of the sensitive operational parameters (i.e. for which a slight variation can induce a huge impact on the process functioning). Sensitivity analyses performed thanks to the PAREX code lead to identify these operatory parameters and pertinent points for process state assessment [15]

Main elements to be followed are major actinides (U, Pu), minor actinides (Am, Np, Cm) and some lanthanides (Nd, Sm). Spectrophotometric in-line analysis is more or less operational. But it is necessary to improve other in-line techniques for some elements (Cm especially). After the priority needs, it would be interesting to follow other cations such as Mo, Pd, Zr, Ru, Fe, Tc. Acidity and pH precise measurements under high activity conditions could also improve piloting, especially when these processes will be industrially implemented.

5. CONCLUSION

After 20 years of research, France and other countries now possess some relevant and effective processes to partition selectively the minor actinides in view of their subsequent recycling in FR reactors. Technical feasibility can therefore be considered as having been achieved. However, several scientific and technological issues are still under investigation to achieve efficient and relevant processes at the industrial scale, in particular with regards to the understanding of the actual molecular processes and origin of selectivity, the chemical process simulation, the solvent cleanup or the relevant continuous industrial contactors (as pulsed column, mixer-settlers).

Now, the next challenge is the demonstration of Am cycle closure. It consists in a large experiment from spent fuel dissolution to $(U-Am)O_2$ pellet manufacturing. The key steps will be on one hand to recycle Am from a concentrated COEX raffinate to improve the compactness of the EXAm process and on the other hand to demonstrate the oxalic coprecipitation of Am with U(IV) to form homogenous $(U-Am)O_2$ oxide suitable for pellet elaboration.

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FRENCH EXPERIENCE AND R&D CHALENGES FOR AN INDUSTRIAL SFR MOX FUEL TREATMENT

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Abstract

With the perspective of growing of fast neutron reactors foreseen in France at the early 1960s, fuel reprocessability was examined at the same time on an experimental scale, pilot scale, and scale 1, mainly in three facilities: AT1, APM, and UP2 400, with the aim of developing an industrial treatment process chiefly based on the PUREX process. A total of about 25 Mt of SFR MOX fuel irradiated at burnup around 100,000 MWd/t, and for some slightly cooled, was reprocessed. All the steps of the process, from the mechanical shearing of the pins to the delivery of finished products, were properly controlled with performance characteristics of recovery yields of uranium and plutonium and decontamination and purification factors from fission products comparable to those obtained during the industrial reprocessing of LWR fuels. This French experience is unique in the world, with regard to both process control and management of waste. With the recycling of 4.4 t of plutonium in PHENIX, it has also demonstrated the closure of the SFR fuel cycle. This feedback shows that the treatment of SFR fuels is a reality. But some developments like mechanical FAs dismantling, fuel dissolution, hulls conditioning, will be necessary in the future to achieve a mature and robust industrial SFR MOX fuels treatment process.

I. Introduction

The growth of sodium fast reactors foreseen in France at the early 1960s was to breed enough plutonium for refuelling these reactors. In this context, the recycling of plutonium was examined at the same time, with the aim of development of an industrial treatment process based on the PUREX process [1], [2], [3]. In addition to the laboratory studies carried out in the hot labs at Fontenay-aux-Roses, the reprocessing of SFR fuels took place at a larger scale in three facilities [4]:

• The AT1experimental workshop at The Hague, which operated from 1969 to 1979 at a maximum processing capacity of 1 kg/day (150 kg/year),

• The Marcoule pilot workshop (APM), operated from 1973 to 1997, whose initial capacity of 2 Mt/year was increased to 5 Mt/year in 1988,

• The UP2-400 plant in The Hague, where reprocessing was performed in dilution with graphite-moderated gas-cooled natural uranium fuels.

This feedback on SFR fuels reprocessing has highlighted the process operations and the devices that still require R&D effort to achieve a robust process for the bulk processing of SFR fuels. The aim of this paper is to present the experience gained in France [5], [6], [7], [8], and the aspects of the process that require improvement or innovation [9], [10].

II. French experience

The periods and the position occupied by the SFR MOX fuel reprocessing campaigns in these three facilities are given in the Figure 1below:
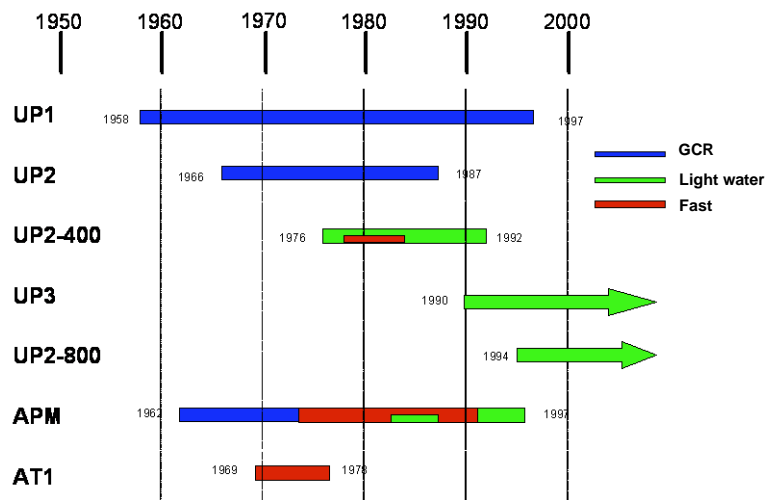
FIG. 1. SFR MOX fuel reprocessing campaigns

II.1. AT1 Experimental workshop

AT1was the prototype fuel reprocessing workshop (Figure 2) for French fast breeder reactors.

Figure 2: View of workshop AT1

It was operated from 1969 to 1979, testing the reprocessing techniques on Rapsodie-Fortissimo and Phenix fuels. As in the other two facilities, the FAs were dismantled in the mechanical cells (CEI) associated with the reactors and the pins extracted were delivered to the reprocessing sites packed in case.

Access to the fuel was obtained by mechanical shearing, pin by pin. The fuel pieces were dissolved in a batch dissolver filled with concentrated nitric acid (Figure 3). Extraction cycles by the TBP were performed in mixers-settlers to separate and purify the uranium and plutonium from the fission products. Conversion to plutonium oxide was carried out by oxalic precipitation.

Figure 3: View of the AT1dissolving cell

More than 15,000 pins of Rapsodie-Fortissimo and Phenix core fuels, irradiated at burnup varying from 40,000 to 120,000 MWd/t and cooling times from three months to more than 24 months were reprocessed at AT1 from 1969 to 1977 thus validating the mains steps of the SFR MOX fuel reprocessing.
When final shutdown was pronounced in 1979, AT1 had reprocessed more than 800 kg of uranium and plutonium.

II.2 APM reprocessing experience

The reprocessing of SFR fuels at the Marcoule Pilot Workshop (APM) was performed from 1973 to 1983 on the TOP (pilot oxide processing) chain (Figure 4), whose capacity was 2 Mt/year. Then the APM was renovated with the construction of the TOR (fast oxide processing) chain commissioned in 1988 (Figure 5), to boost the APM's processing capacity to 5 Mt/year. Note that the TOP and TOR chains were designed in safe geometry to be able to operate without any concentration or Pu mass limit constraints during the processing of plutonium-enriched fuels with a maximum content of 28% Pu/U+Pu.

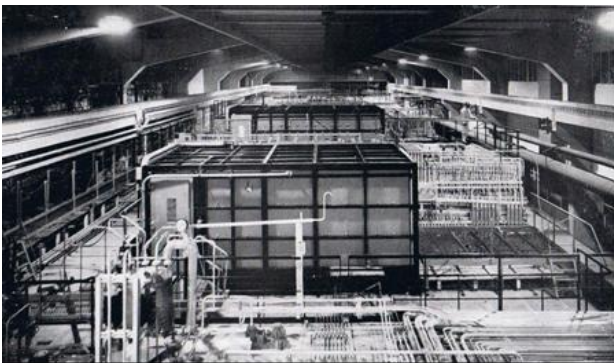Figure 4: View of the APM/TOP chain

From 1973 to 1976, the TOP chain reprocessed approximately 300 kg of Rapsodie-Fortissimo fuel and 1.9 Mt of the German KNK I UO_2 enriched to 6.7% ^{235}U reactor fuel. Then, from 1976 to 1978, the first Phénix core (2.3 Mt) consisting of UO_2 enriched to 26% ^{235}U, and finally the Phénix Pu cores (6.8 Mt of Pu) from 1978 to 1983 were reprocessed.

Figure 5: View of the renovated Marcoule pilot workshop.

From 1988 to 1991, the TOR chain reprocessed 7.2 Mt of Phenix Pu cores irradiated at burnup up to 105,000 MWday/t. During that period and until 1994, it reprocessed also fuels from the German KNK II reactor, consisting of UO_2 enriched to 40-60% ^{235}U and MOX fuels.

The pins laid out in a layer in the mechanical cell were sheared one by one (Figure 6), as at AT1.
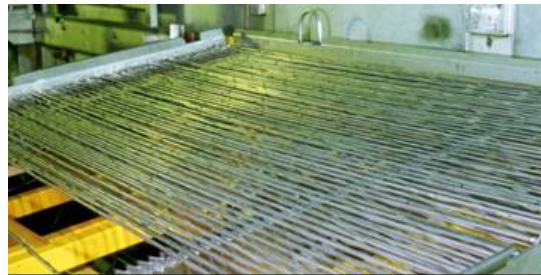
Figure 6: TOR chain mechanical processing cell

Dissolution was performed by boiling concentrated nitric acid in a batch dissolver constituted of a tube and a slab (Figure 7).
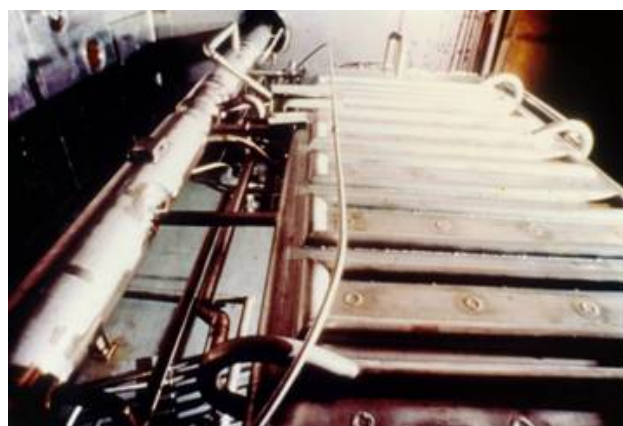

Figure 7: View of the APM/TOR dissolver

The uranium and plutonium extraction and purification cycles were performed in pulsed columns and mixers-settlers.

Note also in the early 1980s the vitrification of the PUREX rafinate coming from the reprocessing of two

tons of Phenix fuel on the PIVER pilot facility.

APM reprocessed a total mass of 13.5 tons of PHENIX core fuels. This reprocessing experience of fast reactor fuel is significant. All the steps of the process, from the mechanical shearing of the pins to the delivery of finished products were properly controlled with performance characteristics of recovery yields of uranium and plutonium and decontamination and purification factors from fission products comparable to those obtained during the industrial reprocessing of LWR fuels.

The campaigns carried out at the APM workshop tested the reprocessing operations over significant periods, provided information about the nature, quantity, and αβγ activities of the effluents and solid waste.

II.3 UP2-400 reprocessing experience

From 1979 to 1984, UP2-400 plant in The Hague reprocessed approximately 10 Mt of PHENIX core fuel irradiated at burnup from 24 to 91,000 MWd/t. This plant was not designed for SFR MOX fuel treatment. Thus, the pins were sheared directly with their case and the fuel dissolution was performed in batch dissolver at low Pu concentration and poisoning of solutions by a gadolinium. For the extraction cycles, the dissolution solution was diluted by the solutions of natural uranium gas cooled reactor fuel dissolution. These campaigns were successful.

III. R&D challenges

Compared to the processing of LWR fuels, the design and composition of SFR MOX fuel assemblies and the modifications of the physicochemical properties of the fuel under thermal conditions and irradiation are specific and affect the process from a safety point of view with large plutonium flux to be managed, the head-end process with the mechanical dismantling of the FAs and the fuel dissolution, and the waste management (cladding conditioning, vitrification).

III.1 Fuel dismantling

The very thick duct tube of SFR FAs makes it impossible to shear the whole assembly, as practiced for LWR FAs. After removal of the sodium, the FAs must be dismantled for the extraction of the pins. This operation was carried out in the mechanical cell of the PHENIX reactor by shearing of the end pieces and by mechanical milling on the corner of the duct tube (figure 8). Then the bundles of pins were extracted and conditioned in cases.
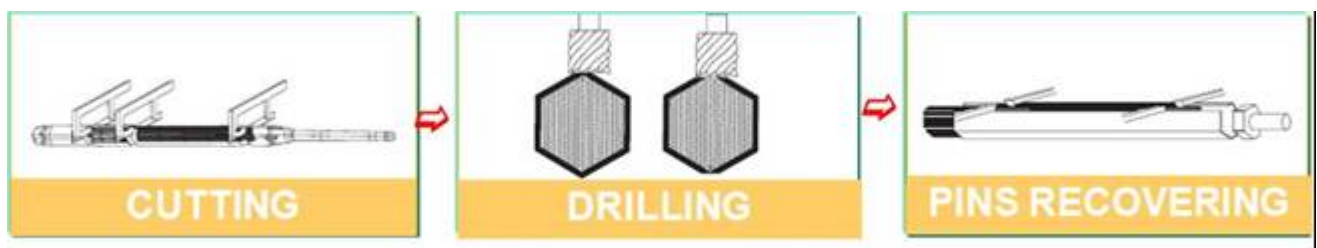

Figure 8: Dismantling of SFR MOX FAs by mechanical milling.

This mechanical dismantling technique is robust and remains possible for low capacity of treatment but generate dust metallic waste. For a great capacity of SFR fuel treatment a more appropriate dismantling process is to be defined.

III.2 Pins shearing

For this operation, the removal or not of the spacer wire depends on the design of the dissolution line, i.e. the shearing tool and the dissolver and the capacity to manage the balls of spacer wire in these equipment.

Experience shows that processing was performed with or without the removal of the spacer wires. The shearing of pins with their spacer wire was carried out without major problems, either pin by pin (AT1, TOP, TOR) or by direct shearing of the cases (UP2-400). Even though the options are still open for the future, the design of a dissolution line that accepts pins with their spacer wire would eliminate a boring mechanical operation.

III.3 Fuel dissolution

There are three aspects to consider: the total dissolution of the uranium and plutonium from the fuel in the boiling nitric acid, the safety-criticality of the operation, and the corrosion resistance of the cladding material to the dissolution environment.

<u>MOX fuel dissolution</u>

Mixed Uranium-Plutonium oxide form is soluble in concentrate nitric acid up to a Pu content of around 35%. Beyond this level, the mixed oxide $UPuO_2$ is considered like insoluble (Figure 9) [11].
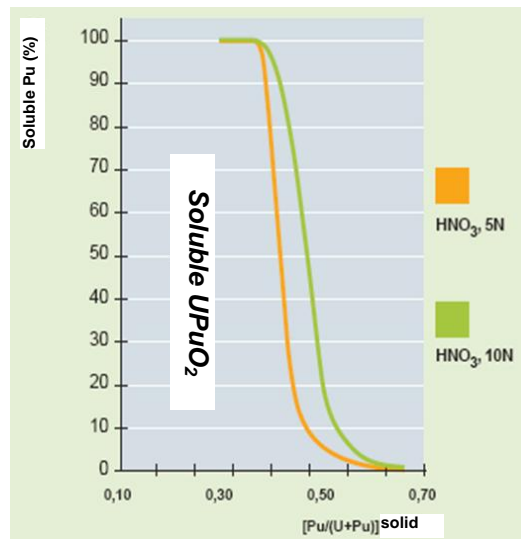
Figure 9: Solubility of solid $UPuO_2$ solutions in nitric acid

Phenix cores (inner core to 18% Pu and outer core to 25% Pu) did not show a particular difficulty of fuel dissolution, unlike RAPSODIE-FORTISSIMO fuel where higher Pu losses were observed for the high burnup fuels, despite aggressive dissolution conditions used (concentrated nitric acid, boiling, and residence time in excess of 6 hours). The Pu losses recovered in the insoluble residues of Phenix fuel dissolution irradiated at burnup ≤100,000MWd/t given on figure 10 did not exceed 0.1%. This good solubility is generally attributed to the COCA fuel manufacturing process used for the fabrication of the PHENIX fuel [8]. This good performance should, also be checked in the future for burnup higher than 100,000 MWd/t, or for any new fuel design fabricated from a co-converted mixed oxide.
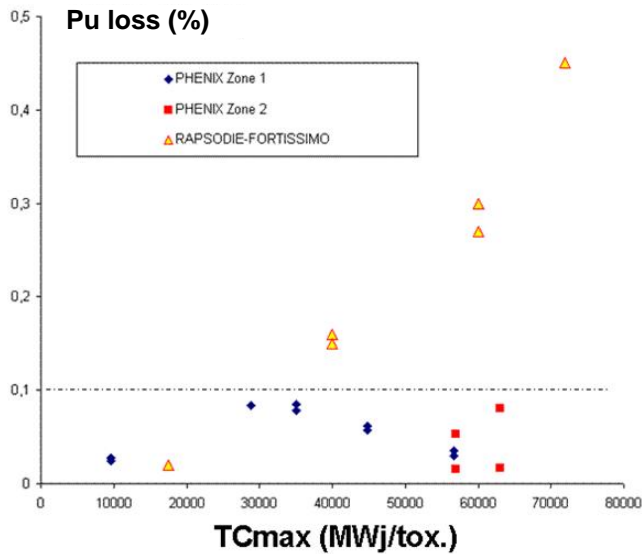
Figure 10: Solubility of RAPSODIE-FORTISSIMO and PHENIX SFR MOX fuels

Criticality

The management of the criticality risk is a key point for the processing of MOX pure solutions at the dissolution and at the extraction cycles. The use of pulsed columns with an adapted geometry will be the appropriate option for extractions. In the past, because of the limited processing capacities of the facilities, the criticality risk at the dissolution step was managed either by the geometry in AT1 and the APM or by dilution and poisoning in UP2-400. The adaptation of these options will have to be evaluated in the future for higher processing capacities of SFR MOX fuels facilities. The other option is to define another dissolution mode like a continuous dissolver (Figure 11).

Figure 11: Prototype continuous helical dissolver

Behaviour of cladding materials on reprocessing

The choice of fuel cladding material is the result of a compromise between durability in the reactor and good behaviour on reprocessing. Hardened and titanium-stabilised steels: 316L, 316Ti and 15-15 Ti [12] have become, each in turn, the benchmark materials for the SFR MOX cladding fuel (Figure 12). The 15-15Ti, the last grade of Phenix cladding material, have retained its integrity in reactor up to maximum doses of 120 dpa, and its corrosion resistance properties in the oxidant dissolution environment (release of limited quantities of iron, nickel and chromium in solution).

This could no longer apply in the future if the FAs designers were to reach higher burnup fuels choose ferritic-martensitic steels, unless to reinforce their structure by nano-dispersion of oxide compounds (ODS steel).
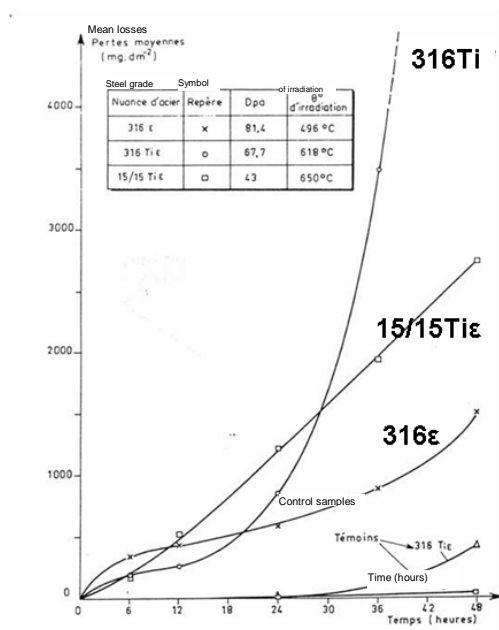

Figure 12: Dissolution behaviour of different grades of Phenix fuel cladding

III.4 Extraction cycles

These operations have not showed difficulties, and the recent enhancements made for the treatment of LWR fuels can been applied in SFR MOX fuel reprocessing plant.

III.5 Waste

The PIVER pilot facility at Marcoule vitrified fission products solutions coming from the reprocessing of two tons of Phenix fuel. Glass containers holding 100% of SFR rafinates were produced in this way. These glasses had a load factor of 8% in FP. With the specifications of the current glasses, this load factor would be limited by the integrated alpha dose over 10,000 years, currently specified as 10^{19} alpha decays per gram, and by the chromium content (corrosion product from the cladding waste) in solutions of fission products, because chromium oxide has a low solubility in glass (maximum Cr_2O_3 content 0.6% in the current specification of R7/T7 glass). In the long term, these limits could be relaxed in the context of a new specification or a new glass formulation.

As long as SFR fuels can be reprocessed with the UOX fuels in the same plant, the SFR rafinates can be vitrified in dilution with the UOX rafinates. This is the scheme applied to the treatment of LWR MOX fuels in La Hague plant today. This was also the principle implemented at the AVM for the vitrification of PHENIX rafinates with dilution by natural uranium GCR rafinates.

The conditioning of high mass of SFR insoluble residues will have to be defined in the future. Two possibilities may be studied. One route is the incorporating in ingots of molten hulls (Figure 13). The second route is the formulation of a special glass to incorporate high content of insoluble residues.

Figure 13: Ingot of molten hulls

IV. **Conclusions**

The three French facilities, AT1, APM, and UP2 400, have reprocessed a total of about 25 Mt of SFR MOX fuel irradiated at burnup around 100,000 MWd/t, and for some slightly cooled. This French experience is unique in the world, with regard to both process control and management of waste. With the recycling of 4.4 Mt of plutonium in PHENIX, it has also demonstrated the closure of the SFR fuel cycle (Figure 14). The multi-recycling of plutonium was also demonstrated with the manufacturing of one fuel assembly with plutonium reprocessed three times (FONTENOY fuel assembly).
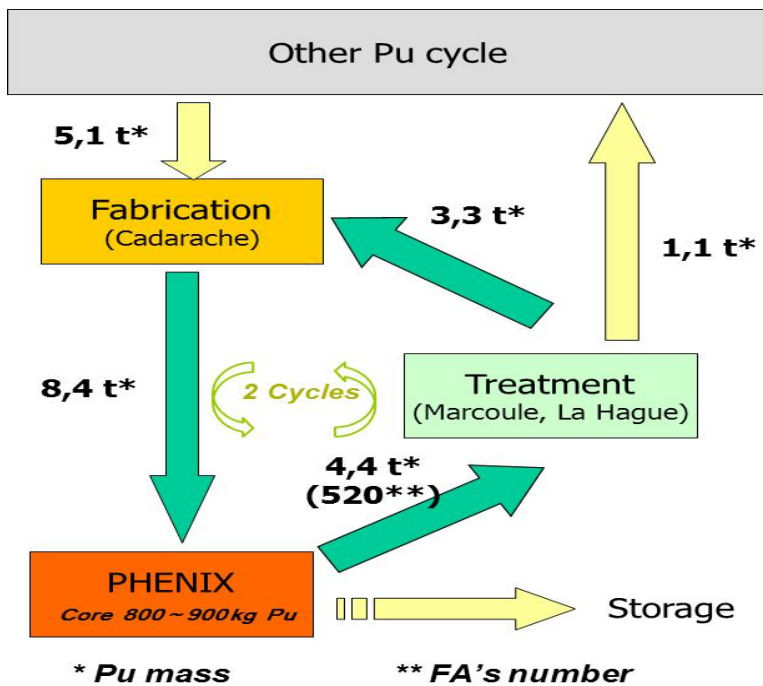

Figure 14: Demonstration in PHENIX of the SFR MOX fuel cycle closure

This feedback shows that the treatment of SFR fuels is a reality. But some developments like mechanical FAs dismantling, fuel dissolution, hulls conditioning etc, will be necessary in the future to achieve a mature and robust industrial SFR MOX fuels treatment process.

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French R&D Program for Multi-Recycling of Plutonium

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Abstract. One of the main issues regarding the future of nuclear energy is to improve its sustainability, in particular through better preservation of uranium resources by increasing the efficiency of its consumption in nuclear reactors. This implies first developing and implementing Fast neutron Reactors (FR), such as the French ASTRID Sodium-cooled Fast Reactor (SFR) project. This also implies implementing multi-recycling of plutonium, which would significantly limit the ultimate waste volume. Based on past experience with hydrometallurgical treatment of spent fast reactor fuel, the CEA has developed an ambitious R&D program to adapt the current PUREX process — for which more than 30 years of experience is available — to the specific requirements of spent FR fuels. Innovations are expected for most of the aspects of the process, in particular for treating the fuel assembly, ensuring safe recovery of plutonium and the reliable confinement of the waste. The main scientific challenges for ensuring safe and reliable multi-recycling of plutonium are reviewed.

1. Introduction

For sustainable nuclear energy, more efficient use of uranium is necessary to preserve natural resources. This is quite straightforward considering that present Light Water Reactors (LWRs) consume less than 1% of the resources required to fabricate their fuel. Compared with an open fuel cycle, a partly closed cycle conserves up to 17% of the natural resources through the recycling of reprocessed uranium in fresh uranium oxide (UOx) fuel and monorecycling of plutonium in mixed oxide (MOx) fuel. At the same time the High-Level Waste (HLW) volume is reduced by a factor of 5 to 7. However, only fast reactors (FRs) allow far more efficient use of uranium resources through higher fission rates for uranium and transuranic isotopes. Theoretically nearly 100% of the natural resources can be exploited in FRs instead of less than 1% currently in LWRs. This quantitative use is not obtained in a single passage in the FR core. Reprocessing of the spent fuel is necessary after the fuel has lost part of its efficiency due to neutron capture by the accumulation of fission products (determining its maximum "burnup"). In spent fuel, the main fissile material left is plutonium mixed with the remaining uranium, fission products, and other transuranics. Depending on the needs of the installed reactor fleet, FRs are capable of generating smaller, equivalent, or larger amounts of fissile material (mainly plutonium) in their core than they consume. The key for full use of the initial uranium resources is to recover and continually recycle the reusable material still present in the spent fuel, i.e. mainly plutonium and uranium [1] [2]. As plutonium is the most efficient fissile material for energy production in FR, this continuous use, recycle and reuse scheme corresponding to a fully closed fuel cycle is often assimilated with "multi-recycling of plutonium", even if plutonium is mixed with uranium (and possibly other transuranics) in the refabricated fuel. In this ultimate closed fuel cycle, allowing sustainable nuclear energy, the FR fleet is then closely linked to the treatment and recycling facilities that refabricate fresh fuel from spent fuel after eliminating the fission products (FP). Fission products (with or without minor actinides (MA), depending on partitioning and transmutation options not discussed here) form the bulk of the ultimate high-level wastes conditioned for geological storage.

France in particular has acquired considerable reprocessing experience through more than 30 years of industrial feedback with the partly closed fuel cycle for its LWR fleet (PUREX Process). Pilot-scale treatment of FR fuel was also assessed with the equivalent of more than 25 metric tons of recovered U+Pu, some of which was recycled in the PHENIX reactor. Considering the increased quantity of plutonium recycled in a fully closed fuel cycle, major issues concerning industrial treatment and recycling of Pu-based FR fuel must still be resolved. This challenge is addressed by the present French R&D program for safe and cost-effective multi-recycling of plutonium whose main subjects are presented here.

2. Rationale for multi-recycling of plutonium

Current recycling in a partly closed fuel cycle as it is industrially performed in France by AREVA (Fig. 1) offers significant benefits by producing around 17% more energy with the same initial resources than in an open fuel cycle: around 10% by mono-recycling plutonium in MOx fuel and around 7% by mono-recycling uranium from the reprocessing plant (RepU) in specific UOx fuel (RepUOx) after re-enrichment. Another key feature is the volume reduction of HLW by a factor of 5 to 7 compared to the spent fuel assembly, with conditioning of FP and MA in glass canisters suitable for safe geological disposal. The recovery of plutonium reduces the radiotoxicity of the HLW glass packages by an order of magnitude and allows the plutonium to be recycled for MOx fabrication. Spent MOx fuel concentrates the remaining (unburnt) plutonium for subsequent reuse after treatment/recycling.
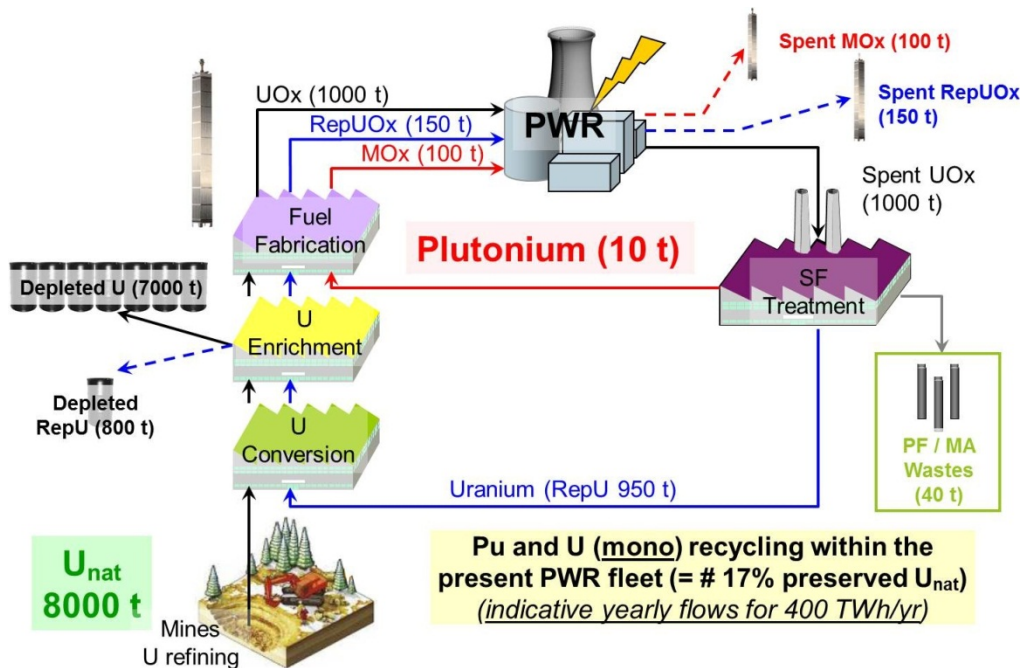
Fig. 1. Plutonium recycling in the partly closed fuel cycle industrially implemented in France.

Despite these important benefits from this type cycle compared with an open cycle, more than 99% of the uranium isotopes from the initial natural resources remain today in the form of depleted uranium (97–98%) and in spent MOx and RepUOx fuel assemblies. Quantitative use of this nuclear material, mainly the ^{238}U isotope, implies considering it as both a fissile and fertile material and in exploiting the fast neutron spectrum to adjust the fissile material mass balance ratio by consuming globally abundant ^{238}U. To initiate this type of cycle before sustaining it by supplying ^{238}U, an initial amount of fissile material is required, namely the plutonium contained in spent LWR fuel and particularly in LWR MOx fuel in which this actinide is more concentrated by the partly closed fuel cycle. ^{238}U is then used to maintain the fissile fraction necessary to sustain the operation of a FR in which it is transformed into ^{239}Pu to replace the fissile material consumed. This stage illustrates the fully closed fuel cycle in which all the initial uranium is fully used instead of less than 1% as in the present fuel

cycle. For the same energy production as with the present French LWR fleet, the fully-closed fuel cycle is illustrated in Fig. 2. Considering the existing stockpiles of depleted uranium in France, resources for a few thousand years are available for nuclear energy production with this type of cycle.
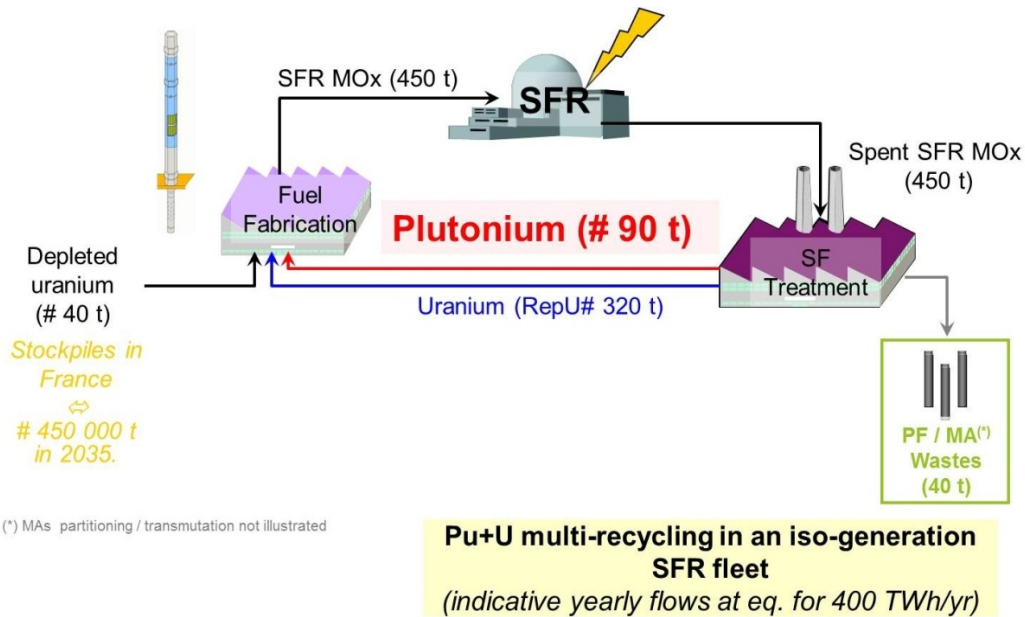
*Fig. 2. Multi-recycling of plutonium in a fully closed fuel cycle
equivalent to existing French nuclear energy production.*

The transition from an open or partly closed fuel cycle to a fully closed cycle is not straightforward. Around 15 t of initial fissile material (plutonium) is required per GWe of FR installed, resulting in about 1.5 t plutonium to be recycled annually. An example of an aggressive FR deployment scenario — one of those currently investigated for more sustainable French nuclear energy production— is illustrated in Fig. 3.
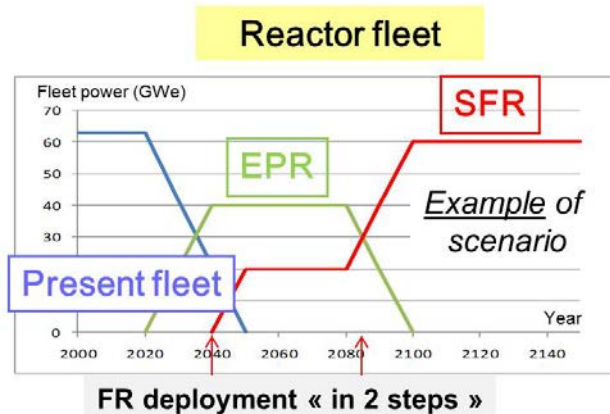
*Fig. 3. An example of a FR deployment scenario envisaged in France
(among other progressive deployment scenarios).*

The consequence of this type of deployment is illustrated in Fig. 4 highlighting the transient treatment and recycling capacity to feed this deployment, followed by the equilibrated multirecycling step, leading to the ultimate closure of the fuel cycle at the end of this century.
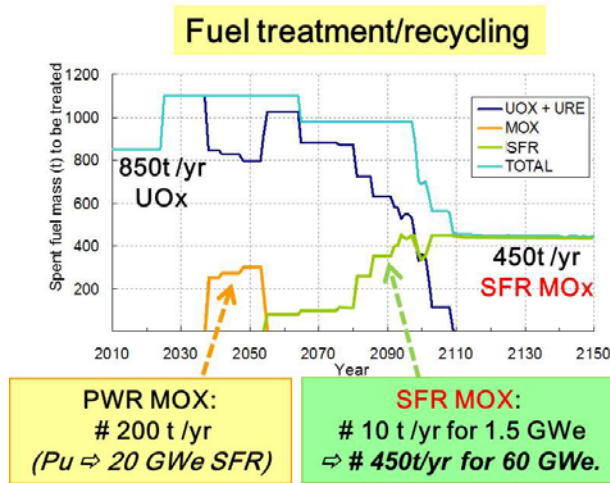
Fig. 4. Consequence of the FR deployment scenario on the fuel treatment/recycling capacities (based on the scenario illustrated in Fig. 3).

This example shows that deploying plutonium multi-recycling is a gradual and progressive process, beginning with the recycling of plutonium from UOx in LWRs, then gradually adding the treatment of LWR MOx to recover plutonium in order to supply the first FR cores, and finally by multi-recycling of plutonium from FR fuel to sustain the FR fleet energy production with maximum preservation of uranium resources.

3. Feedback from experience with hydrometallurgical treatment of spent FR fuel

Compared with standard UOx fuel the treatment of Pu-based fuel (Fig. 5) adds some requirements for the process mainly to deal with the increased quantities of plutonium in the dissolver, in the separation cycles, and in the oxide conversion step. The main modifications (LWR) or innovations (FR) in the process and technology are made necessary by criticality concerns.
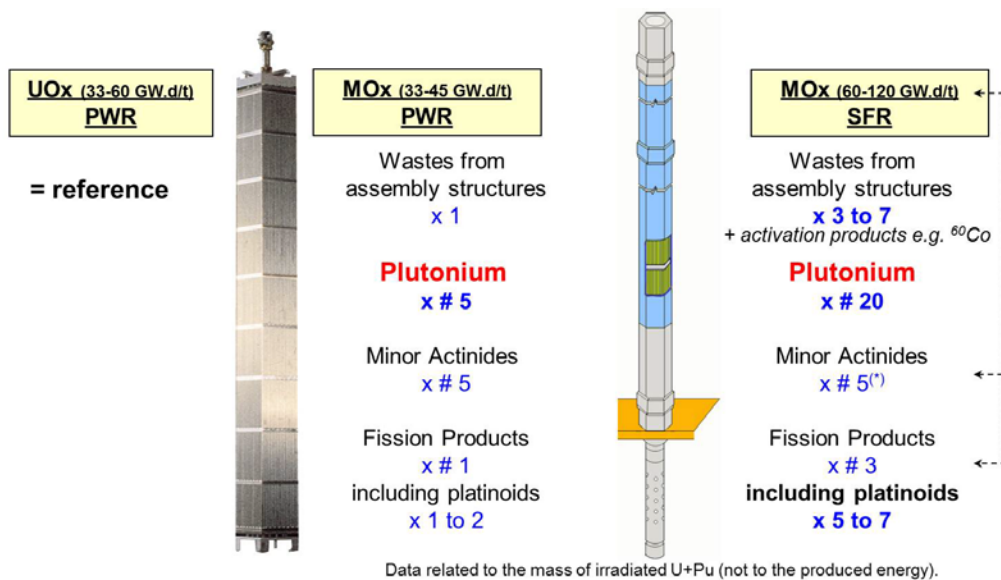
Fig. 5. Main differences between spent LWR and SFR fuel (indicative data).

For waste management purposes, the fission reactions (mainly from Pu isotopes rather than ^{235}U) shift the fission product spectrum towards larger proportions of platinum-group metals (PGM) and higher FP concentrations in spent FR fuel due to higher burnup. Neutron captures by plutonium isotopes lead to significantly higher MA content in spent MOx fuel (although the net MA generation from

plutonium isotopes per unit of energy produced is significantly lower in a fast neutron spectrum). The technological challenge for future industrial treatment and recycling of Pu-based fuels stems also from very different designs between LWR MOx and sodium-cooled fast reactor (SFR) fuel assemblies. FR assembly structures are mainly steel and contain a larger volume of neutron absorbing material which could require changes in waste management. Higher plutonium concentrations in the fuel require specific process steps to prevent plutonium retention in the iron cladding waste or in insoluble fractions in the head-end part of the treatment (fuel dismantling and dissolution). At the same time, more aggressive dissolution conditions to fully recover plutonium can lead to corrosion of the steel cladding with relatively high concentrations of Ni, Cr, Fe present in solution, with consequences downstream (corrosion, waste loading).

France has extensive experience in the treatment and recycling of Pu-based fuels, with industrial treatment campaigns of tens of tons of LWR MOx fuel in the AREVA plant at La Hague, the MELOX industrial LWR MOx fabrication plant, the treatment of tons of FR fuels from Phenix and earlier experimental SFR reactors in pilot plants (AT-I at La Hague, APM-TOP&TOR at Marcoule) and in the La Hague plant (UP2-400, in dilution with spent uranium fuel from graphite gas reactors), or the fabrication of SFR MOx fuel (ATPu plant at Cadarache) for experimental Phenix and industrial Superphenix reactors (Fig. 6 and Fig. 7).
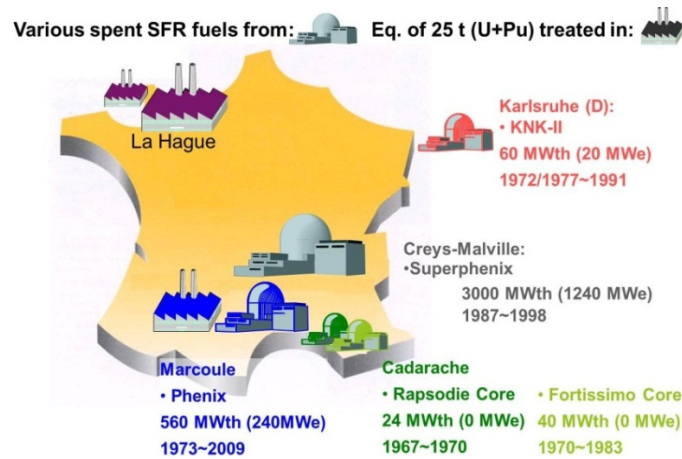
Fig. 6. Illustration of the French experience with sodium-cooled fast reactors and fuel treatment/recycling.
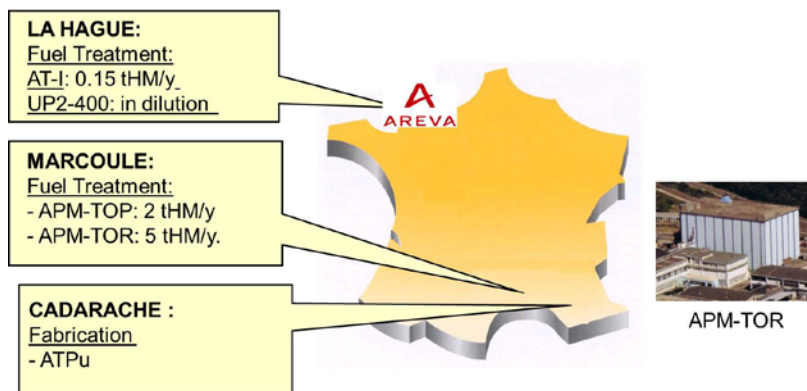
Fig. 7. Main facilities used to fabricate FR fuel and treat spent Rapsodie and Phenix fuels.

For FR fuels, this experience detailed in **[3]** must be followed by a new R&D phase for progressive industrial deployment of the fully closed cycle with the treatment of hundreds of tons of spent Pu-based fuels in a specifically designed plant by advanced processes and technologies and the recycling of the all the recovered plutonium and uranium to supply the reactor fleet with fresh fuel.

4. Overview of the French R&D program

Since 2011, an ambitious R&D program for multi-recycling plutonium has been initiated within CEA. The main R&D subjects towards a fully closed fuel cycle (see Fig. 8) include:

— an industrially scalable head-end process with compact technologies,
— a simplified separation of plutonium and uranium with a higher Pu/U ratio (MA separation not described here, see [4] for more details),
— coconversion of plutonium and uranium, and FR MOx fabrication with increased Pu quantities,
— the management of effluents and specific wastes generated by spent FR fuels.
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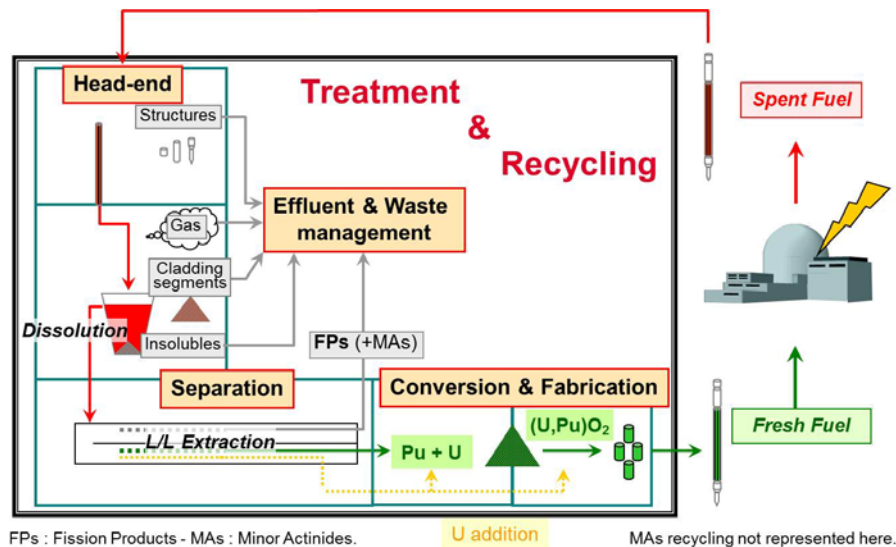
Fig. 8. Illustration of the main R&D subjects included in the program on multi-recycling of plutonium.

Fig. 9 highlights the main differences in the head-end treatment between LWR and FR MOx fuels.

FR fuel assembly concepts lead to more complicated dismantling with existing technologies. Special attention is required to separate the assembly structures from the irradiated fuel material. Access to the spent oxide for hydrometallurgical recovery of reusable actinides is a key objective of the R&D program. Optimizing the disassembly process after having optimized the fuel concept for easier dismantling, handling and transportation is a challenge for technological R&D.

Far higher Pu concentrations in the mixed oxide than for existing spent UOx fuel also requires the design and development of complementary recovery steps from cladding in contact with the fuel and from the solid residues left after the primary fuel dissolution process. Higher platinum-group metal content in the fuel leads to the formation of refractory microphases in the fuel material, which combines with plutonium to form an insoluble intermetallic phase. This is exacerbated in FR fuel due to higher temperatures reached in the core and relatively higher burnup. Locally higher Pu content in the $(U,Pu)O_2$ oxide may also lead to the existence of less soluble portions in the fuel, particularly in the most Pu-rich fuels (e.g. FR fuels, depending on their fabrication process and design and their initial Pu enrichment). In order to ensure quantitative plutonium recovery for recycling with minimal residual plutonium traces in the waste, coupling of the primary dissolution with an additional digestion step must be designed, assessed and optimized for advanced FR fuel treatment. Innovation is also targeted for the more conventional steps such as dissolution of the oxide material in order to obtain compact equipment to address criticality issues and industrial treatment capacities.
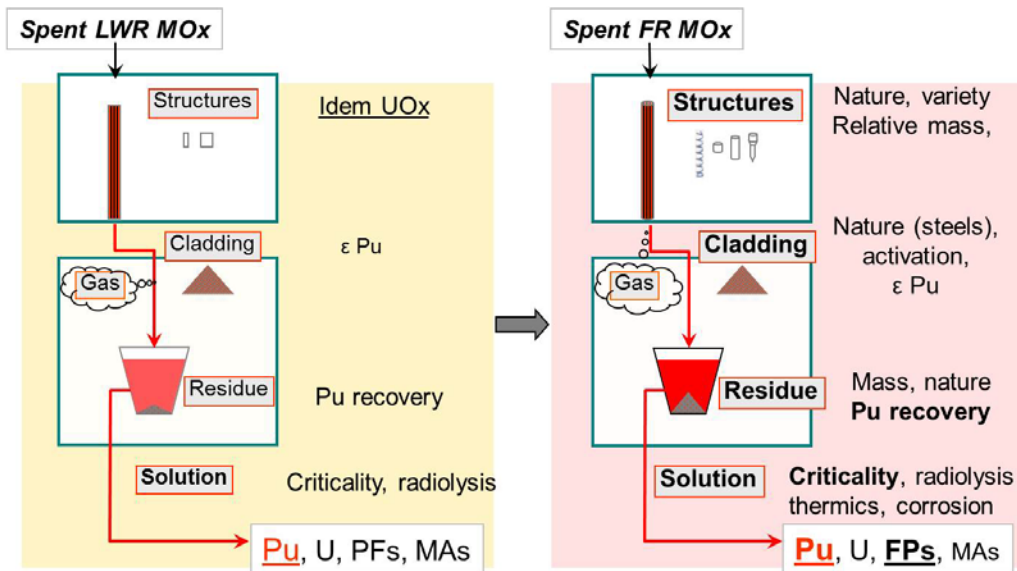
Fig. 9. Main issues for spent Pu-based fuel treatment at the head-end process.

The R&D program in this area is based on the use of experimental irradiated Phenix fuels chosen specifically to sweep various key parameters such as Pu content, burnup ratio, cladding material, etc.

Liquid/liquid extraction methods have been proven very efficient for plutonium and uranium separation and purification to recover more than 99.9% purified actinides. The PUREX process was successfully applied at pilot scale in the Marcoule Pilot Plant (APM) in the 1980s and 1990s. For advanced treatment, a COEX^{TM} type process producing a mixture of plutonium and uranium (Fig. 10) instead of a pure plutonium flow would better meet the criteria of Gen IV systems [5]. A higher Pu/U ratio in the successive purification cycles remains an important issue due to exacerbated radiolytic and thermal effects. Some optimization is also possible by simplifying the process and the management of the liquid effluents and solvent.
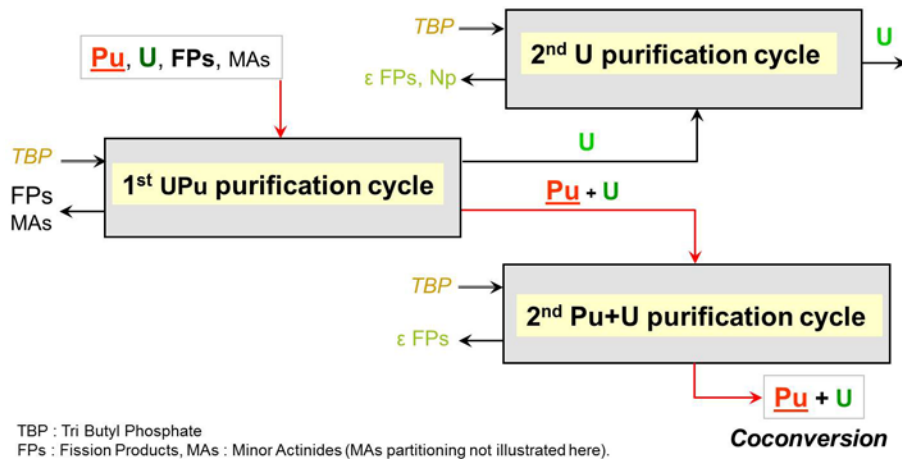
Fig. 10. Separation of Pu and U from FP and MA producing Pu+U and U flows (COEX^{TM} type process).

The ATPu plant at Cadarache fabricated the cores for the Phenix and Superphenix reactors with industrial capacity. The main optimizations involve minimizing the powder grinding steps which generate fine particle fractions. Pu-rich fine particles are the main cause of radioactive material holdup generating doses and complicating maintenance operations. This is an important issue due to transient degraded Pu isotopic composition when recycling plutonium from high burnup UOx or LWR MOx fuels.

Premixing Pu and U in solution instead of by intensive grinding of individual PuO_2 and UO_2 powders is one of the main orientations of R&D on FR fuel fabrication. The potential advantages of coconverting plutonium and uranium in solution into mixed oxide and producing homogeneous $(U,Pu)O_2$ as a starting powder for fabrication needs to be assessed for industrial FR fuel fabrication, then optimized to simplify the integrated coconversion/fabrication process (Fig. 11). The main optimizations concern technological aspects related to the order-of-magnitude increase in capacity during the successive conversion steps: quantitative Pu and U solidification (e.g. by coprecipitation), solid/liquid phase separation then calcination into oxide.
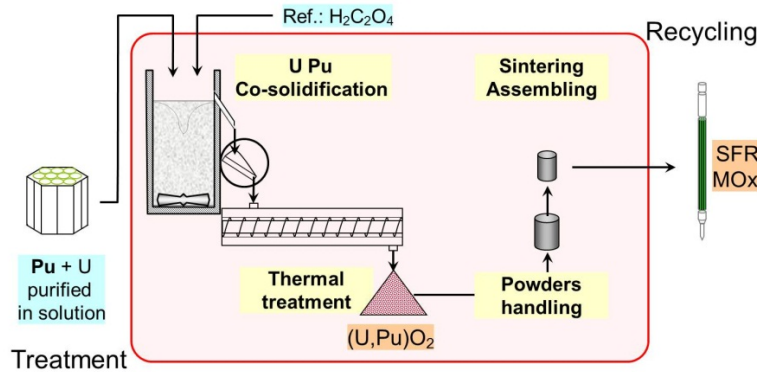
Fig. 11. An integrated co-conversion/fabrication process
is a key-step between treatment and recycling.

R&D on effluent and waste management focuses on the development of conditioning processes and technology to deal with a significantly greater volume of activated steel structures (such as cladding). A melting process tested previously at pilot scale needs further assessment and optimization compared with the present industrial compaction process (optimized for LWR Zircaloy cladding). Optimization of the glass formulation for FP conditioning to accommodate higher concentrations of platinum-group metals and corrosion products from steel cladding is another R&D orientation.
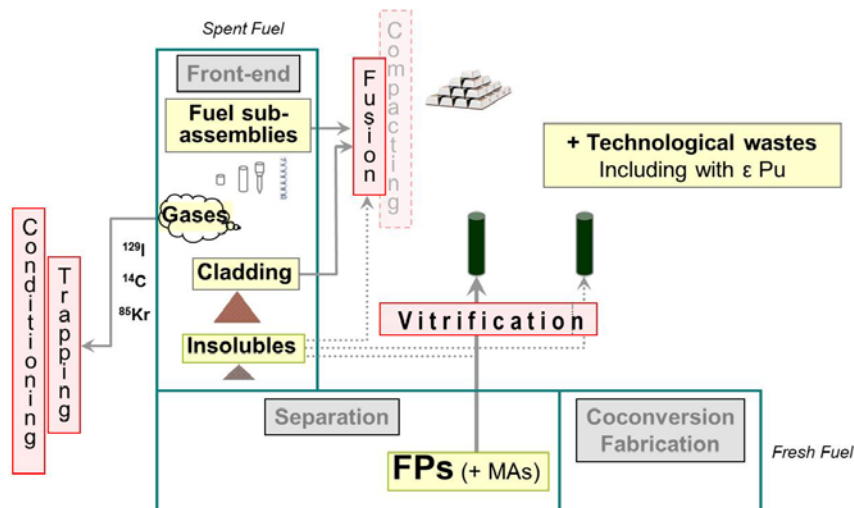
Fig. 12. Management of effluent and waste for a next-generation treatment and recycling plant.

The management of volatile radionuclides (^{85}Kr, ^{14}C, ^{129}I, etc.) is not specific to Pu-based fuel but concerns any future-generation treatment/recycling plant. The development objective is to tend toward minimal emissions through optimized trapping and conditioning methods. Prior assessment of suitable conditioning matrices for storage or geological disposal of each radionuclide is of paramount importance.

Other R&D subjects that have been identified but are not detailed here include:

— process integration by optimizing the interface between each operation and implementing process control using a simulation code and online analysis of key parameters,
— corrosion of materials,
— scenarios for deployment of plutonium multi-recycling.

This R&D program involves various R&D teams in the CEA's Nuclear Energy Division (Fig. 13).
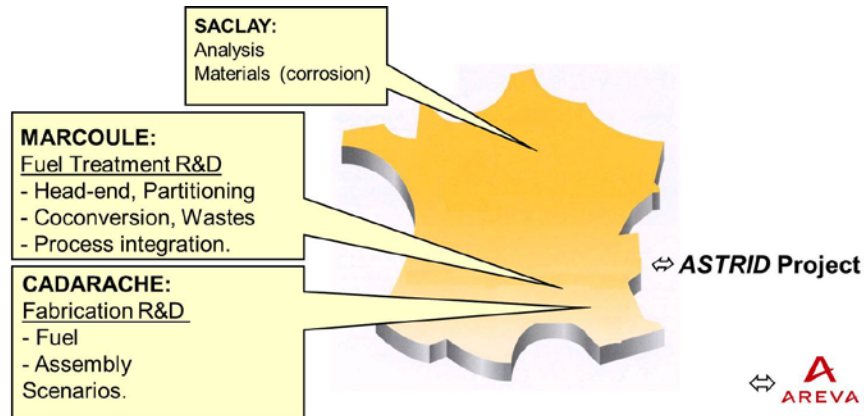
Fig. 13. R&D teams involved in the French program on multi-recycling of plutonium.

In the perspective of a new generation of sodium-cooled fast reactors with innovative fuel and core concepts, the Advanced Sodium Technological Reactor for Industrial Demonstration (ASTRID) project will assess the best solutions for advanced fuel treatment and recycling. This reactor is closely associated with facilities dedicated to fuel fabrication and spent fuel treatment, through progressive deployment of multi-recycling of uranium and plutonium for this reactor at near-industrial scale (Fig. 14).
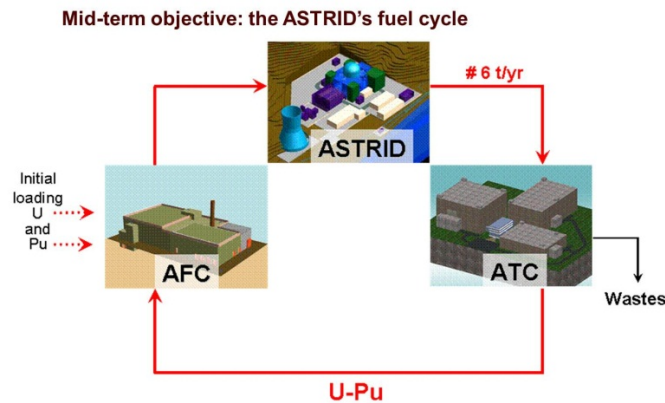
Fig. 14. Schematic representation of the ASTRID fuel cycle (MA recycling not shown).

The initial plutonium for the first cores will originate from spent LWR fuel. The subsequent cores will be supplied by the plutonium and uranium recovered from ASTRID's own spent fuel. This progressive approach is intended to demonstrate the fully closed fuel cycle with an advanced treatment/recycling process and related innovating technologies for Generation IV systems.

5. Conclusion

The French R&D program for multi-recycling of plutonium aims at accompanying the progressive deployment of a fully closed fuel cycle, ensuring optimized use of natural resources and sustainable nuclear energy production. The R&D focuses on enhanced treatment and recycling of Pu-based fuels: first LWR MOx then progressively FR (U,Pu) fuels. The specific properties of these fuels compared to UOx orient the program toward process steps where higher plutonium concentrations and/or flows require modification, optimization and innovative technologies. The design differences between LWR and FR fuels require specific management for the activated and/or contaminated structure materials of FR fuel assemblies, which will be assessed at laboratory and then pilot scale.

ACKNOWLEDGEMENTS

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Selective recovery of americium alone from PUREX or COEX™ raffinate by the EXAm process

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Abstract. Americium is the main contributor to the long-term radiotoxicity and to the heat generation of glasses used for the HLW conditioning. To decrease both impact on the ultimate waste and to avoid the difficult recycling of curium, the CEA has developed the EXAm process for the the separation and the recovery of the sole americium directly from PUREX or COEX™ raffinates. The principle of the EXAm process is to extract americium and light lanthanides from high nitric acid media, leaving curium and heavy lanthanides in the raffinate. A water-soluble amide molecule, TEDGA, is added in aqueous phase to increase Am/Cm and Am/heavy lanthanides selectivity, because of the preferential complexation of curium and heavy lanthanides by this diglycolamide. Many experimental data have been acquired mainly at the extraction-scrubbing step (Am/Cm separation) and were used for the development of a phenomenological model implemented in the PAREX process simulation code. The scientific feasibility demonstration of the EXAm process was then performed on a genuine PUREX raffinate in Atalante CBP hot cell in 2010.

INTRODUCTION

In the framework of the successive 1991 and 2006 Waste Management Act, French government supported a very significant R&D program on partitioning and transmutation of minor actinides (MA) [1,2]. This program aims to study potential solutions for still minimizing the quantity and the hazardousness of final waste, by MA recycling. Indeed, minor actinides (neptunium, americium, curium) are the main contributors to the long-term toxicity of the ultimate waste as well as to the long-term heat power. Recycling them, and particularly americium (Am), would therefore allow significantly decreasing the waste long-term toxicity and the repository surface (thanks to the lower heat power). A gain of up to 6 of the surface repository could hence be reached allowing a very significant preservation of the repository resource [3].

Several scenarios are studied for minor actinide recycling in generation IV fast reactors: (i) either a homogeneous mode where MA are recycled at a low concentration in all the standard reactor fuel, or (ii) a heterogeneous mode in which MA are recycled at a higher concentration in specific targets, at the periphery of the reactor core. Specific separation processes have been developed and demonstrated on some kilograms of spent fuels for both options. Although scientifically feasible, recycling Cm has been anticipated to be difficult to implement due to the very significant neutron emissions of Cm which would require very thick shielding at any step of the fuel cycle. In order to overcome this anticipated difficulty, a recent effort was focused on the recycling of sole-Am with the aim of assessing its viability. Recycling Am could be a good compromise between limiting the anticipated difficulties of the Cm recycling and saving the repository resource for future generations. Based on these findings, the EXAm process was developed in France to separate americium solely from curium

and the fission products directly from a PUREX/COEX[TM] raffinate. An example of fuel cycle including the implementation of americium is illustrated on Figure 1.
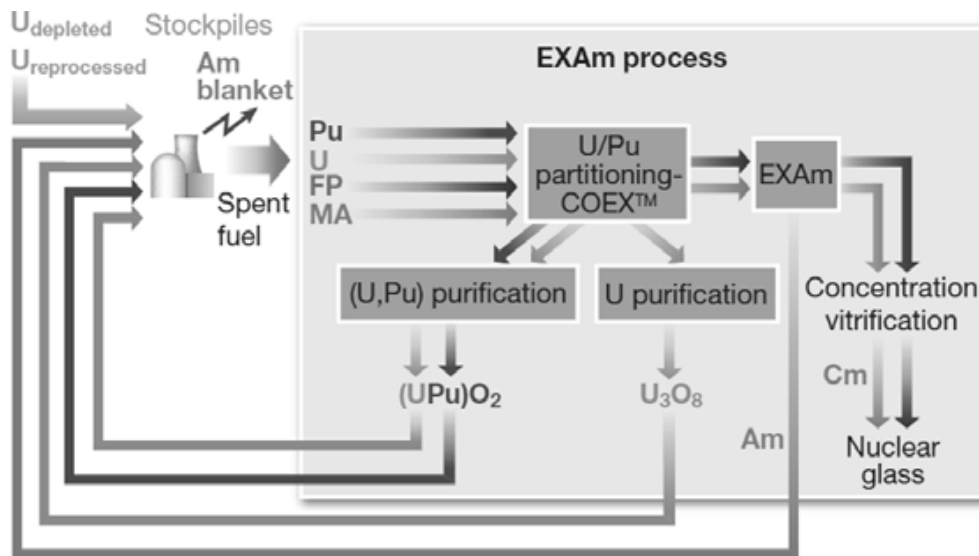
Figure 1: Potential future fuel cycle in which would be implemented the americium recycling [4]

The main difficulty of the sole-Am recovery is to separate americium from curium (Cm) and lanthanides (Ln). Indeed, physico-chemical properties of Am, Cm and Ln(III) are very similar. They are strongly hydrated and their ionic radii are similar. In addition, the acidity of PUREX raffinates is very high so there is a competition between nitric acid and cation extraction. Moreover the element inventory is very large. This is why firstly, in the frame of the 1991 French Act on high active waste, a 3-step strategy was proposed (DIAMEX, SANEX and Am/Cm separation) [5]. The feasibility was demonstrated in 2005 after counter-current hot tests performed on a genuine PUREX raffinate in Atalante facility [6]. Then, in the framework of the 2006 act, the goal was to develop a single cycle process to recover the sole Am(III), directly from PUREX or COEX[TM] raffinates. The so-called EXAm (Extraction of Americium) process has been designed on the basis of the DIAMEX-SANEX process, which was developed for the co-recovery and separation of americium and curium from PUREX/COEX[TM] raffinate and improved by progress accomplished during GANEX process developments [7,8].

In the DIAMEX-SANEX process, americium and curium are co-extracted with lanthanides by a mixture of two extracting molecules: a malonamide DMDOHEMA and a dialkylphosphoric acid HDEHP, diluted in TPH. Actinides are then separated from the lanthanides by selective stripping in aqueous phase using a mixture of two aqueous complexing agents: an aminopolycarboxylate ligand, (HEDTA or DTPA), and a pH buffer polycarboxylic acid (citric or malonic acid) at pH 2-3. This process allows a separation of americium from curium in the extraction-scrubbing section but the low separation factor ($SF_{Am/Cm}$= 1.6) with the HDEHP+DMDOHEMA solvent implies a very large number of extraction and scrubbing stages. This number of stages can be drastically decreased by introducing TEDGA (TetraEthylDiglycolAmide) as a selective water-soluble complexant to maintain Cm and the heavier lanthanides in the acidic aqueous phase. Indeed, diglycolamides have shown a higher affinity for heavier lanthanides(III) and actinides(III) compared to their lighter analogues. Moreover, malonamide DMDOHEMA shows the reverse property and extracts more strongly light Ln(III) and An(III). Combination of these two molecules (DMDOHEMA in organic phase and TEDGA in aqueous phase) allows an increase of the Am/Cm separation factor from 1.6 to 2.5 and therefore leads to an increase of the compactness of the process [9].
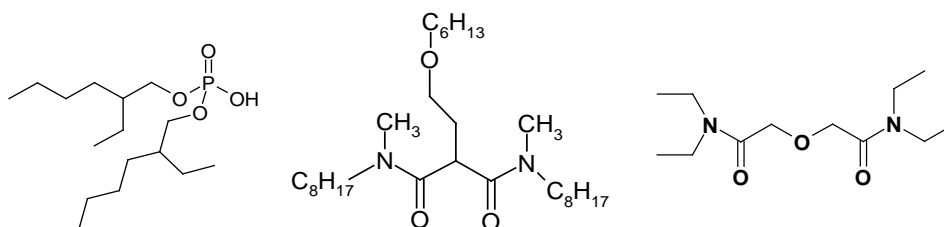
Figure 2: Structure of HDEHP, DMDOHEMA and TEDGA

After selecting the extracting system, batch experiments were carried out to acquire distribution data of the main elements in process conditions. Speciation studies both in aqueous and organic phase were then performed to determine the stoichiometries and stability constants of the different complexes formed with TEDGA in particular. Based on these experimental data, a phenomenological model was developed and implemented in the PAREX process code. The code was then used to calculate a flowsheet able to recover 99% of Am with a high decontamination versus Cm ($DF_{Am/Cm}$ more than 500 is targeted) which was tested first on a surrogate solution then on a genuine PUREX raffinate in ATALANTE hot cells facilities. The paper describes more in details these different steps needed for the development and the validity of the EXAm process.

EXPERIMENTAL PART

In order to develop the EXAm process and in particular to optimize the extraction-scrubbing section in presence of TEDGA, many distribution data of cations were acquired in process conditions, depending on different operating parameters such as TEDGA concentration, acidity, metal loading, etc. As an example, Figure 3 shows the impact of the additition of TEDGA on Ln, Am and Cm distribution ratios and on Am/Cm and Am/Ln selectivities. As shown on Figure 3, lanthanide complexation by TEDGA increases with the atomic number involving a lower extraction of heavier lanthanides (Sm, Eu) in organic phase which will remain with the curium fraction in the process. It is clear from the figure that americium behaviour is very close to neodymium while curium behaviour is somewhere between Nd and Sm ($SF_{Am/Cm}$= 2.5).
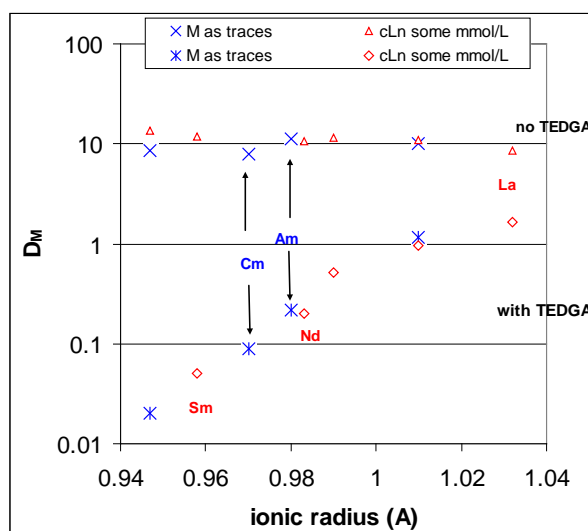
Figure 3: Distribution ratios of Ln and An(III) (organic phase DMDOHEMA 0.6M-HDEHP 0.3M-TPH - Aqueous phase c_{TEDGA} 0 or 0.05M in HNO_3 5M) – 25°C

Although TEDGA is a water-soluble complexing agent, measurements in the organic phase indicated its partial extraction in presence of nitric acid and/or extracted cations. Distribution of TEDGA is a key point of the process as it impacts the extraction properties, the Am/Cm selectivity and the solvent loading capacity. The extraction of TEDGA in organic phase increases with the nitric acid

concentration and ESI-MS experiments indicated the presence of adducts as TEDGA(DMDOHEMA)$_x$(HDEHP)$_y$ in the organic phase [10].

Regarding fission and activation products, zirconium is strongly complexed by TEDGA and forms a non extractible 1:3 while iron and molybdenum remain quantitatively extracted in organic phase even in presence of TEDGA. These two elements must be handled in the other steps of the process.

To obtain a representative modelling of the EXAM process, sufficient insight on thermodynamics aspects is requested. Speciation studies on trivalent lanthanide and actinide complexation by TEDGA were thus carried out in aqueous phase in order to identify the stoichiometries and the stability constants of the Ln-TEDGA complexes. The speciation was studied using different spectroscopic techniques such as NMR, ESI-MS, TRLIFS and molecular dynamics. Stability constants were determined by UV-vis spectrophotometry. Different LnTEDGA$_n^{3+}$ complexes were characterized from La to Lu. The complexes with a low ligand to metal stoichiometry (1:1 and 1:2) were favoured for the lighter half of the Ln(III) series which is consistent with the largest extraction of light lanthanides [10].

La-TEDGA   and   La-TEDGA$_2$ Dy-TEDGA$_3$
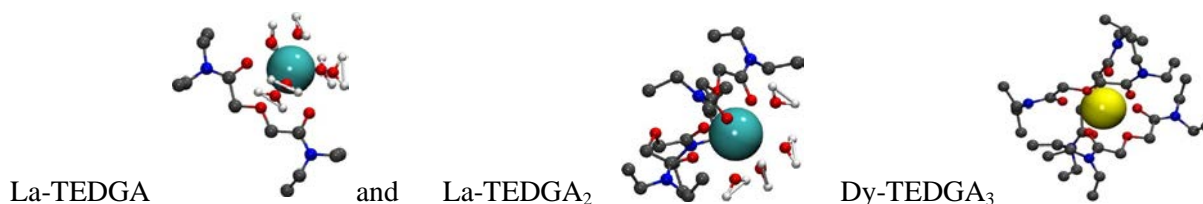
Figure 4 : Molecular dynamic calculations of lanthanide-TEDGA complexes

Speciation studies in the organic phase were also performed. UV-vis spectrophotometry and positive ESI mass spectrometry were used to shown the formation of mixed complexes containing the two extracting molecules in organic phase HDEHP and DMDOHEMA [11].

MODELLING

The modelling of the EXAm process was focused on the two key steps of the process: the extraction-scrubbing section where the Am/Cm separation occurs and the Am selective stripping step.

Am extraction modelling
Speciation studies and distribution data were crucial to determine the number and the stoichiometry of the complexes with TEDGA which have to be considered in aqueous phase. In addition, modelling has to take into account the extraction of TEDGA in organic phase as well as the organic complexes formed between the two extracting molecules (HDEHP and DMDOHEMA) and the 15 different cations potentially present in organic phase (Am, Cm, Ln, Mo, Fe). The whole model at this step includes 56 complexes and the corresponding equilibrium constants [12]. Because of this complexity, the model was adjusted in a relative limited range of acidity: from 4 to 5.5 mol/L.

Am/Ln partitioning modelling
Americium is separated from light lanthanides by selective stripping in aqueous phase. The stripping solution contains a polyaminocarboxylic acid (HEDTA or DTPA) and a pH buffer carboxylic acid (citric or malonic acid) at pH 2-3. The model was built in two steps: the extraction equilibria were first identified and the extraction constant optimized without aqueous reagent. Then the aqueous complexes have been included into the model and the corresponding equilibrium constant were deduced from batch experimental studies [13]. 1:1 complexes between the polyaminocarboxylic and cations have been identified. Used with DTPA, malonic acid is not involved in the complex, unlike citric acid which forms a ternary mixed complex with HEDTA and americium and lanthanides [14].

These models were implemented in the PAREX code and allow the calculation of flowsheets [15]. These studies have pointed out the TEDGA concentration and the feed solution flowrate as the main sensitive operating parameters. A running procedure was also defined: the strategy was to start with a

less efficient process in terms of Am recovery and then improve the recovery efficiency by adjusting the TEDGA flowrate until reaching the targeted performances [16].

ALPHA SPIKED TEST ON SURROGATE SOLUTION

The EXAm flowsheet was first tested in 2009 in mixer-settlers on a surrogate feed containing nominal quantities of lanthanides and other fission products and spiked with [241]Am and [244]Cm. The goal of this test was mainly to validate the model of the extraction-scrubbing section (Am/Cm separation) and to assess the Am/Cm and Am/heavy Lns separation efficiency. At the end of the counter-current test, americium recovery was higher than 97% with a decontamination factor versus curium higher than 1000 (about 5000). The concentration profiles for Am and Cm calculated with the PAREX code were in close agreement with the experimental concentrations measured in every stage of the mixer-settlers which confirm the validity of the EXAm model in the extraction-scrubbing section.

HOT TEST ON GENUINE SOLUTION

The complete EXAm flowsheet (depicted in Figure 5) was tested in April 2010 on a genuine PUREX raffinate in ATALANTE CBP hot cells, in order to confirm the promising results obtained from the previous spiked test. The contactor set-up consisted of 68 stages of laboratory scale mixer-settlers: 16 stages for Am extraction, 16 for Cm scrubbing, 8 stages for Mo stripping, 20 stages for Am stripping and 8 stages for Ln, Fe stripping. As molybdenum, iron and light lanthanides (La, Ce, Pr, Nd) are quantitately extracted along with americium in the solvent, specific steps have to be implemented in the process to strip these elements separately from americium. Molybdenum is stripped before americium using a pH-buffer solution while light lanthanides and iron are stripped after the Am recovery step using specific complexing agents (TEDGA and oxalic acid).

The counter-current test was performed for 60 hours. Americium and neodymium concentrations were checked online by UV-vis spectrophotometry in the different outputs and in some settlers. Laboratory analyses were done in each output flow to support and complete online measurements
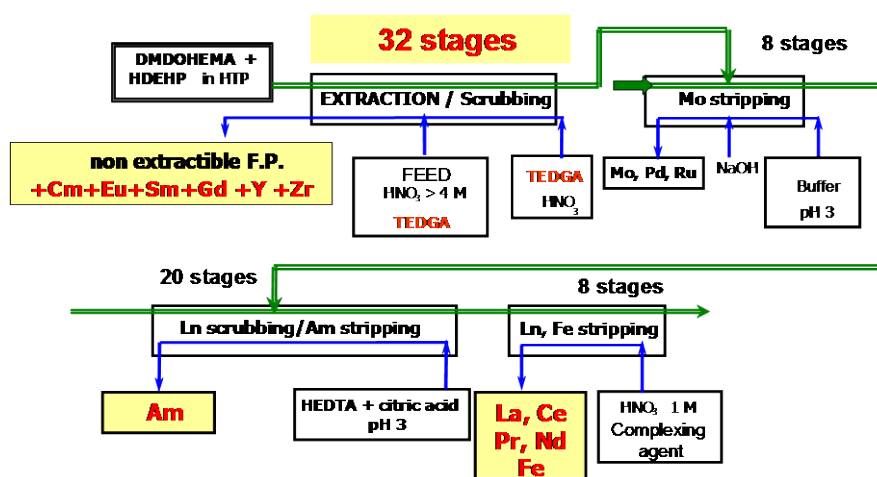
Figure 5: Flowsheet of the counter-current test performed on a genuine raffinate in the process hot cell CBP in 2010

At the steady state, the Am recovery rate was 98.3% with a decontamination factor of americium versus curium of 505 [15]. More than 99% of americium initially in the feed solution was extracted in organic phase after the extraction-scrubbing section but 0.7% of Am was lost in the Mo stripping step which still needs to be improved. The Am output was also well decontaminated versus lanthanides as only 2.2% of Nd (in mass/Am mass) was found with americium (Table 1). The lanthanides were efficiently stripped in the Ln, Fe stripping step. Comparison between experimental and calculated

concentration profiles of the extraction-scrubbing section showed very good agreement for Am and Cm. Based on these results, the scientific feasibility of the sole Americium separation was for the first time demonstrated from a genuine PUREX raffinate.
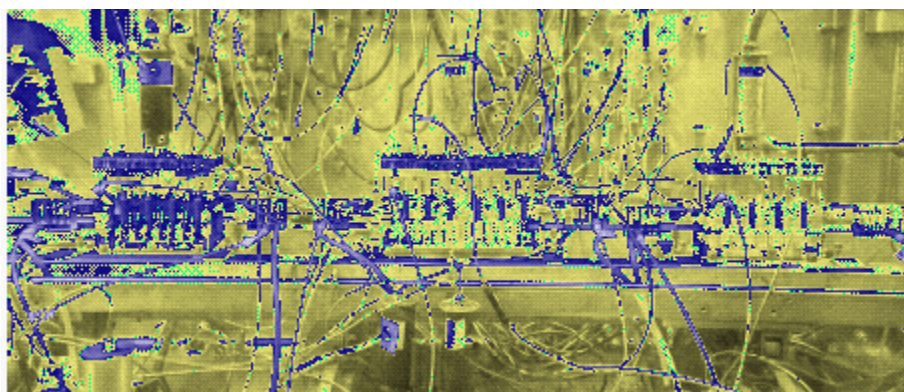
Figure 6 : Photo of mixer-settlers in CBP hot cell

Element (mg/L)	Feed	Raffinate	Mo Stripping	Product	Ln Stripping	Balance (%)	Decontamination factor
Am	220	0.79	0.62	566	0.018	105	
Cm	21.6	10.5	0.0002	0,11	0.0033	136	505
Ce	573	< 1	< 5	< 2.5	960	75	> 585
Nd	1650	3.7	< 5	12.5	2350	113	340
Eu	60	21	< 2.5	< 2.5	< 5	98	> 61
Gd	83	30	< 2.5	< 2.5	< 5	101	> 85
Mo	1000	< 1	420	< 5	< 5	105	> 510
Zr	890	290	< 2.5	< 5	110	101	> 458
Pd	550	< 1	190	115	< 5	95	12

Table 1: Composition of the main flux from samples analyzed at the end of the testl and corresponding mass balances and decontamination factor

CONCLUSION

The feasibility of the sole Am recovery in one cycle process was demonstrated for the first time from a genuine PUREX raffinate of a spent fuel solution. Despite the complexity of the chemical system due to partioning of TEDGA ligand and the necessary to take into account a large number of complexes in both organic and aqueous phase, the extraction-scrubbing step was well modelled thanks to numerous batch experiments and speciation studies. The flowsheets were succesfully tested first on surrogate solutions then on a genuine PUREX raffinate to validate the Am separation.

Now, the next challenge is the demonstration of Am cycle closure. It consists in a large experiment from spent fuel dissolution to $(U-Am)O_2$ pellet manufacturing. The key steps will be on one hand to recycle Am from a concentrated COEX raffinate to improve the compactness of the EXAm process and on the other hand to demonstrate the oxalic coprecipitation of Am with U(IV) to form homogenous $(U-Am)O_2$ oxide suitable for pellet elaboration.

ACKNOWLEDGEMENTS

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Transmutation Scenarios Impacts on Advanced Nuclear Cycles (fabrication/reprocessing/transportation)

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Abstract. In the frame of the French Law for waste management, minor actinides transmutation scenarios have been studied for a sodium-cooled fast reactors fleet using homogeneous or heterogeneous recycling modes. Americium, neptunium and curium can be transmuted once included together in the standard MOX fuel, or the sole Americium can be incorporated in Am-bearing radial blanket. MAs transmutation in Accelerator Driven System has also been studied while Plutonium is recycling in SFR.

Assessments and comparisons of these advanced cycles have been performed in light of technical and economic aspects criteria.

The purpose of this study is to present the results in terms of impacts of the transmutation scenarios on fuel cycle plants (fabrication, reprocessing) and transportations taking into account thermal, radiation and criticality parameters. Comparison with no transmutation option is also presented.

1. INTRODUCTION

In the frame of French Law for waste management, minor actinides (MA) transmutation scenarios have been studied for a sodium-cooled fast reactors (SFR) fleet using homogeneous or heterogeneous recycling modes or a dedicated ADS stratum.

Americium, neptunium and curium can be transmuted once included together in the standard MOX fuel (option named "Core Fuels Recycling (CF)", Fig. 1). Case with the sole Americium has also been considered.

Another transmutation option consists in recycling Minor Actinides (or Americium) in bearing radial blankets (Fig. 2). Finally MA transmutation in Accelerator Driven System has also been studied while Plutonium is recycling in SFR (Fig. 3).

Each of these transmutation scenarios need specific fuel cycle plants (fabrication, reprocessing). The purpose of this study is to present the results in terms of impacts of the transmutation scenarios on fuel cycle facilities. Impacts on fuels transportation have been evaluated.
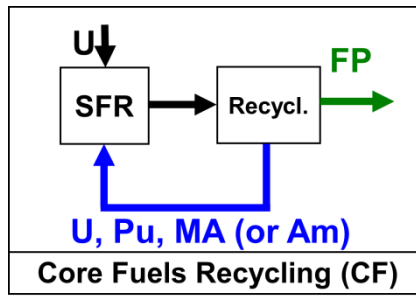
FIG. 1.
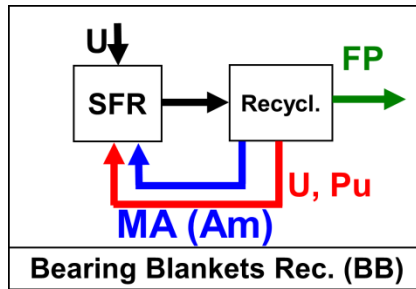
FIG. 2.
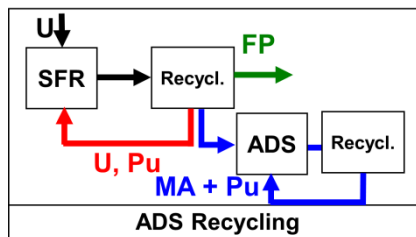
FIG. 3.

2. METHODOLOGY

Transition between actual French fleet and SFR deployment in 2040 is carried out with the simulation software COSI for the different transmutation options [1]. Mass and isotopic compositions in fabrication and reprocessing plants are evaluated. Thus characteristics of the fresh assemblies to produce or spent fuels to reprocess are known in terms of heat release and radiation.

Fuel cycle facilities are evaluated taking into account technical background: industrial experience from French facilities (La Hague reprocessing plants, Melox MOX fabrication plant) and R&D results in separation and transmutation experiments. French regulation is considered for liquid and gaseous releases, for workers occupational exposure and transportation [2], [3], [4].

Fuel cycle facilities or transportation studies provide information on their industrial feasibility for each of the MA or Am transmutation options. Scenarios comparison can be performed by means of various technical criteria. Scenario studies also include economical assessment and waste disposal analysis with / without transmutation not presented herein.

3. IMPACTS ON FABRICATION PLANTS

Different fuel categories need to be manufactured in these studies:

— Standard MOX fuels in SFR comprising MA or Am for homogeneous transmutation. MA mass content in core fuels is 3.9 % in transient period and 1.2 % in equilibrium state. In case of Am homogeneous transmutation mass content is 0.9 % (equilibrium).

— Bearing blankets for heterogeneous transmutation with a 20 % MA content. In case of Am heterogeneous transmutation mass content vary from 20% (transient period) to 10% (equilibrium).

— ADS fuels with 54% MA and 46% plutonium contents (CERCER type with 26.9 % MgO).

Details on fuel characteristics are given in reference [5].

Powder metallurgy process is considered for producing the different fuels. Transmutation scenarios differ from the number of assemblies to be manufactured: MA or Am homogeneous transmutation option need more than 2760 objects when about 200 to 500 are implicated in heterogeneous scenarios (Table 1).

	Core Fuels Recycling	Bearing Blankets Recycling	ADS Recycling
Tons.yr^{-1}	450	29 – 75	20
Assemblies.yr^{-1}	2 760	244 – 522	688
% MA / HM	1.2 – 3.9 MA 0.9 – 2.9 Am	20 MA 20 or 10 Am	54
kW / assembly	1.6 – 1.8 MA 0.7 – 2.9 Am	9.1 MA 3.1 – 1.4 Am	8.3

Table 1.

Constraints increase with curium content. For example thermal constraints set decreasing batch sizes with increasing curium contents. Difficulties also appear on assembly line more specifically for ADS fuels and MA bearing blankets with high thermal releases (Tab. 1) . Heavier protections are necessary. Glove boxes are possible only when there is no MA or Am recycling, hot cells in all other cases.

With high curium content, whole new technology development will be required (more pronouced for ADS option).

Even with less constraints, Am recycling will need R&D for equipment and maintenance qualification.

4. IMPACTS ON REPROCESSING PLANTS

Spent fuels reprocessing plants are based on hydrometallurgy process. Their capacity is nearly the same for different scenarios (about 450 tons per year): bearing blankets and ADS fuels are diluted with spent core fuels.

Transmutation scenarios require new functions to extract and convert minor actinides. Thus innovative minor actinides separation processes are considered: EXAm for Am separation, GANEX for actinides separation.

Studies on reprocessing facilities for core fuels recycling (MA or Am) or bearing blankets recycling (MA or Am) do not show important difficulties. Scientific and technical feasibility has to be investigated for ADS spent fuels.

Criticality constraints have been analyzed in preliminary studies: additional analyzes are required for specific functions (for example conversion of product containing curium).

Thermal and radiation constraints have also been considered. First results show analogy between conversion and fabrication: batch sizes must decrease and protection must be heavier with curium content.

5. IMPACTS ON FUELS TRANSPORTATION

Impacts of transmutation scenarios on fresh and spent fuels annual transportation have been evaluated. Thermal, radiation and criticality constraints have been taken into account to propose cask concepts for normal conditions as shows fig. 4. (example for eight assemblies).
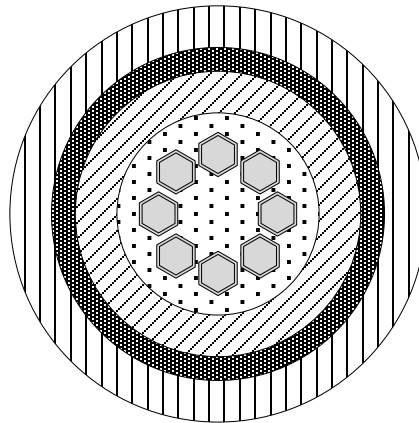
FIG. 4.

No difficulties appear for Am transmutation scenarios (homogeneous or heterogeneous). When fuels contain curium, transport uncertainties increase because of important heat release requiring dividing fresh fuels and technological innovations development.

Considering 1 for no transmutation scenario, annual transportation for MA or Am core fuels recycling is nearly identical (1.1 or 1.2). It increases slightly with Am-bearing blankets recycling (1.5). Effects of transmutation is more important when curium content increases: 3.3

times more transportation for MA-bearing blankets recycling and 5.1 times more for ADS fuels.
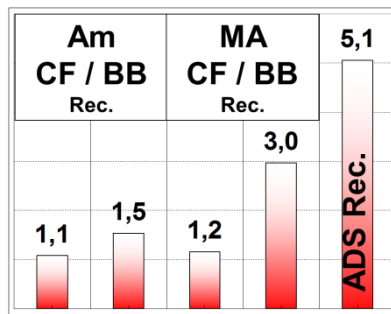
FIG. 5.

6. CONCLUSIONS

This study is the first detailed assessment of plants and transportation in various transmutation scenarios. In case of curium transmutation, studies show large difficulties and uncertainties requiring whole new technology development. This conclusion is more pronounced for ADS option. For Am transmutation, development appears more feasible but needs still to be demonstrated on specific points for industrial extrapolation.

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Polyvalent fuel treatment facility (TCP): shearing and dissolution of used fuel at La Hague facility

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Presented by J Brueziere

Abstract. In order to recycle diverse fuel types, an innovative and polyvalent shearing and dissolving cell is planned to be put in operation in about 10 years at La Hague. This installation, called TCP (French abbreviation for polyvalent fuel treatment), will be set up at the La Hague reprocessing plant. The TCP shearing tool and dissolving equipment will benefit from AREVA's industrial feedback, while taking part in the next steps towards a fast reactor fuel cycle development using innovative treatment solutions. Feasibility studies and R&D trials on dissolution and shearing are currently ongoing. This new installation will allow AREVA to propose new services to their Customers, in particular in term of Fast Reactor (FR) fuel treatment

1. INTRODUCTION

AREVA's La Hague facilities were originally designed to treat irradiated UOX fuels. The past experience illustrates AREVA's ability to industrialize new processes and to treat specific fuels.

This paper will first highlight the main challenges of LWR and FR MOX fuel treatment and then will focus on the way AREVA succeeded in recycling both types of fuels in existing facilities. The last part will explain how the future TCP facility will address the specificities of fuels at the shearing and dissolution step and answer customers' needs, and how this installation represents an important step on the road to FR MOX fuels industrial treatment. AREVA, in parallel to the detailed design of the TCP installation, will initiate discussions with its customers on the interest of this installation for their specific needs and requirements.

2. From UOX to LWR and FR MOX fuels : main specificities

The goal of this part is not to present fully detailed characteristics of MOX fuels (LWR or FR) and their behaviour under irradiation in reactor but only to show differences between these fuels and UOX fuels which impact the treatment process. For both LWR and FR MOX fuels, the key issue is the dissolution step.

In the case of LWR MOX fuels, the design is the same as for UOX fuels, but fabrication process induces potential PuO_2 rich clusters which lead to non soluble plutonium in nitric acid. Typically, for a non irradiated fuel fabricated with MELOX process, less than 1% of the initial Pu is non soluble in the conditions of the solubility test (10 hours in 10 mol/L boiling HNO3). The conditions of irradiation (high temperature reached, long residence time in reactor) allow diffusion between U and Pu leading to a decrease in number and size of PuO2 rich clusters. Consequently, solubility of plutonium is significantly improved.

This quantity of non soluble plutonium, even at low concentrations, is a constraint for criticality demonstration and has to be accounted for through a necessary adaptation of dissolution conditions.

In the case of FR MOX fuels, specificities induce more complexity for the definition of recycling conditions, with a focus on the dissolution step and the structural materials management:

- Quantity of plutonium in the fuel is even higher than in the LWR MOX fuels, up to 20-30% versus 5-10%. This may induce difficulties at the dissolution step, and is a constraint for criticality aspects;

- Stainless steel cladding is much more subject to etching in nitric acid than zircaloy cladding of LWR fuels: the resulting quantities of iron, nickel and chromium in the dissolution solution have to comply with equipment corrosion and with the constraints of the following reprocessing steps (extraction, fission products concentration, vitrification);

- From a mechanical point of view, FR assemblies differ from LWR configuration, with larger quantities of metal to cope with. The fuel pins are positioned inside a hexagonal wrapper tube which make necessary disassembly operations before shearing and dissolution. In the past these operations were realised on the reactor site, to place the pins in specific containers. Mechanical operations are in addition complicated by the presence of a spacer wire coiled around the fuel pins, which has to be managed during shearing and dissolution operations;

- The specific irradiation conditions (high burn-up, high temperature reached in reactor) lead to a restructuration phenomenon in the oxide, which modifies the nature and the quantities of dissolution residues.

In both cases, those MOX fuels differ from our UOX reference mainly by the dissolution step management (solubility, criticality aspects, and mechanical specificities for FR fuels).

Other constraints have to be overtaken:

- Defining an operation point for the Pu/U ratio in top of the extraction cycles and answers safety expectations both in nominal and disrupted modes,

- Dealing with Pu mass limitations in Pu conversion units (thermal constraints on tanks in particular)

- Dealing with limits on the vitrified waste stream: alpha limit due to the higher curium concentration in MOX fuels, but also corrosion products due to stainless steel cladding of FR fuels.

3. AREVA recycling experience for specific fuels

3.1. Specific fuels recycling principles

The initial La Hague plant UP2-400 was designed to process 400 tHM/y of natural uranium oxide LWR used fuels. The two new plants UP2-800 and UP3 were erected in the 80's and 90's to reach a throughput of 1,600 tHM/y of uranium LWR used fuel.

UP3 is a new plant, almost independent from the other facilities existing on site, except the liquid waste treatment. All UP3 facilities were constructed almost at the same time.

On the contrary, UP2-800 was constructed in several steps. Head-end (R1) and separation (R2) facilities were constructed first. Connections were necessary with upstream facilities (fuel storage pools) and with downstream facilities from UP2-400 plant: uranium and plutonium purification and conditioning. New plutonium purification and conditioning facilities, called R4, was constructed some years afterwards, and connected to the already existing separation facility R2. This connection has been realised without significant impact on production thanks adapted design and preparation.

Though initially designed to reprocess LWR fuels with burn-up of 33 GWd/tHM, the La Hague plants have been able to adapt to evolution of fuels, while decreasing the activity of released liquid effluents and radiological impact to environment and workers:

- the increase of burn-up of used fuel with a current licensing for fuel burned up to 60 GWd/tHm
- the recycling of used MOX fuel (60 tons of irradiated MOX reprocessed in UP2-800 plant, 70 tons in AREVA's facilities)
- the recycling of Research and Test Reactor fuel (over 5 tons treated by the end of 2012 in La Hague plant, 23 tons at AREVA's facilities).

The ability to process such fuels out of initial scope illustrates the high flexibility of the La Hague site.

These adaptations were successfully done thanks to operational conditions and procedures adaptations and modifications of existing equipment or process, focused on the dissolution step to take into account the fuels specificities. Indeed, the dissolution solution has to be mixed with UOX stream to comply with downstream constraints as mentioned above.

Such a scheme is already a reality for research test reactors (RTR) fuels at industrial-scale: since 2005, AREVA has acquired a wide industrial experience in RTR UAl fuel treatment at UP3 plant, which was experienced before at UP1 plant in Marcoule. The dissolution of these specific fuels at UP3 is realised in a hot nitric acid solution in the existing dissolver, introducing the fuel into a pit specially designed for RTR fuel. The resulting solution is then diluted with the solution coming from the dissolution of the UOX fuel. The overall rate of the treatment is limited by the amount of aluminium contained in the active glass.

This scheme was also validated through industrial campaigns for LWR and FR MOX fuels as described below.

3.2. *Industrial experience of LWR MOX recycling*

From the beginning of industrial recycling in France, about 70 MtHM of used LWR MOX have been recycled in AREVA plants.

Two campaigns were first carried out on the former plant UP2-400, representing 10 tons reprocessed in total. An extensive R&D program was conducted by the CEA in the 90's to understand MOX specificities and to define optimised treatment conditions, accounting for the higher Pu content. During the campaigns, the resulting dissolution liquor was mixed with uranium to comply with extraction cycles constraints and vitrified waste specifications.

More recently four campaigns representing about 60 MtHM have been carried out from 2004 to 2008 in La Hague UP2-800 plant [2]. A step by step approach from R&D to industrialisation was implemented, with increasing burn-up, Pu content, tons of fuels and treatment flowrate, each campaign giving data to prepare the next one to continuously ensure the safety, environmental and economic operation of the plants

The dissolution step differs significantly from HAO UP2-400 facility to R1 UP2-800. Indeed, HAO facility used a batch process with dissolution conducted at boiling point, whereas R1 process is a continuous process using a rotary dissolver operating between 90 and 92°C. Due to these differences, specific new R&D studies had to be conducted to determine conditions complying with MOX dissolution in current facilities.

These LWR MOX treatment campaigns were successful, which illustrates once again the versatility of La Hague plant to accept a greater range of spent fuels and process. MOX fuel recycling is now a reality.

3.3. *Industrial experience of FR fuel recycling*

FR fuel treatment experience in France covers oxide fuel from Rapsodie Fortissimo and Phenix reactors. A small quantity of fuel was recycled in the pilot AT1 facility at La Hague. But the major experience concerns the Phenix reactor, with 10 tons recycled in the former UP2-400 plant in La Hague between 1979 and 1984, and 16 tons in Marcoule pilot reprocessing facility (APM) from 1978 to 1992 [1].

Phenix fuel treated in La Hague plant had a broad range of characteristics, with a maximal burn-up of 90 GWd/t.

The Phenix fuel treatment at La Hague UP2-400 facility included the following steps:

- The shearing step: the UP2-400 facility received fuel pins from dismantled Phenix assemblies in welded containers from which all traces of sodium have been eliminated. The fuel pins, placed in a case, were sheared with their spacer wire, using the existing HAO shearing machine.

- The dissolution step: the dissolution was conducted in nitric acid at the boiling point, in a batch mode in HAO facility ;

- The extraction step: the dissolution liquor was mixed with UNGG dissolution solution to reach the Pu/U ratio complying with extraction step.

These campaigns were successful, as for Marcoule APM campaigns, and thus, FR MOX treatment was demonstrated at pilot-scale.

4. Towards a specific dissolution facility for treatment of specific fuels

4.1. TCP facility: main principles

The TCP (polyvalent fuel treatment) facility is a specific unit to be implemented at the La Hague plant, dedicated to shearing and dissolution of a wide range of fuels. This installation will allow the treatment of irradiated and non irradiated fuels. The key objective of this unit is to offer our Customers a tailor-made treatment solution, on an industrial scale, taking benefit from existing functions but without impacting main plant capacity.

Today, three main fuel families are identified as candidates for treatment via TCP: light water reactors MOX fuels, research reactors used fuels, and fast neutron reactors MOX fuels. All these fuels are likely to be reprocessed at La Hague using current plant, but with capacity limits due to design optimization for UOX irradiated fuels.

Regarding LWR MOX fuels, the fuels range from manufacturing scraps to irradiated fuels (up to 60 000 MWt/d burn-up).

The second family consists in research reactors used fuels. These fuels differ strongly regarding enrichment, geometry, material, but still can be dissolved in a single equipment in TCP dissolution cell. In addition to current reprocessing process at UP3, TCP will bring more flexibility, address a larger quantity of fuels and open the door to dedicated solutions for specific features (i.e. innovative Al or Si management).

The third fuel family is the used fuels arising from the fast neutrons reactors; such as Phenix fuel pins, or future ASTRID fuels (irradiated and manufacturing scrap). For these fuels, TCP will also offer more flexibility in dissolution conditions for optimizing management of plutonium and other FR fuels specificities.

The TCP process consists in shearing, dissolution and, when necessary, oxidizing digestion for undissolved particles. The shearing tool will allow the shearing of fuel assemblies (15*15, 16*16, 17*17) and also fast reactor fuels with space wire conditioned in case, thanks to specific shearing packages adapted to the fuels. The shearing tool will present a greater modularity and operational flexibility than the existing shearing tools currently operated at La Hague. After shearing, the hulls will be immersed in a dissolution equipment. This equipment will be designed to offer a wide scale of dissolution conditions in a single and mutualised equipment. The dissolution may be followed up by an oxidizing digestion step. In dilution in the solutions of UOX, the dissolved fuel will then go through the next steps of separation process, using the existing equipments and installation, as already operated for RTR and MOX fuels. This will be done with the use of buffer tanks that allow specific isotopic management and facilitate the integration of TCP flow in the treatment process of UOX in order to maintain a good operating flexibility.

4.2. TCP facility: a step towards the future

TCP is planned to be put in operation during the next decade, after feasibility is demonstrated and engineering and construction steps are fully implemented. At that time, the progress of fast neutron reactors development program should lead to a natural integration of TCP as a key part of industrial feasibility demonstration of fuel cycle. TCP role can range from bringing significant amount of plutonium out of used MOX fuels in order to manufacture fuel for first cores to treat fast reactor used fuel for implementing a full closed cycle demonstration.

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Moreover, TCP will also provide key information and data regarding the treatment operations of specific fuels at an industrial scale, completing the already on-going R&D programs and the industrial feed-back. It could for instance allow the characterization of hulls after dissolution if these hulls are taken from the dissolving equipment and sent to laboratories. TCP, as one of the steps towards a large-scale fast reactor fuel treatment, offers a great opportunity to extract a maximum of information regarding the behaviour of fuels and thus to assess industrial feasibility of FR fuels treatment. TCP will then increase our industrial know-how while providing treatment services for a wide range of fuels.

5. Conclusion

AREVA has already demonstrated that specific fuels recycling is a reality within its current facilities. To go further and ensure a greater capacity without impacting UOX fuels treatment, AREVA plans to implement a new TCP facility dedicated to fuels requiring adapted shearing and dissolution conditions.

Besides, TCP design will greatly benefit from AREVA and CEA feed-back and optimizations, making it an innovative and industrial step towards the recycling of the future.

The design is in progress and is on time to include customers' needs in terms of type and quantities of fuel.

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Research and development for the fabrication of minor actinide-bearing fuel materials and technologies

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Abstract. The transmutation of minor actinides (MA) in 4th-generation reactors can be envisioned in homogeneous or heterogeneous mode. Minor actinide-bearing blankets (MABB) -- fuel for heterogeneous transmutation comprising 10 to 20% MA dispersed in a UO_2 matrix -- are largely unknown and warrant further research on the fabrication and properties of the materials, on their evolution under self-irradiation, and on their behavior in the reactor. This article summarizes progress in co conversion of uranium-americium compounds by oxalate precipitation or ion exchange resins. It also describes current R&D on MABB fabrication by powder metallurgy or spherical particle metallurgy. The fabrication processes in teleoperated shielded cells are discussed together with the technologies applicable to MABB fabrication equipment.

1. Introduction

The transmutation of the minor actinides (MA) in 4th-generation fast reactors can be envisioned in homogeneous or heterogeneous mode. Homogeneous recycling consists in incorporating the MA (Am, Np and Cm) in small quantities not exceeding a few percent in the reactor driver fuel. Heterogeneous recycling concentrates the MA in dedicated fuel assemblies containing 10 to 15% MA, placed in the core periphery. In this way the operation of the driver core is dissociated from the transmutation function.

The homogeneous mode has been a subject of a number of research programs [1],[2]. The heterogeneous mode has been widely investigated with the development of inert matrix transmutation targets (composed of minor actinide oxide and inert matrix, such as MgO or Mo) [3] but not so much with the development of minor actinide bearing blankets (a mixing of minor actinide oxide and fertile fuel: UO_2). The CEA has therefore focused its research effort on the second transmutation mode with the objective of defining simple and robust processes and technologies to fabricate AmBB[1] assemblies for transmutation in ASTRID[2]. The qualification procedure adopted by the CEA includes 4 phases:

—— selection,

—— feasibility, in which the technological and process-related choices are defined,

—— optimization of the technological choices,

—— qualification of the fuel.

The selection phase determines the fuel specification requirements. The feasibility phase involves analytic or semi-integral irradiation experiments on an individual pellet or cladding segment. Integral experiments on full-scale pins or capsules are performed during the optimization phase. The final

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[1] AmBB: Americium-Bearing Blanket
[2] ASTRID: Advanced Sodium Technological Reactor for Industrial Demonstration

qualification phase is carried out on a complete assembly. Figure 1 illustrates this approach in the case of heterogeneous fuel for transmutation.
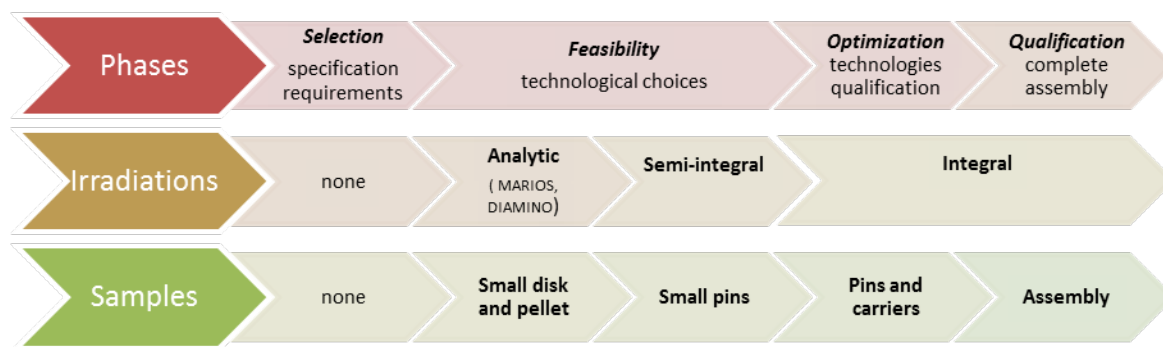
Figure 1 : Qualification procedure in the case of heterogeneous fuel

Americium was initially preferred for this research because of the difficulty of working with curium and the lower radiotoxicity of neptunium. In addition, americium isotope 241, obtained from aged Pu, is preferred for our studies given the scarcity of reprocessed americium.

Following a separation step, the fabrication of a minor actinide-bearing blanket for the heterogeneous mode consists in two steps: *conversion*, yielding a mixed oxide powder (UO_2, AmO_2) from an actinide solution, and *fabrication* to obtain fuel pins.

This article first summarizes the specific aspects of working with minor actinides (Am, Cm, Np), then describes the current state of research on $(U,Am)O_2$ co-conversion and pellet fabrication for MABB, and finally discusses the related technological developments.

2. Specifics of Minor Actinides

The minor actinides, especially Am and Cm, are gamma or neutron emitters and require remote operation in a shielded cell, unlike current (MOX) fuel which can be handled in a glove box. This very severe constraint implies the development of processes as simple as possible, limiting the number of steps and relying on technologies compatible with automatic and remotely controlled work [4].

In addition, the high alpha activity of the MA, especially curium, exacerbates the difficulty of controlling contamination in the fabrication lines. Processes such as milling, forced sieving, granulation, and grinding, which generate fine powdery and thus contaminating particles, must be avoided.

Although the behavior of high-density fuel (>95% of the theoretical density) is still better known, another concept with a lower-density microstructure and controlled open porosity is being investigated for use with the MABB. This microstructure is intended to enhance the release of helium and fission gases during irradiation, thus limiting the risk of fuel swelling [1].

In addition, industrial processes include additives such as lubricants or pore-forming agents. Considering the significant radiolysis and/or thermal decomposition phenomena likely to be encountered with alpha- and gamma-emitting MA, the use of organic additives must be limited or avoided in favor of stable compounds.

Finally, the high oxygen potential of americium compared with uranium and plutonium could lead to americium sublimation during sintering or a deviation from stoichiometry. It is therefore important to fully control the MABB sintering conditions.

3.   Co-Conversion of Minor Actinides

Research on enhanced separation [5], [6] has led to the development of a complete process for the extraction and dissolution of actinides from spent fuel for conversion to oxide. Similarly, work on the conversion of actinides alone has led to many processes, of which the best known are:

⸺   chemical precipitation followed by calcining,

⸺   binding to a substrate by impregnation or ion exchange, followed by suitable heat treatment,

⸺   the sol-gel route,

⸺   thermal denitration based on evaporation of nitric acid solutions.

For the heterogeneous mode and the fabrication of mixed oxides for MABB, research has focused on co-conversion of $(U,Am)O_2$ following the EXAm enhanced separation process [7].

3.1.   *Description of (U, Am)O$_2$ Co-Conversion Processes*

3.1.1.   *Chemical Precipitation of (U,Am)O$_2$*

For chemical precipitation processes it is important to control the quantitative and simultaneous precipitation of the relevant actinides to obtain the target composition and guarantee the homogeneity of their distribution in the solid. Among other possible chemical coprecipitation routes, only the oxalate method meets these criteria for uranium-actinide(III) mixtures. Precipitation as an oxalate is an industrially proven process for recycling plutonium at oxidation state IV. In addition, U(IV)-Pu(III) coprecipitation has been investigated by the CEA since 2007 for the design of an industrial facility [8]. Logically, therefore, the co-conversion process by the U(IV)-Am(III) oxalate route is also investigated in CEA laboratories to synthesize $(U,Am)O_2$ mixed oxide solid solutions and to optimize the process parameters. The process is based on the following sequence of operations:

⸺   Precipitation of the oxalate precursor in a nitric acid medium

⸺   Synthesis of the oxide solid solution by heat treatment of the oxalate precipitate in inert atmosphere.

In the laboratory the oxalate precursor is obtained in a vortex effect reactor. A free acidity of 1 M and 0.15 M excess oxalic acid were selected to optimize the precipitation yields. Hydrazinium ions are added to stabilize the desired oxidation states (IV for uranium and III for americium); they also affect the structure of the mixed U(IV)-Am(III) oxalate by balancing the charges within the structure.

Both reactants — the solution containing the two actinides and the precipitating oxalic acid solution — are added simultaneously around the edge of the free vortex, figure 2, and a coprecipitate with the formula $(N_2H_5^+, H_3O^+)_{2+2x} U^{IV}_{2-2x} Am^{III}_{2x} (C_2O_4)_5 \cdot nH_2O$ forms almost instantaneously, ensuring a completely homogeneous uranium and americium distribution in the solid. The U(IV)-Am(III) oxalate coprecipitate is filtered and dried at room temperature, then typically calcined for 2 h at 750°C in a tube furnace in flowing argon (10 NL·h^{-1}) to form an oxide solid solution of $U_{1-x}Am_xO_2$.

Figure 2 : Vortex precipitator and coprecipitation device in a shielded cell

3.1.2. *Binding on Ion Exchange Resins (IER)*

Loading of actinide mixtures on an ion exchange resin (an extension of the Weak Acid Resin (WAR) process [9][10] is also being investigated by the CEA for its simplicity and its ability to produce calibrated solids. This technique produces "powder" batches of non-dusty, free-flowable spherical particles (small spheres 100 micrometers in diameter) [11], [12].

The principle of co-conversion to U-Am oxide is based on the use of carboxylic resin beads to bind uranium(VI) and americium(III) cations by ion exchange. The actinide-loaded resin then undergoes oxidizing heat treatment (carbonization in air at 600–1000°C) to eliminate the carbonaceous material, leaving only the intimately blended metal oxides: U_3O_8 (triuranium octaoxide) and AmO_2 or Am_2O_3 (dioxide or sesquioxide). A reduction step is then necessary to adjust the oxygen stoichiometry of the uranium oxide to a value near 2. The process flowsheet is shown schematically in figure 3.

```
┌─────────┐    ┌──────────────────┐    ┌─────────┐
│    U    │    │ Resin selection  │    │   Am    │
│ solution│    ├──────────────────┤    │ solution│
└─────────┘    │Washing/ size     │    └─────────┘
              │ selecting        │
              └──────────────────┘
                       │
                  ┌─────────┐
                  │ Binding │
                  └─────────┘
                       │
                  ┌─────────┐
                  │ Drying  │
                  └─────────┘
                       │
              ┌──────────────┐
              │Heat treatment│
              └──────────────┘
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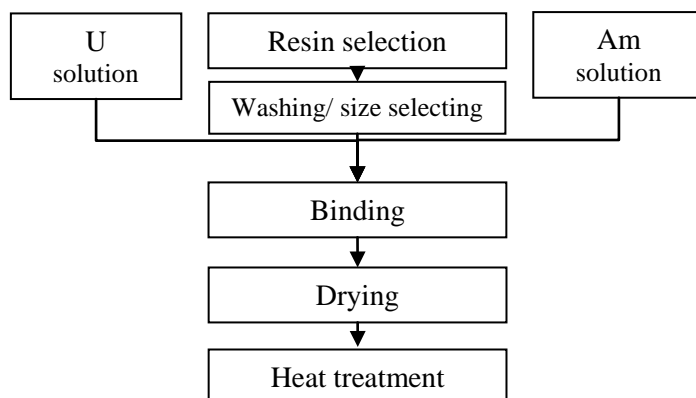
Figure 3: Flowsheet for producing spherical (U-Am)O2 particles

The ion exchange reaction on protonated carboxylic resin is effective only if the pH of the solution in contact with the resin is higher than 4, or at least higher than 3 with multivalent ions such as uranium(VI) or americium(III). The first key step in the process is to prepare an acid deficient actinide nitrate solution [11].

Binding occurs by ion exchange between a protonated acrylic resin and the (U, Am) solution buffered to a pH exceeding 3. The resin is packed in a column and submitted to once-through solution flow. The loaded resin is dried and mineralized, then calcined in a tube furnace in flowing air at up to 800°C.

3.1.3. *Denitration and the Sol-Gel Route*

Denitration processes are based on evaporation of the nitric acid solutions followed by thermal decomposition of the salts. Denitration, and particularly the modified direct denitration (MDD) process developed at Oak Ridge, is compatible with compact facilities but this advantage does not appear to offset its operating constraints, such as additional crushing and milling operations that are difficult to implement in a high-activity environment, as well as effluent ammonia management. It is not a subject of detailed study within the CEA.

The sol-gel route may be of interest for fuel applications requiring relatively calibrated powders even though sol radiolysis phenomena, control of the chemical conditions, and effluent management are obstacles for an application with minor actinides. A sol-gel variant involving internal co-gelation was tested by the CEA with a U-Am mixture.

3.2. *Results and Discussions*

The results of U,Am co-conversion by coprecipitation confirmed the formation of an ideal oxide solid solution of $(U,Am)O_2$. Controlling the precipitation of single-phase mixed oxalate requires short delay blending of uranium(IV) and americium(III). Due to radiolysis, U(IV) is oxidized to U(VI) resulting in precipitation of uranyl oxalate (together with mixed U-Am oxalate) when its concentration exceeds 5 g·L^{-1}. The resulting solid compound is no longer homogeneous. After calcination, XRD[3] analysis of the oxide confirms the formation of a mixed oxide structure with a fluorite structure and a lattice parameter $a = 5.461 \pm 0.002$ Å, and good control of the target Am/(U+Am) molar ratio.

For co-conversion on ion exchange resin, research is concentrated on the uranium phase pending the initial results for $(U,Am)O_2$ expected in 2013. A study using an environmental scanning electron microscope with a heating stage revealed the evolution of a single microsphere during calcination and showed that it conserved its spherical shape.
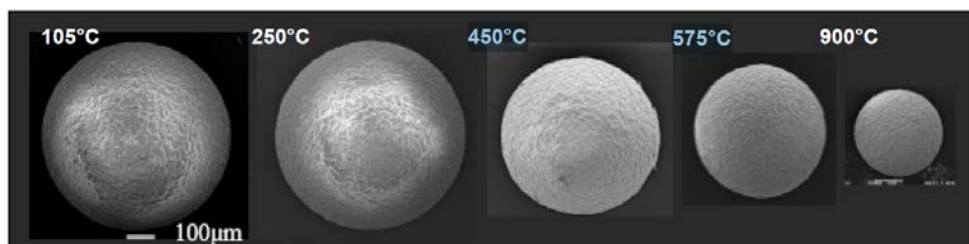
Figure 4 : Evolution of a spherical uranium particle during heating

Pelletizing of this type of spherical particles by the CRMP[4] process has been validated with cerium surrogate: the resulting pellets are dense (95% of theoretical density after sintering) with a homogeneous microstructure [13].

These initial results reveal the potential of this process, which still requires substantial further research. Co-conversion by oxalate coprecipitation remains the benchmark process for co-conversion of mixed $(U,Am)O_2$ oxide because of its maturity and robustness.

4. Fabrication of Minor Actinide-Bearing Blankets

The approach adopted for the fabrication of minor actinide-bearing blankets follows the approach used for qualification of the fuel (figure 1) and began with the MARIOS[5] and DIAMINO[6] analytical

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[3] XRD: X-ray diffraction
[4] CRMP: Calcined Resin Microsphere Pelletization
[5] MARIOS : Minor Actinides in Sodium-cooled Fast Reactors

irradiation experiments. They should be followed by two other analytical irradiations and 2 or 3 semi-integral irradiation experiments before 2020, depending on the results of the post-irradiation examinations.

4.1. *Description of Pellet Fabrication Processes*

Two processes have been selected and are now the subject of feasibility studies in the laboratory: one based on powder metallurgy, and another based on spherical particle metallurgy. In addition, the Sphere-pac process is a subject of technological intelligence because of its simplicity, which is an advantage for manufacturing minor actinide-bearing blankets, although its behavior must still be qualified in fast reactors [14][15].

4.1.1. *Powder Metallurgy for MABB*

Powder metallurgy basically consists in powder preparation, press compaction, and conventional or reactive sintering. During MABB fabrication by reactive sintering, competition arises between the formation of the desired solid solution and its densification. Three processes have been selected by the CEA for MABB fabrication; as shown schematically in figure 5 :

   — A powder metallurgy process involving reactive sintering was used to produce the dense MARIOS samples [16],

   — The UMACS process[7], with conventional sintering was used to produce the DIAMINO samples [17],

   — A simplified process which is a subject of R&D.

These processes differ mainly in the way the powder is prepared for press compaction (figure 5).

4.1.1.1. Powder Metallurgy by Reactive Sintering

Initially, part of the UO_2 powder is blended and milled with all the AmO_2 powder. The remaining UO_2 powder is then added to the primary blend to adjust the composition to the desired Am content. The blend is again milled under the same conditions to ensure homogeneity. The ultimate objective is to enhance the formation of UO_2/AmO_2 reaction interfaces and avoid the formation of unwanted phases and inhomogeneities during reactive sintering. The resulting blend is pressed into pellets. During this step only the press dies are lubricated; no organic or mineral additives are introduced into the blend before press compaction. The compacted pellets are sintered under reductive conditions for 4 h at 2023 K.

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[6] DIAMINO : Dispositif d'Irradiation d'Actinides MIneurs dans Osiris (Irradiation experiment of Minor Actindes in Osiris Reactor)

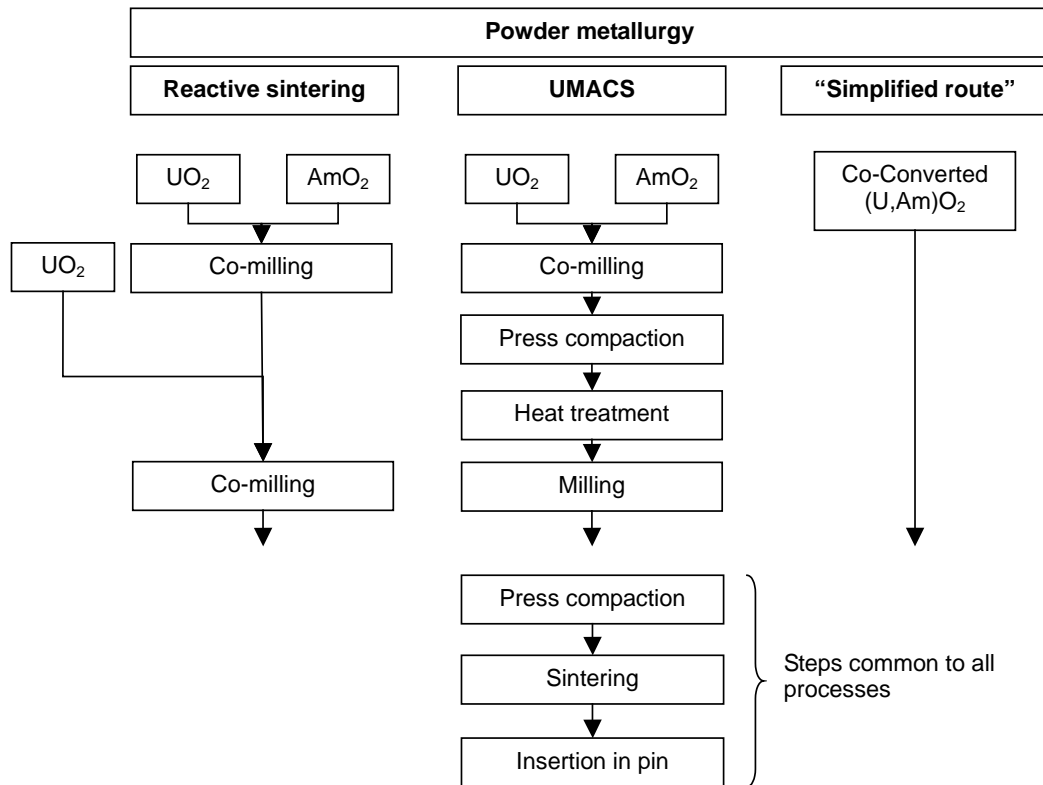[7] UMACS: Uranium-Minor Actinide Conventional Sintering

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                          Powder metallurgy

    Reactive sintering            UMACS            "Simplified route"


        UO₂      AmO₂        UO₂      AmO₂        Co-Converted
                                                   (U,Am)O₂

  UO₂      Co-milling            Co-milling


                            Press compaction


                             Heat treatment


         Co-milling               Milling



                            Press compaction       Steps common to all
                                                    processes
                               Sintering


                            Insertion in pin
```

Figure 5 : Powder metallurgy processes investigated for the production of MABB

4.1.1.2. UMACS

The UO_2 and AmO_2 powder precursors are first blended by co-milling in the required proportions. This essential homogenization step favors the formation of reactive interfaces between UO_2 and AmO_2. This step therefore determines the homogeneity of the resulting phase and the absence of unwanted phases. The resulting blend is then pressed into pellets to ensure intimate contact and enhance the interdiffusion necessary to form the solid solution at high temperature (solid-state reaction). The resulting pellets are then heat-treated to obtain the desired solid solution.

The temperature is selected to allow the compound to be synthesized without excessive densification which could be unacceptable for the subsequent milling step. During heat treatment the atmosphere is controlled to favor interdiffusion without reduction and/or sublimation of the americium oxide that has not yet reacted. The pellets are then milled to obtain a dispersed product suitable for press compaction into pellets. Milling also eliminates any microstructural defects such as porosity formed by Kirkendall effect or defects remaining from initial precursor porosity. The resulting powder is then again pressed to form pellets, which are sintered during a dedicated cycle at high temperature in controlled atmosphere. At this stage the americium is already combined with the uranium in a solid solution, which considerably reduces the risk of sublimation.

4.1.1.3. Simplified Route

The simplified route requires co-converted powders having specific characteristics (flowable, sinterable, dust-free). The $(U,Am)O_2$ solid solution will already be present after calcining of the oxalates, allowing conventional sintering. The initial results are expected in 2014.

4.1.2. Spherical Particle Metallurgy

The CRMP spherical particle metallurgy also includes press compaction and sintering. The flowability and hardness of the spherical particles co-converted on ion exchange resin (Section 3.1.2) are

intrinsically favorable to press compaction. Moreover, the spherules are non-dusty and therefore facilitate the implementation of minor actinides. Figure 6 illustrates the simplification provided by the CRMP process.
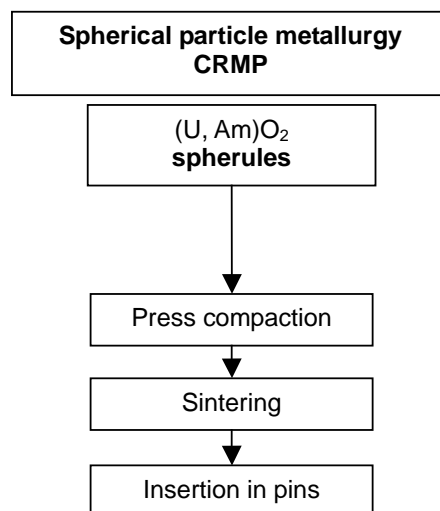
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┌─────────────────────────────┐
│  Spherical particle metallurgy │
│            CRMP               │
└─────────────────────────────┘
        ┌─────────────────┐
        │   (U, Am)O₂      │
        │   spherules      │
        └─────────────────┘
                │
                ▼
        ┌─────────────────┐
        │ Press compaction │
        └─────────────────┘
                │
                ▼
        ┌─────────────────┐
        │    Sintering     │
        └─────────────────┘
                │
                ▼
        ┌─────────────────┐
        │ Insertion in pins │
        └─────────────────┘
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Figure 6 : Spherical particle metallurgy: the CRMP process

Studies are currently in progress on uranium and uranium-cerium pellets (cerium is used as a surrogate for americium). Based on the encouraging results obtained to date [18], the first $(U, Am)O_2$ pellets could be tested in 2015–2016.

4.2. Results and Discussion

The fabrication of MABB by powder metallurgy with reactive sintering leads to competition between the formation of the solid solution and its densification. Consequently, it is difficult to obtain high densities (>95%) reproducibly with controlled porosity [19]. The UMACS process, whose main advantage is that it separates the formation of the solid solution from its densification, is capable of producing dense samples with high density and homogeneous microstructure. Both processes were used to fabricate the minidisks for the first MARIOS and DIAMINO analytical irradiation experiments, which demonstrated their feasibility at laboratory scale.

Their complexity and the presence of contaminating steps remain major obstacles for the fabrication of full-scale pellets (optimization phase: figure 1). Our research effort in the coming years will therefore focus on the "simplified route" using a solid solution of co-converted mixed oxide powder. One of the main difficulties with this approach will be to control the morphology of the coprecipitated powder and guarantee its suitability for press compaction and its sinterability with significant quantities of minor actinides.

At the same time, the CRMP process — more innovative but less mature — will be investigated to demonstrate its feasibility at laboratory scale. The initial results expected in 2015–2016 will allow us to evaluate the true potential of this process.

4.3. Structural and Thermodynamic Aspects

In the heterogeneous mode, regardless of the actinide content, the microstructure, or the process considered, the structural and thermodynamic aspects of the U-Am-O systems have a major impact on fuel fabrication and particularly on the sintering step. The effort currently focuses on americium via the U-Am-O system study and its implementation in $U_{1-x}Am_xO_{2\pm\delta}$ (MABB) fuel. Comparing these binary systems and their thermodynamic properties shows that the $U_{1-x}Am_xO_{2\pm\delta}$ solid solution cannot be described by a simple substitution of Am(IV) for U(IV). Introducing Am in the UO_2 fluorite

structure results in complete reduction of Am(IV) to Am(III) and partial oxidation of uranium to conserve the electroneutrality of the structure [20]. In addition, the reduction of $AmO_{2-\delta}$ to Am_2O_3 occurs before the formation of the solid solution by heat treatment under reductive conditions [21]. Understanding these mechanisms is vital for the fabrication process.

5. Technologies

The existing Atalante facilities at Marcoule in France are sufficient to meet the needs of the feasibility phase, i.e. the production of disks, pellets or short fuel pins. The fabrication equipment is entirely satisfactory, but involves manual operation limited to small quantities (a few tens of grams). They are not capable of fabricating full-scale objects for the integral experiments (figure 1). This is the main area for development and technological innovation in the near future. Research focuses on the technological obstacles such as an automatic press in a teleoperated shielded cell, as well as on innovation. The initial results are expected for 2016. A program of modeling and design assistance based on virtual reality are associated with each technological development to minimize the development costs. Technological developments are a major issue in R&D for transmutation.

6. Conclusion

Research work in the feasibility phase for the qualification of minor actinide-bearing fuel or blankets involves analytical or semi-integral irradiation experiments. Research focuses on MABB fabricated from co-converted $(U,Am)O_2$ powder. The "simplified route" and CRMP process have been selected to produce pellets with co-conversion by oxalate coprecipitation and by ion exchange resin, respectively.

The main advantage of co-conversion by oxalate coprecipitation is its maturity; the challenge is to obtain flowable powder directly suitable for press compaction. Co-conversion on IER is also being investigated for its simplicity and its ability to produce calibrated solids. The first tests with $(U,Am)O_2$ will allow us to evaluate the interest of this route.

Equipment and facilities are currently available to perform experiments on pellets or cladding segments. The objective of future work is to ensure a supply of minor actinides and develop the means to produce full-scale materials for irradiation in the ASTRID reactor.

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Overview of the Main Achievements of the FP7 EURATOM Collaborative Project ACSEPT

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Abstract. Nuclear power plays a key role in limiting European Union's greenhouse gases emissions, and makes an important contribution to improve EU's independence, security and diversity of energy supply. However, its social acceptance is closely linked to an enhanced safety in the management of long-lived radioactive waste contributing to resource efficiency and cost-effectiveness of this energy and ensuring a robust and socially acceptable system of protection of man and environment. Among the different strategies, partitioning and transmutation (P&T) allows a reduction of the amount, the radiotoxicity and the thermal power of these wastes, leading to an optimal use of geological repository sites. ACSEPT successfully addressed the partitioning issues by focusing on the development of advanced separation processes, both aqueous and pyrochemical. Head-end steps, fuel refabrication, solvent treatment, waste management were also taken into account. In aqueous process development, the SANEX, innovative SANEX and GANEX flowsheets were designed and tested in hot cells. In pyrometallurgy, studies on actinide back-extraction from aluminium and exhaustive electrolysis allowed the validation of two flowsheets developed from more then 10 years in Europe. A training and education program including seminars, workshops, brainstorming meeting but also student exchanges and support to post-doctorate fellowships was a key point for maintaining and increasing a high expertise level in actinide separation sciences in Europe. Six month after the end of ACSEPT, and when its follow-up, SACSESS, just begins, it is time to highlight its main achievements.

1. Introduction

Consistently with potentially viable recycling strategies, ACSEPT provided a structured R&D framework with the ambitious objective to develop chemical separation processes compatible with fuel fabrication techniques, in view of their future demonstration at the pilot level (Figure1).

For several decades, many European countries have chosen the strategy of closed fuel cycle, currently involving (i) the reprocessing of spent nuclear fuels to recover uranium and plutonium (both fissile materials that can be recycled) and (ii) the vitrification of long lived radionuclides (the final waste being expected to be disposed of in deep geological repositories). Nevertheless, the sustainability of an advanced fuel cycle relies on the possibility to maximise the energy usage of nuclear spent fuel and to provide improved waste forms for long-term storage: the removal of minor actinides (i.e.: Np, Am, Cm, Cf) with U and Pu from the waste and their recycling in fast neutron reactors, will significantly reduce the radio-toxic inventory. Therefore, the separation of all significant Trans-Uranium (TRU) elements and their incineration in fast neutron reactors or Advanced Driven Systems is a key feature of advanced fuel cycles. However, new reprocessing technologies (spent fuel dissolution, actinide

separation and fuel refabrication) are required to address the challenges, which cannot be met by current generation of chemical plants. Two strategies are proposed for the recycling of the actinides issuing from the various forms of future nuclear fuels (oxides, carbides and nitrides or metallic fuels): (i) their homogeneous recycling in mixed fuels (via a prior group separation of the actinides: GANEX concept) and (ii) their heterogeneous recycling in targets or core blankets (via their selective separation from fission products).

Both aqueous separation processese and pyrochemical process could be implemented to recover the actinides. This paper sumarizes the main achievements of the project in these domains, including integration studies as well as training and education.
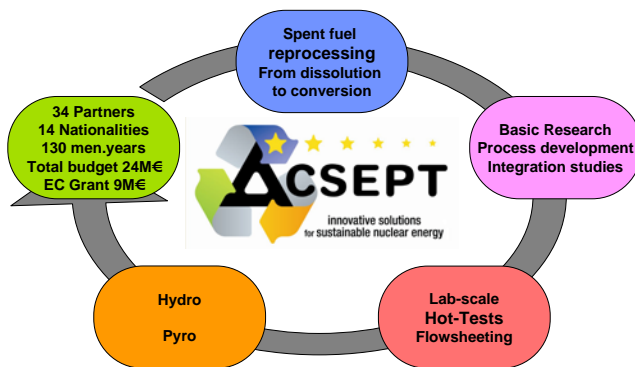

Figure 1: the ACSEPT Project

2. Aqueous separation process developments

The first domain addresses the hydrometallurgical separation (i.e. applying chemical liquid-liquid extraction) of actinides from irradiated nuclear fuels of the metal oxide (UOx or MOx) type. First, the fuel is dissolved in hot nitric acid, the so-called head-end step. Next, the actinides are separated from fission products and from corrosion products via several consecutive extraction processes (Figure 2). Finally, the product solution(s) containing the actinides are converted into solid actinide products from which new fuels or targets can be fabricated.
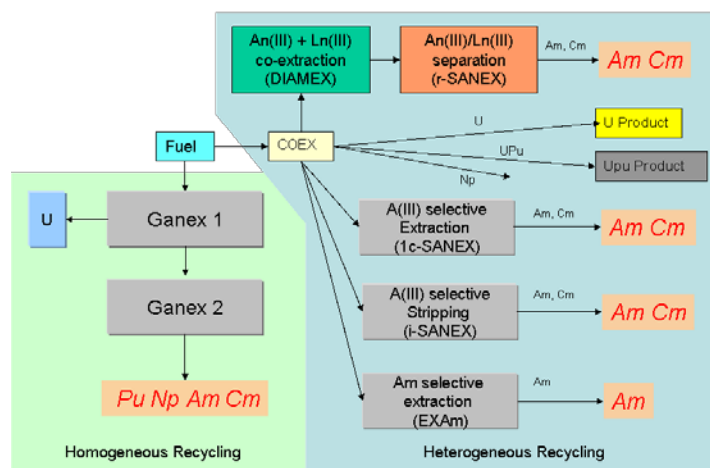
Figure 2: The aqueous separation processes developed for the homogeneous and heterogeneous recycling strategies

The first separation process, the commercially implemented PUREX process, separates U and Pu, leaving behind the so-called high active raffinate (HAR), which is currently vitrified. The PUREX process can be modified to co-separate Np. The separation of the remaining actinides, Am and Cm, from the HAR had been studied in previous projects, making use of the DIAMEX and the r-SANEX processes. Aim of the ACSEPT process was to simplify this process scheme by merging the DIAMEX

and SANEX processes into one process. Another route followed was the development of GANEX (Grouped Actinide Extraction) processes. Aim is developing processes co-managing all transuraium elements (TRU = Np, Pu, Am, Cm), avoiding pure Pu products. A GANEX process is advantageous regarding non-proliferation issues and is well suited for the homogeneous recycling of actinides.

2.1. Head-end steps

A substantial effort was made in ACSEPT to assess the dissolution of different fuel types. Both conceptual studies and experimental work were performed. One of the key steps in any further work programmes considering reprocessing options for future fuels is to develop a 'process specification'. Existing technologies can then be assessed against the specification and technology gaps can be highlighted. Then R&D can be targeted towards these areas. This is particularly important in the area of head end which takes the spent fuels and provides the feed solution to the primary separation plant.

Experimental and mechanistic studies have advanced the knowledge of dissolution chemistry of (unirradiated) bulk-phase MOx and the associated plutonium-rich regions. Also, these and future planned developments in the dissolution of plutonium dioxide with Ag^{2+} will allow further assessment of dissolution in the presence of insoluble fission products which are also present in dissolver sludge.

2.2. Ligand desing and assessment

During the project, more than 120 new molecules have been synthesized and tested for their potential ability to be used in one of these separation processes.

Among the lipophilic compounds able to separate Am(III) from Eu(III) in the organic phase, $CyMe_4$-BTPhen (Figure 3 left) is one of the more promising new molecules. It actually extracts Am(III) with a very good selectivity over Eu(III) and with extraction kinetics faster than the current reference molecule, $CyMe_4$-BTBP. Unfortunately, distribution ratios are very high, which may cause problems in the back extraction part of the process. CA-BTP (Figure 3 right) has also been demonstrated to be an extracting agent selective for actinides(III), eliminating certain drawbacks of CyMe4-BTBP such as low solubility or slow kinetics. Unfortunately CA-BTP is not suitable for 1c SANEX or GANEX applications due to the formation of a precipitate at the acidity required for the above processes.
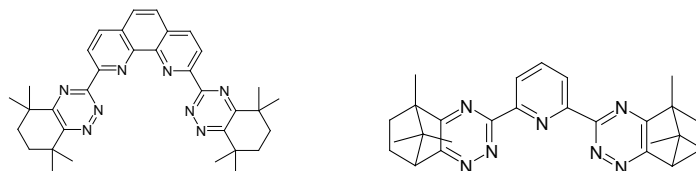
Figure 3: CyMe$_4$-BTPhen (right) and CA-BTP (left)

Regarding the hydrophilic complexing agents, 3 new molecules have shown remarkable properties: PyTri-Tetraol, SO$_3$-Ph-BTP (figure 4 right) and SO$_3$-Ph-BTBP (figure 4 left). These ligands do in fact complex Am(III) selectively over Eu(III) in a nitric acid aqueous phase ([HNO$_3$] > 1 mol/L). They may therefore be used in an *i*-SANEX or GANEX process in order to separate An(III) from Ln(III).
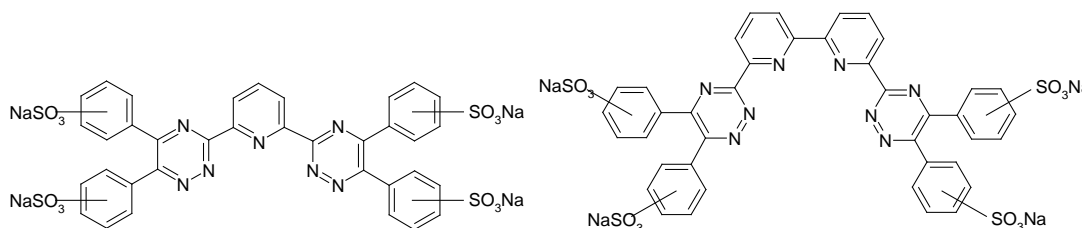
Figure 4: SO$_3$-Ph-BTP (left) and SO$_3$-Ph-BTBP (right).

2.3. Process development

One of the main goals of ASCSEPT was demonstrating novel process options such as 1c-SANEX, *i*-SANEX and GANEX processes. Applying some of the chemical systems developed, several process tests were successfully performed using lab-scale counter-current contactor setups.

Computer codes were used to calculate flow-sheets for lab-scale demonstration tests of 1c-SANEX, *i*-SANEX and GANEX tests to be performed in counter-current centrifugal contactor setups. These calculations are based on equilibrium and kinetic data collected in the optimisation studies.

2.3.1. 1c-SANEX
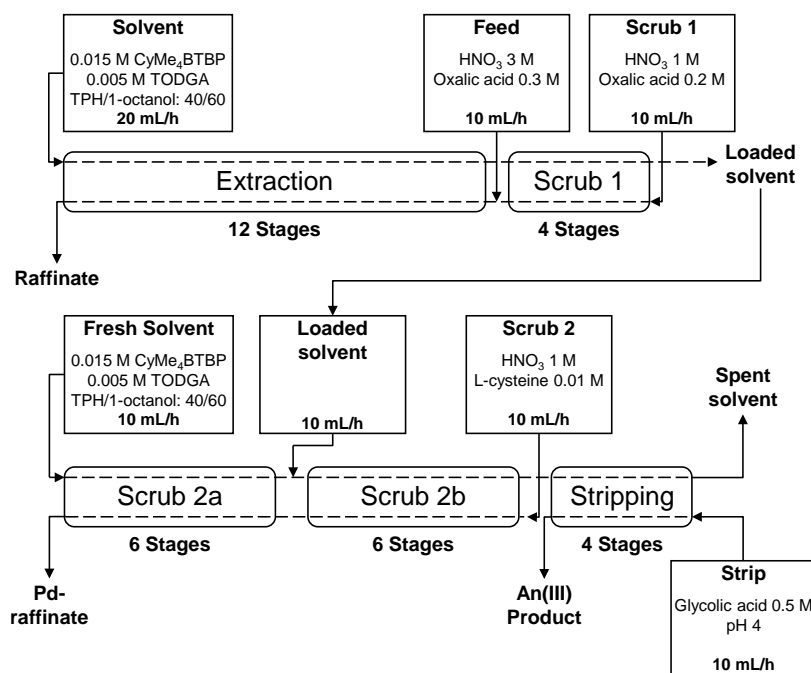
Figure 5: 1-cycle SANEX process flow-sheet.

A spiked 1c-SANEX test was performed using the system developed in ACSEPT. A flow-sheet was calculated (Figure 5) and the test was performed using a spiked synthetic PUREX raffinate as feed solution. The co-extraction of Zr and Mo was prevented using oxalic acid. Co-extracted Pd was selectively stripped using an L-cysteine scrubbing solution. The recovery yield in the product solution was 99.8% for Am(III) and 99.4% for Cm(III). Except for Y(III) (8.8 % of the initial amount), the product solution contained only low concentrations of Pd (0.8 % of the initial amount) and Ln(III) (< 1 % of the initial amount). Experimental and calculated concentration profiles were in good agreement.

2.3.2. *i*-SANEX

A hot *i*-SANEX process demonstration was carried out using a system based on the co-extraction of Am(III), Cm(III) and Ln(III) into a TODGA + TBP solvent followed by selective stripping of Am(III) and Cm(III) using a buffered DTPA solution (Firgure 6).

Feed solution was a genuine raffinate from a PUREX hot test performed earlier. The test performed successfully. The recovery yield was > 99.8% for Am(III) and 99.9% for Cm(III). Moreover, the Ln(III) decontamination was excellent (less than 2% by weight of Ln(III) versus An(III) in the final product). Calculated concentration profiles were in good agreement with experimental results.
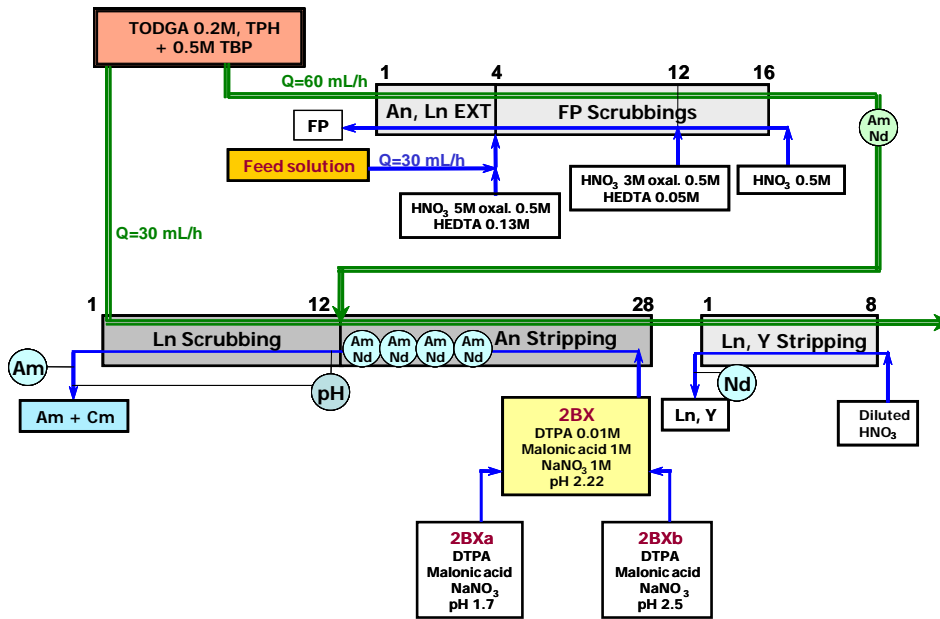
Figure 6: Optimized process flowsheet for the i-SANEX hot test.

2.3.3. GANEX

Based on the EURO-GANEX system (see III.1.3.2.3) a flow-sheet was developed and optimised. Several process tests were run using spiked surrogate feed solutions containing Pu in nominal concentration (10 g/L), giving feedback to the flow-sheet calculations towards a final flow-sheet for the hot test (Figure 11).

Before the hot EURO-GANEX process test a GANEX 1st cycle process had to be run to prepare the genuine feed solution. 117 g fast reactor fuel was dissolved in 6 mol/L HNO_3. U was extracted from this solution in a GANEX 1st cycle process, leaving a raffinate solution containing 10 mg/L U, 18.3 g/L Pu and 240 mg/L Am. This solution was adjusted to 10 g/L Pu and 5.9 mol/L HNO_3 and used as feed solution in the hot EURO-GANEX test.

The hot EURO-GANEX test (Figure 7) was run on two consecutive days (day 1, extraction/scrubbing; day 2, stripping). Analytical results demonstrated the high efficiency of this flowsheet.

Figure 7: EURO-GANEX flow-sheet for the hot test.

2.4. Actinide co-conversion

In the various concepts for future nuclear systems, co-management of two or more actinides (and possibly an "inert" element) has often been put forward recently. It improves and simplifies the nuclear fuel cycle for many reasons, particularly when dealing with minor actinides, noticeably at the back-end of the spent fuel treatment and at the front-end of the fabrication of a new fuel.

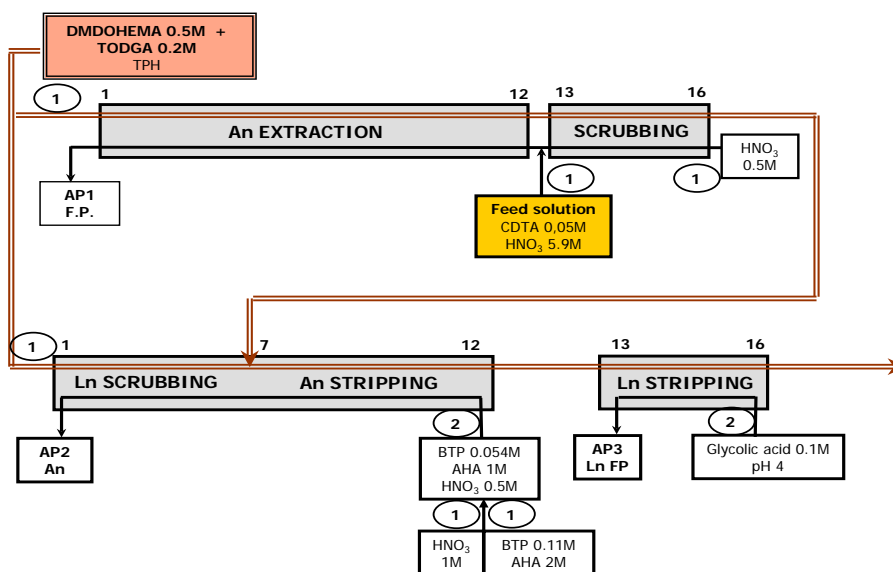Then, actinide co-conversion processes can play an important role by closing the actinide co-partitioning steps and producing in the same time mixed actinide solid compounds used as starting materials for the fabrication of new objects. Different co-conversion concepts are today conceivable, based on co-precipitation operations, sol-gel transition, matrix infiltration, thermal co-denitration or other related techniques.

For the development of innovative fuel cycles such as those conceived in GenIV reactors, uranium based material was taken as the reference fuel matrix material within the ACSEPT project, whereas in EUROPART inert matrix material (zirconium based) was investigated.

The internal gelation route in continuation of the EUROPART project was studied. Synthesis of ascorbate- hydroxyl- uranyl sols directly from uranium trioxide and ascorbate- nitrate hydroxyl-uranyl sols from uranyl nitrate and ammonium poliuranates (ADU) has been elaborated using the Complex Sol-Gel Process (CSGP). Among the innovative methods for such co-conversion of mixed actinides solutions, the method based on the application of the so called "solid extractants" (SEXs) was studied.

From the results that have been obtained through the cooperation of all groups it can be concluded that the internal gelation, the GSGP as well as the solid extractant based Co-conversion route are suitable methods to fabricate UO_2 microspheres containing trivalent actinides for the heterogeneous recycling of MA in Gen IV reactors.

3. Pyrochemical separation process developments

In pyrometallurgy, the objectives of the ACSEPT were to develop pyrochemical separation processes beyond the current state of the art, as an alternative option for the longer term. The work was centered on the two reference cores of process identified during EUROPART (Figure 8), and aimed at the validation of the scientific feasibility of each technological brick, at laboratory scale. Indeed, studies were not limited to the recovery of actinides, but also focused on the head-end steps, on the salt purification and recycling and on the waste conditioning, the ultimate goal being to propose a reprocessing scheme allowing actinide fluxes suitable for fuel refabrication.
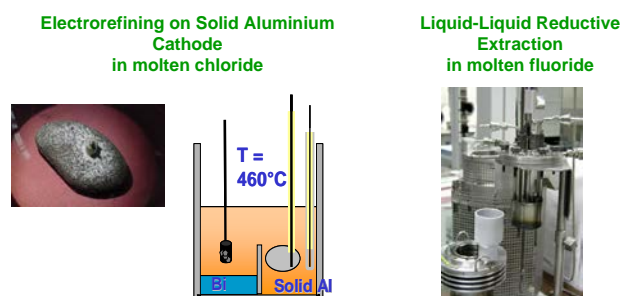
Figure 8: The two reference pyro processes developed within ACSEPT

3.1. Head-End Steps

The head-end steps cover all operations taking place ahead of the core of process, i.e. mainly the decladding, the thermal treatment and the conversion of the fuel into a form suitable for its dissolution in the molten salt solvent. Apart from conversion of oxide fuels by chlorination in the view of dissolution in chloride salts, head-end steps were not a priority in the frame of the previous projects

PYROREP and EUROPART. Within ACSEPT, the work focused on the thermal treatment of the fuel, and on its conversion into metal or fluorides.

Along with the recent developments in the head-end of reprocessing technology, a novel technique of thermal treatment for actinide recovery from irradiated fuel has been proposed and successfully tested at PSI (InVap). The method is aimed to separate the short-lived and neutron absorbing Fission Products (FPs) from irradiated fuel into the gas phase when thermal release is promoted by means of inductive heating under controlled redox conditions. After the operational parameter optimization, the InVap was shown to give good reproducible signals at the highest operational temperature of 2300°C. Post-annealing gamma spectrometry examination showed that almost no detectable activity was left in the samples.

At CEA, the feasibility of hydrofluorination with an "in situ" HF gas generation set-up was assessed. Some elements on thermodynamics and kinetics of hydrofluorination reaction were learnt thanks to this study. The reliability of the hydrofluorination set-up through a chemical reaction involving "in situ" HF gas generation was demonstrated. This set-up could be implemented in a hot cell.

At CIEMAT and CNRS-LGC, the so-called direct reduction process, consisting in an electroreduction of solid oxides into metal in a molten salt solvent, was studied. This route is the reference process for the conversion of spent fuel in USA, Japan and Korea, but there was no expertise within the European community before the start of the ACSEPT programme.

3.2. Process Development

The main objective of this activity has been defined as the development of the processes involved in pyrochemical separation of actinides, according to the reference technologies selected within the last projects: liquid-liquid reductive extraction and electrorefining of actinides onto solid aluminium cathodes.

3.2.1. Exhaustive electrolysis

The exhaustive electrolysis technique has been studied in order to evaluate feasibility of the process for purification of the salt from electrorefining. A dedicated experimental set-up has been designed, manufactured and successfully tested during the project. The main parts are chlorine gas producing inert anodes and a quartz electrolyser with an Inconel gas tightened lid enabling precise manipulation with the electrodes. A series of galvanostatic electrolyses aimed to the selective recovery of An have been carried out in molten LiCl-KCl electrolytes, followed by an experiment focused on a complete recovery of all actinides with certain portion of Ln in a multistage electrolysis. Concentration of An has been decreased from 2.1 down to 0.7 wt.% during selective part of the experiment, when the current density was above -2.0 mA·cm^{-2}. Then co-deposition of actinides and Nd has been carried out up to recovery of all actinides with average current density > -4.0 mA·cm^{-2}.

3.2.2. Recovery process development for An recovery from An-Al alloys

A chlorination route has been investigated in ITU for recovery of An from the An-Al alloys formed during the electrochemical separation processes. The chlorination route consists in three steps: Vacuum distillation for removal of the salt adhered on the electrode, chlorination of the An-Al alloys by $Cl_2(g)$ or $HCl(g)$ and sublimation of the formed $AlCl_3$. A very efficient chlorination (up to 99.8% conversion) with no volatilisation of U has been achieved by $Cl_2(g)$ already at 150°C. A major part of $AlCl_3$ (between 85% and 94%) has been removed already during the chlorination. The chlorination by $HCl(g)$ enabled higher reaction temperatures, which indicated higher process rates. A complete conversion of UAl_3 to non-volatile chlorides was achieved at 300 and 350°C during 20 h, while 99.6% was chlorinated during 4 h at 350°C. During the experiment using U-Pu-Al alloy prepared by electrorefining, somewhat lower efficiency of chlorination step was achieved, but still minimum 97% of the alloy was chlorinated with no An losses by volatilisation.

An actinide oxidative back-extraction process has been developed in CEA for recovery of An from the Al matrix obtained by a reductive extraction process using liquid Al as extractant in molten fluoride media. Bibliographic and the thermodynamic studies have shown the advantage of using chloride media for the process and the experimental conditions has been predicted (salt composition, working temperature 700°C). The recovery of Pu and Am has been quantitative in a single stage, whilst U is the most difficult actinide to be back-extracted and cannot be fully recovered in a single step.

3.3. Salt treatment for recycling

The pyrochemical treatment of spent nuclear fuel must aim to minimise the amount of waste created in order to demonstrate industrial and economic feasibility. Therefore, it will be advantageous to recycle the salt used in the main pyrochemical processes as much as possible. Furthermore, the separation of fission products from the salt will not only minimise the final highly active (HA) waste volume, but will also remove the large water-soluble component that could potentially cause significant issues for disposal.

3.3.1. Exploratory studies of distillation in fluoride salts

At CEA, distillation was considered for the decontamination of the $LiF-AlF_3$ salt used in the pyrochemical liquid-liquid extraction process for the treatment of spent carbide or oxide fuel. In order to facilitate the adjustment of the $LiF-AlF_3$ composition to that required in the main process, it was also investigated whether it is possible to recover several fractions during the distillation, one being enriched in AlF_3, which would then be removed. The first important observation was the substantial reduction of the volume of FP-containing waste as 95% of the solvent salt can be recovered and recycled. However, although it was possible to obtain a phase enriched in aluminium compared to the initial solvent, its composition does not meet the requirements to fully optimise the flowsheet. For the successful implementation of fluoride salt distillation for clean-up and recycle, further work is required on development of the technology and apparatus to give better temperature control.

3.3.2. Evaluation of the processes for chloride salt decontamination

Zeolite ion-exchange was confirmed as the only demonstrated process for removing all of the fission products simultaneously, although the efficiency for the AMs (Cs/Rb) was particularly poor. A number of practical aspects of the zeolite-salt interaction were studied, including the implementation in column geometry, the effect of temperature and relative quantities, and competition effects.

Precipitation of the lanthanide FPs is feasible using a wet argon sparging process. This process does not increase the overall salt volume and yields $LnOCl$ or Ln_2O_3. It could be a relevant alternative to carbonate or phosphate precipitation

3.4. Waste Conditioning

3.4.1. Assessment of sodalite as a matrix for conditioning chloride wastes

The general aim of the work, performed jointly between ENEA, Polimi and CEA, was the evaluation of sodalite as a matrix suitable for containment of chloride salt wastes coming from pyroprocesses. The sodalite powder thus synthesized was then sintered by using a Hot Uniaxial Pressing equipment. The results of the leaching tests under static conditions show a significant release of the elements, especially at 90°C. Furthermore, SEM analysis puts into evidence an irregular surface and an underneath structure of the sample after 30 days of leaching, while a lot of small holes appear on the surface of the sample after 150 days. The initial dissolution rate determined by dynamic leach test using a soxhlet device can be estimated between 12 and 16 $g/m^2/d$ which is a too high value. All these data demonstrate that sodlaite is not a relevant matrix for for a high level wastes conditioning matrix.

3.4.2. Studies on chlorapatite as a matrix for spent chloride salt confinement

The potentialities of other oxychloride phases, like chloroapatite, $Ca_{10}(PO_4)_6Cl_2$, and chlorospodiosite, Ca_2PO_4Cl, have been studied, especially in terms of leaching behavior. These preliminary results are very positive, because the leaching study on sodalite was concluded by the fact that this oxychloride was not durable enough for high level waste. However, in order to study more precisely the leaching behavior of these phases, it would be necessary to optimize the densification parameters, and to perform two more leaching tests, under dynamic conditions with pure water at 100°C on a monolithic sample, in order to estimate the initial dissolution rate r_0 (soxhlet test) and also in static conditions on powder, in order to increase the S/V ratio, at 90°C, to estimate the residual leaching rate.

3.4.3. III.2.4.3 Studies on metallic matrices for conditioning metallic fission products

The electrochemical behaviour of copper-nickel alloys for conditioning metallic fission products has been studied in a synthetic groundwater. In aerated conditions, copper and copper alloys are covered by porous oxide/hydroxide layers which do not allow surface protection towards corrosion. Nevertheless, when nickel percentage increases into the copper matrix, corrosion resistance increases principally due to an improvement of film resistance. In aerated media, nickel and nickel alloys are passive. However, for nickel alloys passivation kinetic is reduced and samples are more sensitive to crevice and pits certainly related to discontinuities in the passive layer. In CO_2 saturated water, the difference between corrosion currents recorded on copper and nickel alloys are less marked. Copper and copper alloys have nearly the same behaviour than in aerated-only conditions. Nevertheless, with acidic environment the oxide layer is thinner (partial oxide dissolution) and this accelerates corrosion. Nickel and nickel alloys are more sensitive to this change of acidity. In fact, in such conditions, nickel is in a pre-passive domain which induces changes in the passive layer properties. The film could be less homogeneous and allow the diffusion of aggressive species towards the interface, therefore inducing an important increase of corrosion currents in comparison with those recorded in aerated conditions. Under this storage conditions, copper addition will be limited to 30 wt.%. Moreover, a localized corrosion could occur and disposal procedures have to prevent crevice or pitting corrosion. Given the weakness of the passive film induced by the presence of copper oxide within nickel oxide, the best compromise must be looked for, between the copper content in the volume of the material (for mechanical properties) and within the passive film for a greater corrosion resistance.

4. Integration – cross-cutting issues

All this work was carried out consistently with previous system assessments while still keeping an eye open on innovative routes. The studies helped to assess the most promising processes or process options and finally to propose relevant of viable flowsheets and technology elements for future integral tests and demonstration at the lab-scale.

The System Studies work package covered a range of work. The work undertaken by NNL had the initial aim of collating feedstock data in order to define a likely fuel type envelope for various separation processes and to obtain a notional map of the quantity and type of feedstock in terms of relevant isotopic content and other parameters. A theoretical calculation of various irradiated fuel parameters from basic data produced by the RED-IMPACT project was produced. This has shown that most fuels in a 2004 survey of reactor burnup and initial enrichment from European stations are within this envelope. The envelope calculation produced several different irradiated fuel parameters in order to aid in the design of separation processes.

This task was focussed on online monitoring for molten salts processes. Two different techniques were developed: the first one, the LIBS device (Laser Induced Breakdown Spectroscopy, also called Laser Ablation coupled with Optical Emission Spectrometry (LA-OES)) were developed by CEA teams. In the frame of a PhD thesis, UEdin manufactured and characterized microelectrodes to in situ analysis in molten salt.

In order to foster and strengthen the links between partitioning and transmutation with a view to consolidate future actinide recycling strategies, ACSEPT carried out studies to pave the way towards more integration between Partitioning and Transmutation. First the design of the MARIOS experiment which was implemented within FP7 FAIRFUELS was realized in ACSEPT to optimize the timing of FAIRFUELS. ACSEPT investigated also fuels and targets dissolution, conversion of separated elements to solid precursors prior to fuel fabrication. Conceptual reviews as well as system studies were carried out, which led for apart to the implementation of an experimental program within FP7 ASGARD. These actions contributed to reinforce the consistency of the research in the field of P&T.

Experimental results were integrated by carrying out engineering and systems studies on aqueous and dry (pyro) processes to prepare for future demonstration at a pilot level. However ACSEPT did not intend to deliver a picture of what could be a preliminary design of a future demonstrator, which would require a more technico-economical approach, out of its scope. The philosophy of process studies is rather to integrate the technical results generated within the technical domains so as to provide an early feedback on R&D, taking into account scale-up criteria. This guarantees the sound basis for the future design of a demonstrator.

5. Training and education

ACSEPT contributed to develop the integration of European education and training in the field actinide chemistry, to combat the decline in student numbers, teaching establishments and young researchers. thus providing the necessary competence and expertise for a sustainable development of nuclear energy. It provided an infrastructure which supported co-operative work among the European nuclear community.

ACSEPT supported the funding of post-doctoral students (two students funded on the first half of the project), the exchange of students between partners (11 students, 2–3 month stays) and helped students attending conferences, ACSEPT training sessions or summer schools. Two ACSEPT International workshops (Lison 2010 and September 2012 as a session of ATALNTE 2012 conference) allowed the young scientists to highlight their work and fostered the visibility of the Project..

6. Conclusions

After four years of work, major progress was achieved in ACSEPT. In aqueous reprocessing, efforts allowed the realisation of four hot-test. In pyrometallurgy, promising routes for the recovery of actinides from aluminium have been demonstrated. In addition, progress was also made in head-end steps (oxide to metal route, thermal treatment), salt recycling (fluoride salt distillation) and waste conditioning (metallic matrices). Last but not least significant efforts were made for dissemination activity and training of students, helping developing nuclear skills in Europe.

With the technical advances within ACSEPT it should be possible to propose options to Governments, European utilities as well as technology providers. A technically feasible strategy for recycling actinides will certainly produce positive arguments:

—— European decision makers and public opinion could be convinced that alternative solutions to nuclear waste management are now available.
—— The way towards a sustainable energy supply is paved.

DEVELOPMENT OF MECHANICAL PRESS FEATURE FOR FABRICATION OF SOLID AND ANNULAR PELLETS.

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Fabrication of Plutonium bearing fuel for different types of reactors is being carried out inside leak tight glove box train at Advanced Fuel Fabrication Facility, Bhabha Atomic Research Center, Tarapur. All the operations inside the glove box are carried out either manually or semi-automated way through gauntlets. As per the requirement solid as well as annular MOX pellets are fabricated using mechanical rotary press. Mechanical rotary press green pellet's acceptance is sensitive to the combination of granules size and powder characteristic. Process parameter also very as per the compaction of fresh powder and clean reject oxide(CRO).The rate of production on mechanical rotary press depends on turret revolution per minute(RPM) and the turret rpm is optimized considering the die size.die fill, dwell time & number of station available on the press.

The present paper describes the development of mechanical rotary press feature for fabrication of solid and annular pellets and highlights its associated issues.

INTRODUCTION

Advanced fuel fabrication facility (AFFF) , BARC tarapur is engaged in fabrication of plutonium bearing mixed oxide fuel for different type of reactors . Presently AFFF tarapur is manufacturing mixed oxide (PuO_2+UO_2) fuel pellets and elements for fast breeder reactor . The nature of material handled demands that the fabrication of the product to be carried out in leak tight glove boxes . So all the equipments required for the fuel fabrication are handled inside the glove boxes under negative press and process operation and maintenance are carried out either through gloves or through automation & remotezed system .

The conventional "powder to pellet" powder metallurgy route for fabrication of MOX fuel involves mechanical milling & mixing of UO_2 and PuO_2 powder , pre compaction , granulation and final compaction to a green density of 55 % - 60% of theoretical density . *(Fig – 1 shown the flow sheet for MOX fuel fabrication by conventional method)*. The compaction of powder and granulation is being carried out by mechanical rotary press for fabrication of solid as well as annular MOX pellets . The compaction in rotary is done as plunger follow cam profile (track) and final load is applied as it passes through compaction roller .

The present paper describes the development of mechanical rotary press feature for fabrication of solid and annular pellets and highlights its associated issue.

ROTARY PRESS DESCRIPTION: -

Rotary press is a machine for application of pressure under controlled condition of load, speed, and direction for compaction of powder and granules .

The compacted green pellets acceptance is sensitive to powder characteristics , granules size , shape and distribution, additives added and flow ability .

The other parameter which influence the compact qualities are die & plunger material, dimensions of final product, density requirement of final product , compression ratio and shrinkage during consolidation of compact . In rotary mechanical press , each compaction cycle consist of die fill , weight adjustment ,double acting synchronized compaction , dwell time and ejection . The pre compaction of ceramic powder are carried out at 5-8 tsi and final compaction at 18-20 tsi . *(Fig -2 shows the compaction cycles of mechanical rotary press)*

DEVELOPMENT OF ROTARY PRESS (FEATURE) : -

Development of rotary press started with single pressure (compaction) roller with constant turret rpm for making the pellets . *(Fig -3)*

To increase the performance of rotary press number of feature are incorporated on machine

1. Dwell time control by reducing turret speed.

2. Ejection under load 10-20 % of compaction load is applied by top plunger on pellet during ejection. This is required to avoid lamination cracks of the pellets. If this load is more vertical cracks can occurs.

3. Hydraulic compensation: -

    To the provide the Cushioning effect on compact during compaction .

    To apply the constant load even there is change in granules characteristic.

4. Weight adjustment - After die fill a small jerk is given to bottom plunger to settle the powder & remove entrapped air .

5. Hopper with stirrer or vibrator to free flow of powder / granule. It helps in proper die fill.

6. Pre-pressing before final compaction *(Fig -4)*

    20-40% of final compaction load is applied through pre-compaction roller before final compaction.

7. Compaction zone adjustment in die : -

    Both top & bottom rollers displaced simultaneously maintaining   the applied load. This allows us to change the compaction zone in die to use full die depth which increases the die life.

8. Annular pellet compaction :-

    Rotary press has been developed to make annular pellets .For making annular pellet, core rods need to be fixed on press for top & bottom plunger.

9. Online plunger cleaning system *(Fig -5)*

    During the fabrication of annular pellet top plunger needs regular cleaning . Rotary press has been developed for online cleaning of top plunger .

10. Glove box integrated mechanical rotary press. *(Fig -6)*

ADVANTAGE :-

1. Easy maintenance

2. Simple tooling for solid / annular pellets , i.e easy core rod fixing & replacements .

3. High production rate .

CONCLUSION:-

The above development leads to enhancement of quality of product *(Fig -7 &8)*, fast production and reduction in rejection of product

SCRAP RECYCLE STEPS

FUEL FABRICATION STEPS

PuO$_2$ — UO$_2$

Oxidized Scrap → Attritor Milling

Precompaction& Granulation

Compaction

Microwave/ Thermal Processing

Sintering

CRO

Dry Centreless Grinding

Rejects ← Vacuum Degassing

Stack Making

Rejects ← Pellet Loading

Fuel Element Welding

Decontamination

Decladding Reject Elements ← Wire Wrapping

Packing & Transport

FLOWSHEET OF PFBR MOX FUEL

FIG.-1

Rotary press compacting sequence

Upper compression roll

Upper raising cam

Cam body

Upper lowering cam

Cam body

Lower pulldown cam

Weight adjuster cam

Bottom of stand

Ejection cam

Lower pulldown cam

Lower compression roll

Fill   Scrape off   Underfill   Compression   Ejection   Knock off

FIG -2

BASIC ROTARY PRESS

FIG -3

PRE PESSING BEFOR FINAL COMPACTION

FIG -4

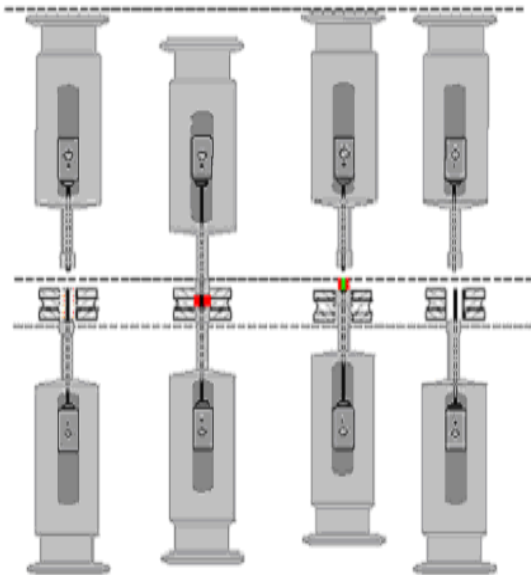**Online plunger cleaning system**

FIG -5

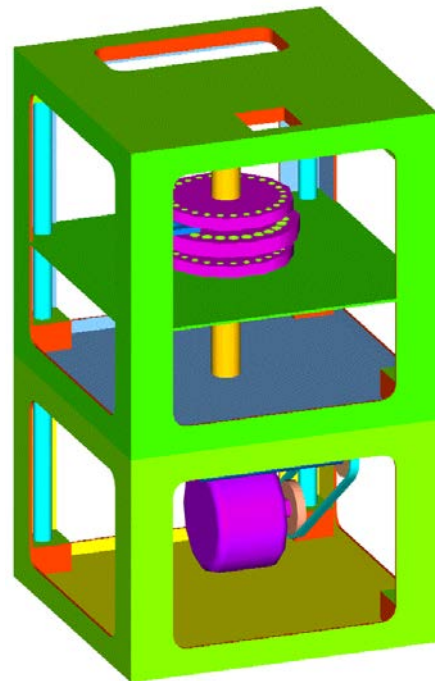**Glove box integrated mechanical rotary press**

FIG -6

(Fig -7) ANNULAR PELLETS

(Fig -8) SOLID PELLETS

Challenges in the design of Waste Management Plant (WMP) for Fast Reactor Fuel Cycle Facility (FRFCF).

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Abstract. A 500 MW, Prototype Fast Breeder Reactor (PFBR) is being constructed by DAE at Kalpakkam, Tamilnadu. Fast Reactor Fuel Cycle Facility (FRFCF) is also being planned as an integrated facility in close proximity to PFBR to cater to the need of closing the fast reactor fuel cycle. The design of waste management plant of FRFCF is one of the important and challenging tasks in FRFCF. The high burn up, short cooling period and high fissile content of spent fuel input from fast Reactors to FRFCF are the main reasons for the difficulties / challenges posed in the management of wastes from FRFCF. Separation of actinides and Platinum Group Metals (PGM) from high level liquid wastes, higher waste oxide loading in vitrified waste product from high level liquid waste management, development of better sorbent and chemical treatment method for achieving higher decontamination factors in the treatment of low and intermediate level liquid wastes and separation of plutonium from spent / de-graded solvent waste are some of the challenges which are addressed in this paper. Solid waste management is also associated with major challenges because of high volume of alpha contaminated wastes. Proper segregation, assaying, conditioning and treatment for volume reduction are planned. Management of significant amount of solid wastes generated as fuel hardware components (alpha and non-alpha) through proper storage and retrieval for future conditioning / disposal are also addressed in this paper. This paper describes the challenges faced during the design and solutions provided for each system.

1.   Introduction

Design of Fast Reactor Fuel Cycle Facility (FRFCF) at Kalpakkam is a first time effort in the history of Indian three stage Nuclear Power Programme aiming at construction and operation of an integrated facility to close the fuel cycle for Prototype Fast Breeder Reactor (PFBR). The FRFCF, an integrated facility in close proximity to PFBR, comprises of co-located five plants namely. Fuel Reprocessing Plant (FRP), Fuel Fabrication Plant (FFP), Reprocessed Uranium Oxide Plant (RUP), Core Sub assembly Plant (CSP) and Waste Management Plant (WMP). Utilities required for all the plants in the facility are drawn from a common services plant.

The plant design of WMP incorporates systems for treatment and conditioning of the radioactive liquid and solid wastes generated from different plants of FRFCF and also the secondary waste generated from WMP itself. Certain specific nature of spent fuel input from PFBR Viz., high burn up (〜100,000 MWD/Te), short cooling period (〜1 Yr) and high fissile content poses major difficulties / challenges in the management of radioactive wastes at FRFCF. The quantity of waste generation is quite substantial compared to the existing thermal reactor fuel processing. Another major difficulty in waste management is the association of higher alpha contamination in every stream of waste. These aspects makes waste management, a challenging task in FRFCF.

Prime importance is given to waste minimization, segregation and categorization at the design stage itself. Volume reduction is taken as the key factor while choosing the technologies used for management of wastes so that the radioactivity is effectively contained [1]. The treatment schemes are

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selected by adopting the principles of ALARA ("As Low As Reasonably Achievable") such that the annual dose to general public due to discharges to the environment through different routes is within the prescribed apportioned limit for this facility as provided by regulatory authority.

2. Features of Waste Management Plant

WMP consists of three major blocks Namely Main Process Building (WMP Building), Solid waste Treatment Plant (SWTP) building and Near Surface Storage and Disposal Facility (NSSDF). WMP building houses treatment and conditioning systems for Liquid Wastes. Hull compaction system and containerisation system for alpha bearing solid wastes are also planned in WMP building. SWTP building houses treatment and conditioning systems for low level non alpha bearing solid wastes (Category-I). Different engineered barrier facilities like Stone Lined Trenches (SLT), Reinforced Cement Concrete Trenches (RCCT) and Special Vaults (SV) are provided at NSSDF for disposal of non alpha solid wastes (category I, II & III). Alpha Storage Facility (ASF) block is provided as a part of NSSDF for interim storage of conditioned alpha bearing solid wastes (Category IV) [2].

3. Treatment Scheme and Process Description

3.1. Liquid Wastes

Liquid wastes are broadly classified as (a) High Level Liquid Wastes (HLW): higher specific activity (> 1Ci/lit), higher concentrations of long lived radionuclide (Transuranic/TRU) and higher decay heat (b) Intermediate Level Liquid Wastes (ILW) : moderately low specific activity (1- 1000 mCi/lit), very low concentrations of long lived isotopes (TRU) and very low decay heat (c) Low Level Liquid Wastes (LLW): low specific activity (1- 1000 µCi/lit), insignificant trace concentrations of long lived isotopes (TRU) and no decay heat (d) Organic Liquid Waste (OLW): degraded solvent generated from FRP, specific activity in the range of 0.1 – 1 mCi/lit with low alpha contamination [2].
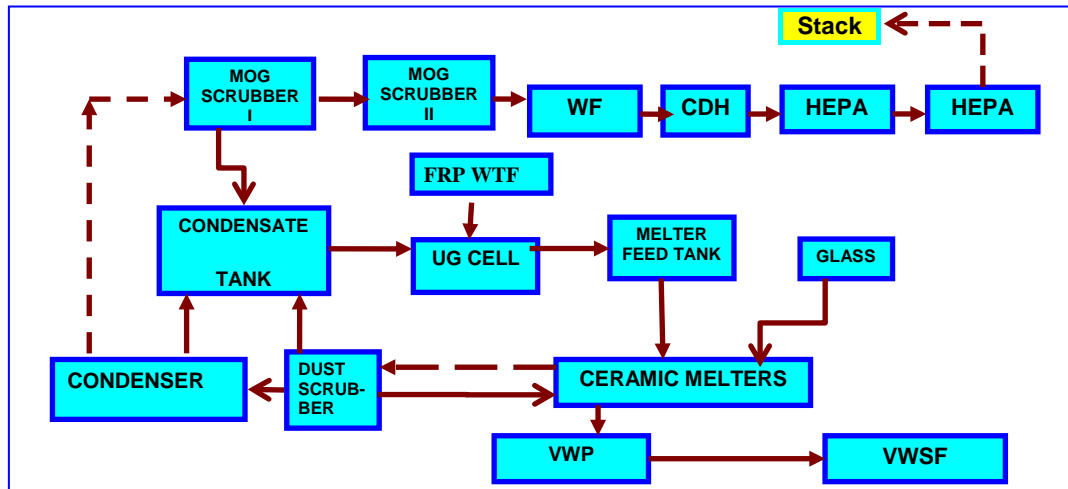

FIG. 1. HLW TREATMENT SCHEMATIC

a) HLW is treated by direct vitrification route in continuous feed Joule Heated Ceramic Melter (JHCM) with extensive off-gas treatment system. The treatment schematic for HLW is given in Figure 1. The concentrated acidic HLW after adequate cooling period in waste tank farm of FRP is transferred to receiving tank at WMP through pipe-in-pipe transfer line placed inside shielded waste transfer trenches. Secondary waste generated during vitrification process is returned back to FRP via same trench route for concentration. The off gas generated during vitrification in JHCM passes through dust scrubber, condenser, two stages of scrubbers, washable filter (WF), chiller-demister-heater (CDH) and two stages of high efficiency particulate air (HEPA) filters before releasing to the environment through stack. JHCM is operated in continuous mode of feeding and product glass pouring in intermittent mode. The product canister filled with vitrified glass product is sealed followed by surface decontamination. Sealed and surface decontaminated product canisters are transported in shielded cask to Vitrified Waste Storage Facility (VWSF) at Kalpakkam for interim storage.

b) ILW generated in FRP are of two type; acidic ILW and alkaline ILW, with wide radioactivity spectrum. ILW is transfered from waste tank farm of FRP to receiving tanks at WMP through transfer lines similar to HLW transfer. Acidic ILW with low total dissolved solids (TDS) and moderate concentrations of TRU are directly treated along with HLW stream through vitrification route. Alkaline ILW stream with high TDS and trace TRU contamination are treated by ion exchange process followed with two stages of chemical precipitation as per schematic given in Figure - 2. Cesium and Strontium specific organic cat-ionic ion exchange resins are used in ion exchange process. The loaded resins are eluted and the eluate is concentrated for vitrification along with HLW. The downstream solution from ion exchange process is treated by two stages of chemical precipitation process for removal of ruthenium and other radionuclides. The precipitates from chemical treatment steps are fixed in cement matrix and the filtrate from second stage precipitator is routed to delay tanks for treatment along with LLW.
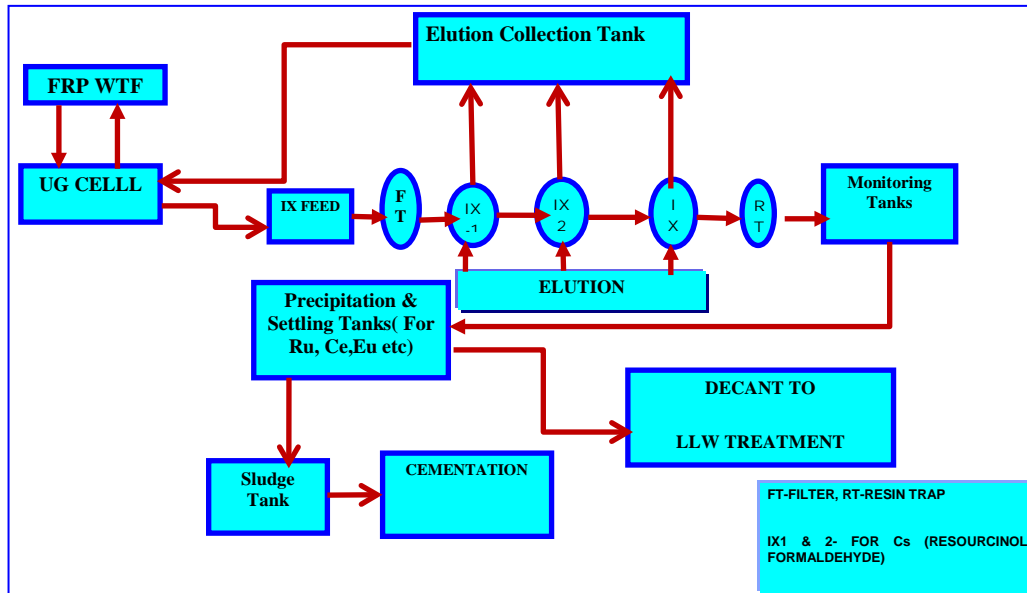

FIG. 2. ILW TREATMENT SCHEMATIC

c) LLW generated from all facilities of FRFCF are received in underground stainless steel lined RCC delay tanks at WMP via over ground pipe line. Depending upon the chemical nature and specific activity, LLW is received in separate compartments of delay tank. Segregation as detergent waste and non-detergent waste are done at the source of generation for ease of treatment. Category-II and III wastes are treated by chemical treatment method.

Continuous sludge blanket clarifier is used for precipitation. Online mixer is used for chemical mixing. The dilute sludge is dewatered by continuous solid bowl centrifuge before cementation of sludge. The decant of clarifier is transferred for sea discharge after monitoring. The potentially active wastes (PAW) like steam condensate, wastes from sinks and showers etc., are monitored prior to transfer for sea discharge. The active decontamination of protective wears is also a part of LLW management system.

d) The spent solvent waste generated in FRP are treated by alkaline hydrolysis process. OLW is received in UG receiving tank at WMP from waste tank farm of FRP via transfer lines similar to HLW transfer. OLW is pre-treated for removal of alpha contamination before subjecting to alkaline hydrolysis process. The Alkaline hydrolysis process is a batch process with a cycle time of 4h - 6h. The reaction between OLW and alkali is accomplished by heating the reaction mixture by steam in a jacketed vessel with agitator and reflux condenser. The top organic phase (Dodecane) in the reactor is incinerated along with incinerable Cat–I solid wastes. The middle phase is subjected to evaporation for separation of organic and aqueous phase. The bottom aqueous phase is immobilized in cement matrix in cementation cell. The OLW treatment schematic is given in FIG. 3.
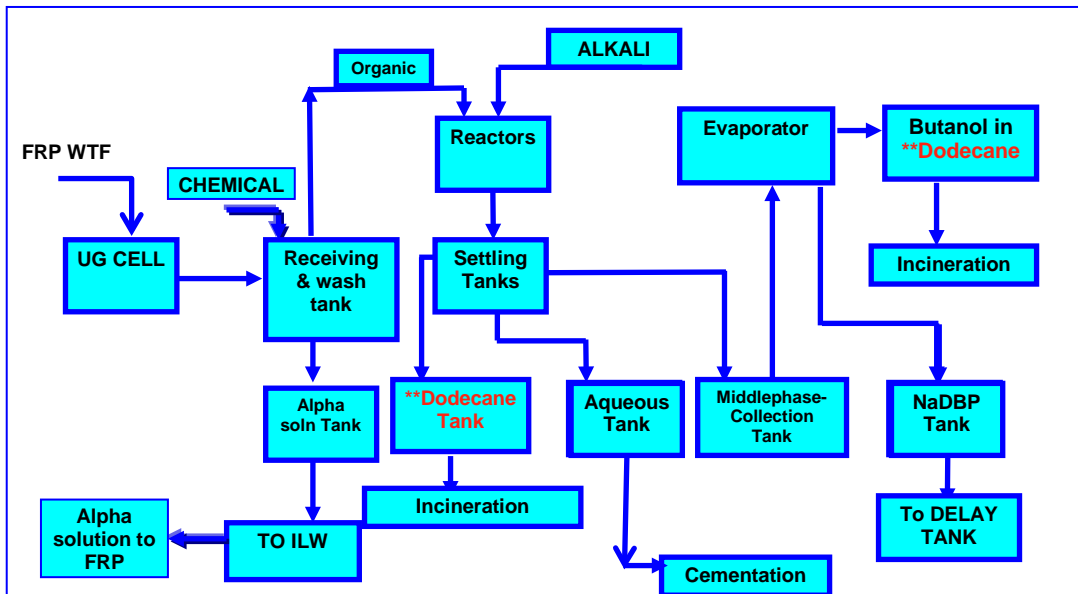
FIG. 3. OLW TREATMENT SCHEMATIC

3.2. Solid Waste Management

The management schematic for solid wastes is given in FIG. 4.
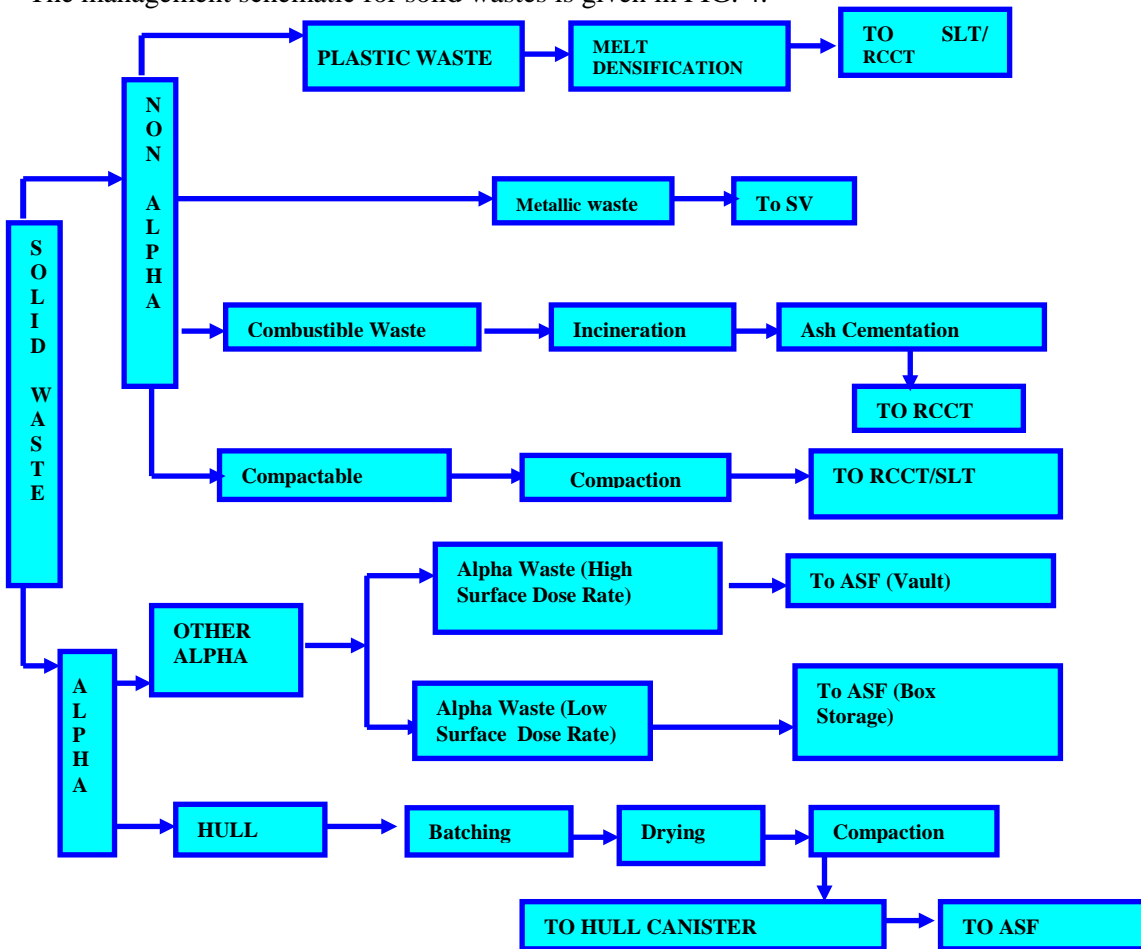

FIG. 4. SOLID WASTE TREATMENT SCHEME

Non-alpha (Cat-I) solid wastes like HEPA waste and compactable wastes are subjected to compaction. Plastic wastes (Cat-I) like PVC shoes, rubber gloves etc., are volume reduced by melt densification process. Combustible wastes (Cat-I) like tissue paper, cotton waste etc., are subjected to incineration along with dodecane waste. Disposable solid waste packages up to 20mR/h contact surface field (Cat-I) is disposed off in SLT and packages above 20mR/h and up to 50R/h surface field (Cat-I, Cat-II & Cat-III) are disposed off in RCCT. Cat-III solid wastes like fuel hardware having dose rate above 50R/h (Cat-III) are stored in SV for subsequent processing / disposal in RCCT. SLT, RCCT & SV are all located in NSSDF. High active hull wastes (Cat-IV) from FRP are repacked in standard canisters after compaction. High active alpha contaminated metallic waste and hardware components (Cat-IV) from FRP are also packed in standard canisters. After remote lid welding and surface decontamination, these canisters are stored at ASF located in NSSDF. Alpha bearing Solid wastes with associated Low beta-gamma contamination (Cat-IV with surface field<200 mR/h – contact handleable) from FRP and FFP are packed in sealed double polythene bags and over packed in SS drums at the source of generation. Four such drums are placed in a custom designed special type rectangular steel box. These rectangular boxes are stored in ASF. Individual boxes at ASF have ventilation supply and exhaust connected to a Negative Pressure System through a common plenum.

4. Design Features

Process safety and industrial safety aspects are considered during design of facilities at WMP. Radiation protection aspects like shielding, ventilation, zoning and man and material movement aspects are taken care during design stage. Sufficient process margins are considered to take care of the variations in annual generations. Redundancies are provided for the critical process / process equipment for maximum availability and minimum down time of the plant. Decontamination/decommissioning aspects of all equipment inclusive of Joule melter is also considered during the design. Accordingly, three independent bays of vitrification blocks are provided as one for working, another for hot stand by and the third for decommissioning and refurbishment. Each of the vitrification bays is provided with three hot-cells namely feed and off gas cell, melter cell and welding and decontamination cell segregating operations involved with handling of liquids and soilds. All utilities to the three vitrification bays like services, material handling and remotization, ventilation systems etc., are physically separated from each other in order to facilitate ease of operation, decontamination and decommissioning. In-cell equipments are designed for minimum maintenance and long life period matching with plant life.

The maintenance prone self-shielded Ion Exchange column assemblies, valves and pumps in the ILW treatment system, agitator and pneumatic valves of OLW management system, in-cell cranes, power manipulator, master slave manipulators, in-cell trolley systems etc., are designed and located with the criteria of ease of operation and maintenance with limited man-rem exposure. Proper segregation of low level liquid waste is done according to its nature and specific activity. Detergent wastes are totally isolated from non- detergent wastes from treatment consideration. All treatment systems for liquid wastes inclusive of LLW treatment system are planned inside closed vessels connected to separate vessel off-gas system by which contamination of equipment location area is prevented by design.

Proper segregation, categorization and volume reduction are considered as prime design objective for solid waste management. Large volume Category-I solid wastes are provided with volume reduction treatment systems like incineration system for combustibles, mechanical compaction system for compressible like filters and metal scraps, thermal compaction system (Melt densification system) for plastics and cement fixation system for treatment concentrates. The incineration system is designed for incineration of separated do-decane stream from OLW treatment system along with combustible solid wastes.

All treatment systems are provided with separate off gas treatment units, separate ventilation systems and remote handling systems for proper control of operational exposure. Improved off gas treatment scheme is adopted by using multistage scrubbers and filters so that the radio and chemical toxicity release to the environment through the gaseous route is minimum.

NSSDF is designed within the close proximity (~3 Km) of FRFCF so that radioactive material transportation is within the nuclear facility and not through public domain. A detailed geology and

hydrology studies were done for the NSSDF site before its selection. Based on the conditioned waste generation rates of different categories, disposal facilities with different engineered barriers like SLT, RCCT and SV are designed. All disposal facilities are designed for disposal of wastes in un-saturated zone. These disposal facilities are designed as discrete modules which can be constructed periodically over the years utilising a common material handling system to reduce investment cost. Care is taken in design that at no time excavation activity will be there at locations downstream to existing disposal modules. SV is designed as a transit storage module for non alpha high surface field wastes like fuel hardware waste components prior to disposal in RCCT / reconditioning treatment. Alpha storage facilities at NSSDF are designed for above ground interim storage of alpha bearing solid wastes prior to their ultimate treatment process / disposal in repositories.

Only fully established and proven processes are designed and included in WMP. However, WMP is designed with adequate expansion space and provisions for extension of required services for implementation of new processes under development like vacuum distillation of separated do-decane from OLW treatment system, actinide separation process for HLW, volume reduction and decontamination processes for alpha bearing soild wastes etc. The design of WMP is made in such a way that the inclusion of processes under development at a later stage will be possible without shutting down any of the operating processes.

5. Design Improvement and Challenges of WMP

Improved design provisions are incorporated in WMP based on the operational experience of the earlier plants. The challenges posed in HLW management are due to higher concentrations of actinides in HLW and higher concentrations of Ruthenium. Adequate cooling period of HLW is planned to avoid the problems associated with Ru volatility in melter. In HLW treatment process, improved design feature like three independent bay of vitrification system providing for redundancy and adaptability for incorporation of design changes in melter, minimum activity inventory in liquid form inside melter cell by providing a separate Feed and Off-gas cell, closed pouring system for prevention of spread of contamination, improved material and refractory selection in melter design, cell ventilation filter at the source, improved off gas treatment system etc are implemented. These design changes contribute to not only improve the process efficiency but also has provided improvements in decommissioning aspects, life of melter, decontamination factor with respect to vitrification process and radiation protection aspects. Development of process and validation is underway for actinide partitioning of HLW through hydrometallurgical processing employing different synthesized solvents like organophosphorous based CMPO and TEHDGA [3]. Development of suitable glass matrix and new melter technology like cold crucible technology is also underway to increase the waste oxide loading in vitrified glass product [4]. Accordingly, the design provisions are made in the HLW management system to incorporate implementability of the new processes without taking any shutdown of the plant.

The challenges posed in ILW management are high TRU content in acidic ILW stream and higher concentrations of Ru, Tc, Ce etc. WMP is designed to vitrify acidic ILW stream directly along with HLW. The design of alkaline ILW management system incorporates multiple steps of IX treatment and precipitation treatment so that high net decontamination factors can be achieved. Development of new sorbents / ion exchangers and new chemical reagents for removal of radionuclide like Ru, Ce, Tc [5] etc is under advanced stage of development which can be implemented in the process system at WMP. Spent solvent waste is likely to have higher concentrations of TRUs which requires to be removed before subjecting the waste to hydrolysis treatment. Separation of TRUs from this stream through two different routes namely oxalic acid / uranus are under development. The design of OLW Management system is done for incorporation of this step as and when the process is validated. Such pre-treatment steps and multiple processing steps improve the processing efficiency, volume reduction factor and over all DF of the process.

Considering the potential of trace contaminations by TRUs in LLW stream, LLW treatment processes are planned in completely closed vessels with vessel off gas treatment system to prevent air born contamination in plant areas.

Cladding hull wastes from fast reactor fuel reprocessing facility is a heat generating source unlike similar waste from thermal reactor fuel reprocessing. Design provisions are made in the ventilation system of hull processing cells and conditioned hull storage vaults to ensure temperatures are within acceptable limits even during station black out. Cladding hull wastes is a high level waste requiring retrievable storage till disposal in deep underground formations. Considering the cost of such space, a volume reduction process of hull compaction is under development and accordingly, WMP is designed to accommodate this processing step. Volume reduction processes like incineration, compaction and melt densification which provide high volume reduction factors to the large volume inventory wastes providing savings in disposal space are adopted with separate off-gas treatment and area ventilation system in the management of Category-I solid wastes. Proper segregation of solid waste and assaying provision is also incorporated in design of solid waste management system.

At NSSDF, new design features are incorporated in the above ground engineered barrier facilities like SLT, RCCT and SV. The salient aspects are disposal in unsaturated zones, top levels above design based flood levels, under drain and over drain systems, maximum utilization of disposal space, modular constructions with common extendable material handling systems etc. A significant amount of fuel hard ware component waste which is mainly contaminated with short lived isotopes like Co^{60} and Mn^{54} are generated having high surface filed. SV is designed to retrievably store them for an interim period for subsequently processing / disposing in RCCTs. New alpha transit storage facilities are also designed with the consideration of remote handling and retrievable above ground storage. All the transit storage facility is designed with proper shielding, ventilation and radiation protection aspects so that during operation and maintenance time, man-rem exposures are minimum. Treatment processes for combustible alpha bearing solid wastes are under development. The ASF for such of these unconditioned wastes are designed with high levels of safety with a planning to retrieve and process in future by using validated technologies. Space provisions and logistics are planned adjacent to ASF for implementing this at a later stage.

6. Design Safety, Radiation Protection and Environmental Aspects.

The waste management facility is designed without compromising safety of the plant, personnel and environment, incorporating safety from collection of waste to disposal of waste. The civil structures of WMP building and ASF are designed for functional under Safe Shutdown Earth Quake (SSE) conditions. The floor level of the building is sufficiently raised so that it is above design based flood level considering 1000 years of return period inclusive of tsunami, tide surge, storm and rains. The Class III power supply systems are located at higher elevations for reliable availability. The power supplies are provided with redundancies with equipment locations and routings in such a manner that fire in one system does not affect the functioning of redundant system. Transfer of active liquid waste from reprocessing facility is carried through underground shielded tunnel in double containment SS pipe with provision for collecting leakages, if any. Design provision is made for monitoring activity in the secondary pipe by continuous air monitoring system during liquid transfer. The double containment is provided with proper sloping on either side to aid gravity drainage and to prevent stagnations. Stress analysis of piping and pipe supports and equipment and equipment supports related to High level liquid waste management system are carried out for integrity under process conditions and during SSE conditions. Closed pouring ventilation system has been designed for joule heated ceramic melter, which will prevent spread of contamination due to gaseous activity while pouring of vitrified waste glass into product canister. Remote operation for IX system, separate maintenance area for agitators of alkaline hydrolysis reactor, valve and pumps cubicles for ease of operation and maintenance etc., are provided in the IL and OL waste treatment system. Independent remotely operable inline cementation system is provided for cement fixation of sludge generated from treatment of IL and OL wastes. Hot cells handling Cladding hull wastes and the hull storage facilities are designed to take care of heat generation in waste mainly due to short lived radio-nuclides.

The facility has been separated into different radiation zones namely Red, Amber, Green and White based on planned activities inside the building. Once through filtered air is supplied to green zones of the building and are exhausted through amber and red zones so that air flow pattern is from low active area to high active area which prevent cross contamination and in turn create progressively higher negative static pressures. The exhaust air is filtered through pre and HEPA filter banks before

dispersal to atmosphere at 75 m elevation through RCC stack. The exhaust fans are provided with Class-III supply with redundancies to ensure reliable operation. Instrumentation interlocks are provided in the ventilation system to keep the building at negative pressure with respect to atmosphere. All operations involved with high active liquid and solid wastes are planned inside shielded cells with remote operation gadgets like Radiation shielding windows, Master Slave manipulators, Power manipulators, remotely operable in-cell cranes, welding machines, special trolleys etc. Redundancies have been considered for all major equipment of supply and exhaust ventilation system, process tanks, Off-gas filters etc., and for liquid transfer lines and transfer operations. Radiation monitoring instruments and radiation surveillance systems are provided inside the plant areas with Distributed radiation Protection Console (DRPC) instrumentation with redundant Class-II power supply connections to ensure their reliable operation.

In order to ensure minimum release of radioactivity to environment, the waste management systems are planned with high decontamination factors. The activity in Category V, IV and III are concentrated and contained in stable matrices like vitrified glass forms or cement matrix with a high DF. Off gases generated from these treatment systems are treated in Off gas cleaning equipment like scrubbers in series, chiller for dehumidifying, demister, heater, composite filter and HEPA filters before releasing to environment at 75 m elevation through stack achieving a DF of around 10^6. Continuous air monitoring of the stack releases is done to ensure releases within statutory limits. All filtering equipments are provided with 100% redundancy in order to operate the facility continuously. The off gas treatment systems are located at higher elevations with respect to corresponding liquid waste treatment systems to provide for natural draft. Category-II liquid wastes are treated by chemical treatment thereby providing a DF of 10 to100 and the treated liquid is discharged to sea along with Category-I liquid wastes after providing adequate dilution and monitoring before discharge ensuring activity concentrations within their permissible limits as stipulated by regulatory authorities. The conditioned Category-I, II and III solid wastes are disposed in engineered barrier facilities at NSSDF with provisions for active surveillance of ground water, soil and atmospheric air to ensure early detection and remedial action in the event of accidental release of activity to environment. The conditioned Category-IV wastes are stored in above ground engineered barrier facilities.

7.   Future Plans and Provisions

Waste management facility of FRFCF has been provided with various future plans for incorporating processes under advanced stage of development and demonstration. The major provisions are actinide separation unit for separation of actinides from high level waste and dodecane purification system.

Separate area adjacent to the waste management facility has been planned to locate the actinide separation unit. In order to receive and transfer HLW between the reprocessing facility, high level waste treatment block of WMP and future Actinide separation plant, design provisions for extension of underground (UG) trench lines with double containment piping system has been given. Design provisions are also given to extend all necessary utilities inclusive of man and material movement provisions to the future actinide separation plant from WMP without shutting down any of the operating systems at the time of extension.

Vacuum distillation for refining separated n-dodecane from alkaline hydrolysis process of spent solvent treatment system is also in advanced stage of development. A separate hot cell is provided in WMP and is located adjacent to IL/OL processing cells with all necessary external extensions of process piping, utility piping, remote handling systems etc for incorporating the vacuum distillation process under development. In addition to above, design provision is made for incorporating a pre-treatment process for removing fissile content from spent solvent waste for recovery.

Other future plan is space provisions in WMP for incorporation of a reverse osmosis treatment unit and bio de-nitration treatment system at the downstream of LLW treatment system aiming at Zero discharge of radioactivity to environment through liquid waste treatment route.

8.   Summary

Design of FRFCF at kalpakkam is a first of its kind in the history of Indian three-stage Nuclear Power Program aiming to close the fuel cycle for PFBR. Management of wastes arising from reprocessing of

high burn up, short cooled and high fissile content fast reactor fuel and the corresponding fuel cycle facilities like fuel fabrication plant, reconverted uranium oxide plant and core sub assembly plants pose lots of challenges. The design of waste management plant has addressed all these concerns and with the support from development of new processes like actinide separation, modification of glass matrix formulations, development of new sorbents, separation of fissile content from spent solvent waste, hull compaction system etc., the challenges are reasonably met providing the required high decontamination factors at waste management plant so that radioactive discharges to environment is well within the limits imposed by regulatory bodies. The design improvements have also reduced the waste volume considerably which are required to be disposed and stored. Design has incorporated process safety, industrial safety and radiation safety at all levels inclusive of safety during severe conditions like earth quake and tsunami and thereby reducing the risk of man-rem exposure to occupational workers and public at large.

Acknowledgements

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New extraction agents based on the 2.6-disubstituted pyridines for HLW partitioning

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Abstract. Synergistic extraction mixtures of 2.6-bis(1-(3-methylphenyl)-1H-tetrazol-5-yl) pyridine (MeATP) with chlorinated cobalt dicarbollide (CCD) in m-nitrobenzotrifluoride (F-3) proposed for selective extraction of the transplutonium elements (TPE) in acidic media ($\beta_{Am/Eu} > 100$). In nitric acid the extractability of actinides decrease in the range: Am(III) > Pu(III) > Pu(IV) > Pu(VI) > U(VI) > Np(V) and $\beta_{Am/Np} > 2000$. Among the HLW components Cs. Sr. Tb-Tm. Pb. Pd. Ni and Co extract remarkably. The fundamental technological flowsheet for separation of TPE. cesium and strontium from PUREX-process raffinate was developed and tested. The separation factor of americium and the sum of rare-earth elements on the three-stage countercurrent extraction is about 1000.

1. Introduction

Transplutonium elements have very high radiotoxicity and prolonged half-live periods. Recovery of TPE and its transmutation allows to simplify the process of HLW final disposal. Dialkyl-substituted triazinylpyridines (BTPs) effectively separate americium and europium in moderately acidic media (up to 1 M HNO_3) [1]. but have low stability in to acid. Countercurrent test were carried out with the mixture of 0.01 M iPrBTP and 0.5 M solubilizer – dimethyldioctyl hexylethoxy malonamide as extractant. To prevent BTP degradation. the hydrazinium nitrate was added into wash solution [2]. but after two cycles the extraction efficiency decreased by 40 %. We have found that 2.6-bis(1-aryl-1H-tetrazol-5-yl)pyridines (ATP) have very high stability to hydrolysis and γ-radiolysis [3]. The characteristics of the ATP change slightly after irradiation up to dose 2.4 MGy or 24-hours boiling with 6 M HNO_3. The main goal of our work was to develop and to test the fundamental technological flowsheet on the base of ATP for separation of TPE. cesium and strontium from PUREX-process raffinate.

2. Experimental Procedure

2.1. Reagents and methods used

The 2.6-bis(1-(3-methylphenyl)-1H-tetrazol-5-yl) pyridine (MeATP. Fig. 1) used in this work were synthesized in St.-Petersburg State Technological Institute (Russia) [3].
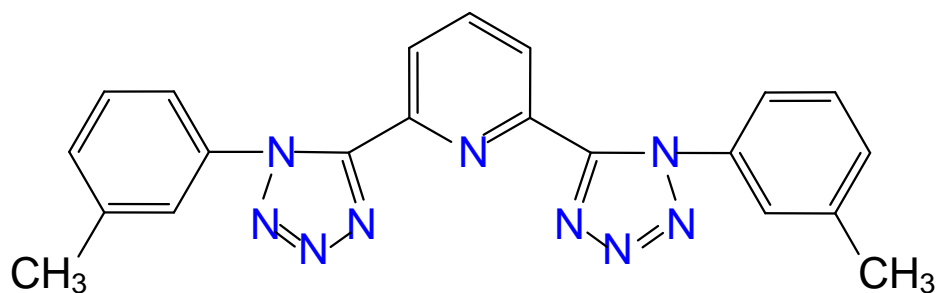
FIG. 1. Structure of the 2.6-bis(1-(3-methylphenyl)-1H-tetrazol-5-yl) pyridine (MeATP)

Meta-nitrobenzotrifluoride (F-3. RHODIA. France) was used as diluents for MeATP. Cesium salt of chlorinated cobalt dicarbollide (CCD) was produced by "KatChem" Co (Czech Republic). Process solutions were prepared by exact weighing portions of substance.

To determine the distribution ratios of radionuclide. organic and aqueous phases were poured into polyethylene test tube and stirred at $20\pm2^{o}C$ for 5 min. As follows from the preliminary test data. this duration was sufficient to establish equilibrium. The phases were separated by centrifugation; then samples of each phase were taken into polyethylene tubes. Radiometric measurements were conducted on scintillation gamma-spectrometer using a 51×51 mm NaI well detector (Canberra).

2.2. Results and discursion

Actinides and fission product extraction by extractant 0.02 M MeATP – 0.02 M CCD in F-3 from HNO_3 media was studied. It was found that actinides distribution ratios decrease from Am(III) to Np(V): Am(III) > Pu(III) > Pu(IV) > Pu (VI) > U (VI) > Np (V) with separation factor $\beta_{Am/Np} > 2000$ (Fig. 2).
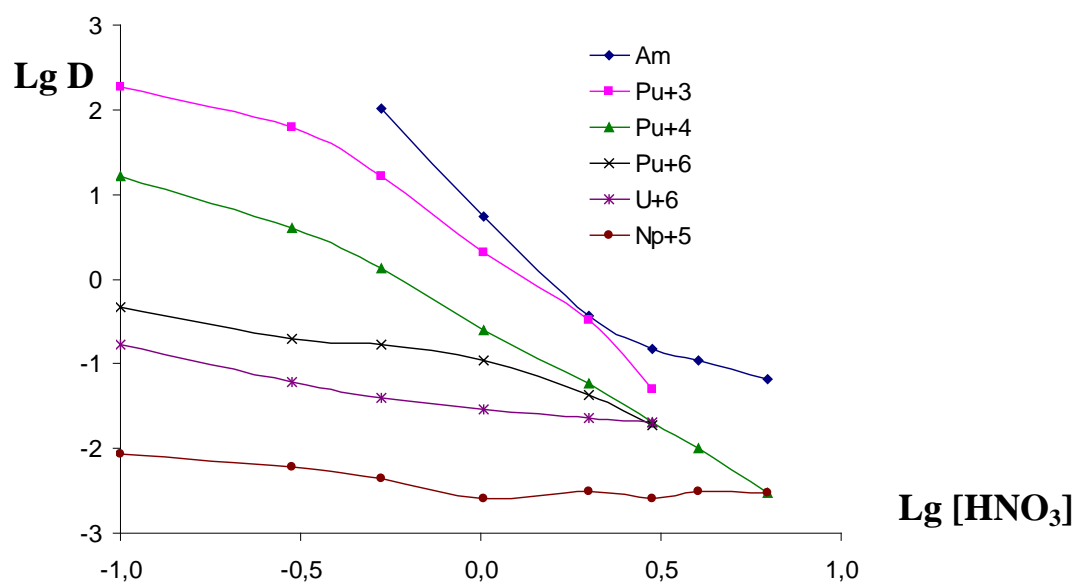
FIG. 2. Extraction of actinides by extractant 0.02 M MeATP – 0.02 M CCD in F-3 from HNO₃.

Among the HLW components Cs. Sr. Pb. Pd. Ni and Co extract remarkably (Fig. 3).
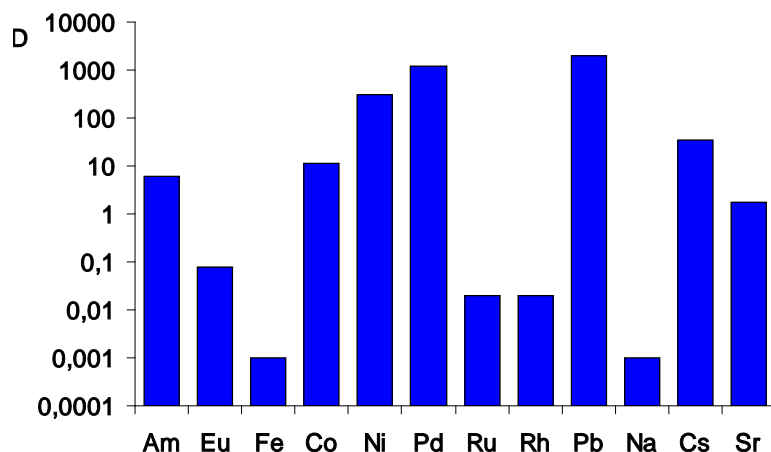
FIG. 3. Extraction of radionuclides and sable components of HLV by extractant 0.02 M MeATP – 0.02 M CCD in F-3 from 1 M HNO₃.

The extractant 0.05 M MePhATP + 0.05 M CCD in F-3 was used as it provided the high distribution coefficients of Am and demonstrated the adequate capacity for REE. The solution simulating the high-level raffinate of PUREX - process arising from reprocessing of MOX fuel with burn-up of 26 GW*d/t was used as simulated HLW. The high content of REE is the characteristic feature of this solution.

2.3. The flowsheet development

The Am/Eu separation factor begins to increase on attaining the phase volume ratio of Org:Aq =2:1. Further increase of extractant excess has no influence on selectivity. After three successive contacts of extractant with fresh simulated HLW the value of Am distribution coefficient is equal to 1.04. which affords the effective extraction process under counter-current conditions.

A series of other metals. including REE. is extracted in combination with americium. To produce more pure americium. these metals should be removed by selective stripping. The complexones like citric. oxalic and oxyethylidene diphosphonic acids were unsuccessfully tested as selective stripping agents for REE. In composition of stripping agent some substances were introduced which form cationic particles in acidic medium capable of displacing Am and Eu cations from extract into aqueous phase. Hydrazine. acetamide and carbamide were tested as such cation displacing agents. The application of acetamide or carbamide permits to obtain the distribution coefficients of Am and Eu which are needed for effective separation of them at the stage of selective REE stripping. The solution of 0.3 M

carbamide in 0.3 M HNO_3 is chosen as selective stripping agent. The simulated HLW solution and such strip agent are mixed in any ratios without precipitation.

As a strip agent for all radionuclides the solution of methyl ammonium carbonate (MAC) with DTPA additions is chosen. Intercycle regeneration of recycled solvent is to be conducted by 3M HNO_3.

As a result of the studies the flowsheet has been elaborated for extraction separation of americium and REE (scheme and relative flowrate are given in Fig. 4).
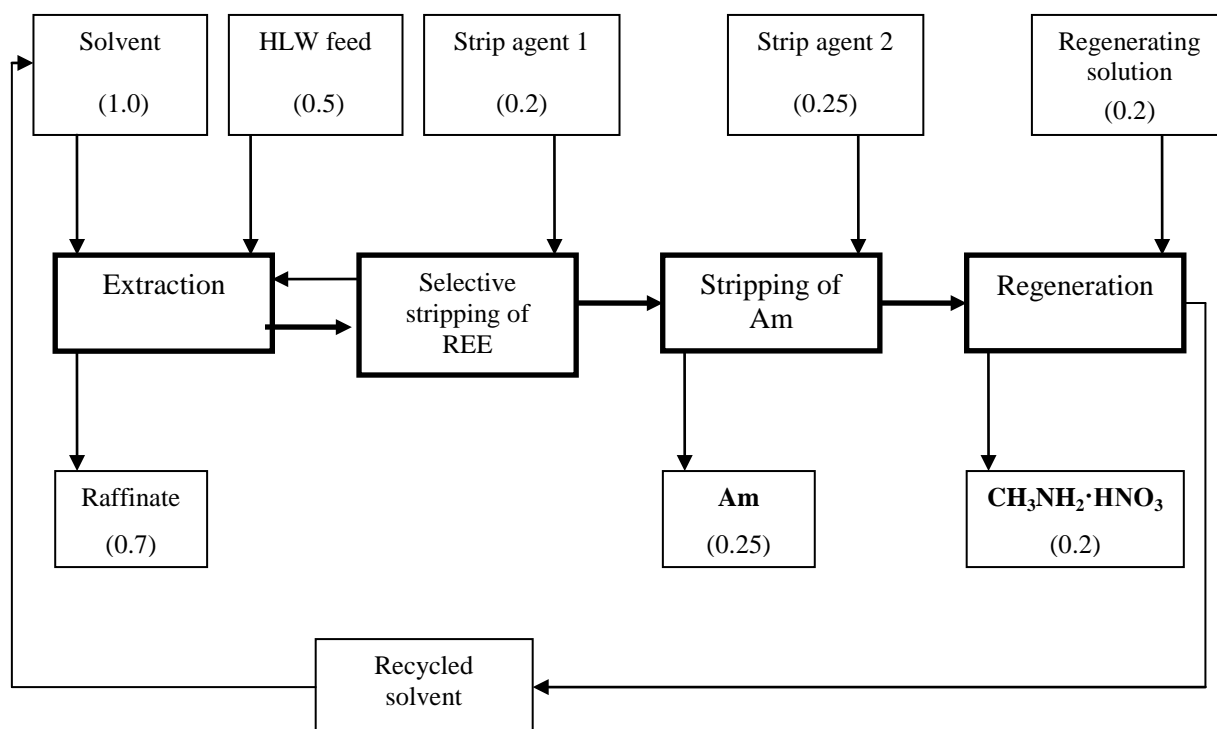
FIG. 4. The flowsheet for extraction separation of americium from HLW

In connection with the detected kinetic features of the extraction system MeATP+CCD in F-3 – HNO_3. which prevent the dynamic testing on the vibration minicolumn. it was decided to replace these tests by a combination of static tests. Two options of the static tests were used: cross-current and counter-current. Experiments in crosscurrent conditions consist of three successive contacts of fresh simulated HLW solution with one portion of extractant. The scheme of countercurrent tests presented on Fig. 5. In accordance with these two procedures the main operations of the flowsheet for REE – TPE separation were modeled.
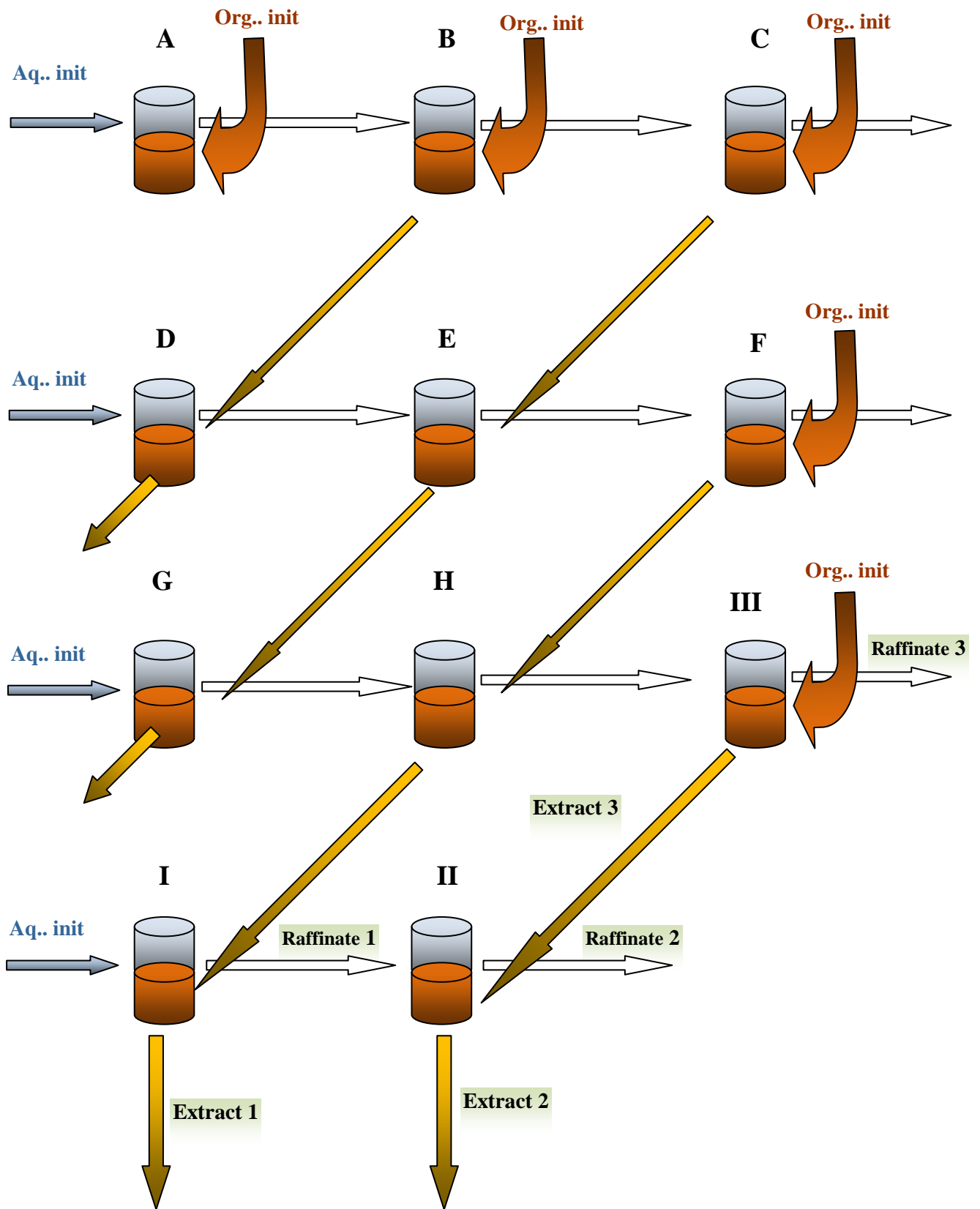
FIG. 5. Schematic diagram of experiment in countercurrent regime

2.3.1. Extraction

Experiments on modeling the countercurrent extraction were performed in the regime of crosscurrent which adequately models the saturation of extractant by recoverable radionuclides.

At the first stage the nitric acid (3M HNO_3) containing 10^{-3} M $Eu(NO)_3$ with addition of Am^{241} and Eu^{152} traces was used as initial solution. The results obtained are presented in Table 1.

Table 1. Distribution ratios of Am^{241} and Eu^{152} over stages of crosscurrent flowsheet

Stage number	1	2	3
Distribution ratio of Am	11.24	12.47	11.33
Distribution ratio of Eu	0.21	0.18	0.04
Separation factor	54	69	283

On the basis of the data given in Table 1 the following conclusions can be drawn:

- value of Am distribution ratio remains constant at all extraction stages;

- value of Eu distribution ratio decreases at the expense of displacement effect at each subsequent stage of extraction process. resulting in considerable increase of separation factor (more than 200).

At the second stage the simulated solution contained a mixture of REE in concentrations corresponding to their content in real PUREX-process raffinate. The results obtained are shown in Table 2.

Table 2. Extraction of REE according to crosscurrent flowsheet

Component	Concentration in simulated solution. g/l	Concentration in extract. g/l (after third stage)
HNO_3	0.5 M	below 0.01 M
Y	2.2	Not determined
La	5.76	below 0.01
Ce	10.8	below 0.01
Pr	4.9	below 0.01
Nd	19	below 0.01
Sm	3.6	0.27
Eu	0.7	0.32
Gd	0.54	0.40

It is evident that only Sm, Eu and Gd are left in extract under conditions of complete saturation of extractant with REE. Americium is extracted by 99.7 % under these conditions. The other REE are displaced into aqueous phase and the separation factor of Am and REE attains 50.

At the third stage the simulated solution contained the main stable components of real PUREX-process raffinate (Table 3) with addition of trace quantities of Am^{241} and Eu^{152}.

Table 3. Composition of simulated HLW (1 M HNO_3)

Elements	Concentration. g/l	Elements	Concentration. g/l
Cs	0.941	La	0.339
Rb	0.11	Ce	0.635
Sr	0.235	Pr	0.288
Y	0.129	Nd	1.118
Zr	0.75	Sm	0.212
Mo	0.936	Eu	0.042
Ba	0.45	Gd	0.032
Na	2.84	Cr	0.255
Fe	1.6	Ni	0.255
Pd	0.24	Co	0.27

The results obtained are given in Table 4.

Table 4. Distribution ratios of Am^{241} and Eu^{152} over stages of crosscurrent flowsheet

Stage number	1	2	3
Distribution ratio of Am	7.15	0.27	0.11
Distribution ratio of Eu	0.30	0.009	0.004
Separation factor	24	30	28

Based on the data given in Table 4. the following conclusions can be drawn:

- values of Am and Eu distribution ratios decrease at each subsequent stage; this is connected with reducing the concentration of free extractant due to co-extraction of palladium and nickel;

- value of Am and Eu separation factor is constant at each stage.

Hence. the purification ratios of Am from REE should be attained in the range of 30 ÷ 200 at extraction stage depending on HLW composition.

2.3.2. Selective stripping of REE

The selective stripping of REE was checked in countercurrent regime. Extract was produced by one contact of extractant with simulated feed solution containing 9.5 g/l REE in 1 M HNO_3. The solution of 0.3 M $(CO(NH_2)_2)$ in 0.7 M HNO_3 was used as selective strip agent. The results obtained are shown in Table 5.

Table 5. Distribution ratios of Am^{241} and Eu^{152} over stages of countercurrent flowsheet

Stage number	1	2	3
Distribution ratio of Am	9.4	9.0	14.0
Distribution ratio of Eu	0.31	0.19	0.17
Separation factor	30	50	84

The obtained data point to the practically complete (by 99%) scrubbing of extract from europium. The americium losses with REE strip solution do not exceed 7.5%. In the process flowsheet this strip product is combined with feed and thus there are no TPE losses generated.

2.3.3. Stripping of TPE and regeneration of extractant

All the investigated components of HLW are completely recovered by the solution of methyl ammonium carbonate (MAC) with DTPA additions. In operation of extractant regeneration by 3 M HNO_3 solution the complete washing of methylammonium from organic phase is achieved on three stages at Org/Aq ratio of 2:1. After such washing the extractant does not differ in properties from the fresh one. For performing the tests we used the same portion of extractant subjected to regeneration more than 20 times. No changes in its extraction properties were observed. The conducted static tests data was used to calculate distribution of the main HLW components over products of the flowsheet (Fig. 4) for separation of TPE from HLW. The calculation results are presented in Table 6.

Table 6. Distribution of main components of HLW (% of initial value) over products of process flowsheet for separation of TPE from HLW

Component	Raffinate	Strip product Am	Regenerating solution	Recycle extractant
^{241}Am	< 0.3	> 99.0	< 0.01	< 0.1
^{152}Eu	> 99.0	< 0.7	< 0.01	< 0.01
Total REE	> 99.8	< 0.1	< 0.01	< 0.01

The results obtained confirm the possibility of using the mixture of 0.05 M MeATP + 0.05 M CCD in F-3 for selective recovery of TPE fraction directly from PUREX-process raffinate.

2.3.4. Distribution of stable components of simulated HLW

The experiment on investigating the behavior of stable components of HLW was performed under static conditions. The scheme of crosscurrent test consist of one extraction, one REE stripping and three TPE stripping stages. The simulated HLW (Table 3) three times diluted by 1 M HNO_3 was used as feed solution. The application of the diluted solution allows avoiding the extractant saturation and makes it possible to obtain the data on distribution of

all metals. Composition of REE strip agent: 0.3 M carbamide in 0.7 M HNO_3; TPE strip agent: 1 M MAC + 5 g/l DTPA in water. The experimental results are given in Table 7.

Table 7. Distribution of ^{241}Am and stable components of simulated HLW over main products (% of content in initial HLW)

Product	^{241}Am	Eu	Ce	Co	Cr	Cs	Ba	Fe	Gd	La	Nd	Rb	Sm	Sr	Zr	Ni
Raffinate	4	40	76	8	92	5	74	88	41	79	61	14	45	11	58	48
Strip product REE	23	17	0	7	-	12	10	-	11	0	1	30	22	28	4	-
Strip product TPE (stage 1)	76	3	0	62	0	43	1	0	6	0	0	27	1	50	6	57
Strip product TPE (stage 3)	0.4	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0

It is evident that only cobalt, nickel, rubidium and lead are co-extracted with TPE. These elements are adequately stripped by carbonate strip agent and do not accumulated in recycle extractant.

3. Conclusion

The fundamental flowsheet scheme for recovery of TPE from PUREX-process raffinate by the synergistic extraction mixture MeATP and CCD has been elaborated. A possibility of using the extraction mixture 0.05 M MeATP + 0.05 M CCD in F-3 for selective recovery of TPE. Cs and Sr directly from PUREX-process raffinate has been demonstrated. The separation factor of ~1000 has been achieved for Am and REE sum. As to the investigated stable components of HLW, only cobalt, nickel, rubidium and lead are co-extracted. All these elements are effectively stripped by carbonate strip agent and are not accumulated in recycle extractant.

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Metallic Fuel Casting Development and Parameter Optimization Simulations

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Abstract. One of the advantages of metallic fuel is the abillity to cast the fuel slugs to near net shape with little additional processing. However, the high aspect ratio of the fuel is not ideal for casting. EBR-II fuel was cast using counter gravity injection casting (CGIC) but, concerns have been raised concerning the feasibility of this process for americium bearing alloys. The Fuel Cycle Research and Development program has begun developing gravity casting techniques suitable for fuel production. Compared to CGIC, gravity casting does not require a large heel, which must then be recycled during subsequent casting operations, does not require application of a vacuum during melting, and is conducive to re-usable molds. Development has included fabrication of two separate benchscale, approximately 300 grams, systems. To shorten development time computer simulations have been used to ensure mold and crucible designs are feasible and to identify which fluid properties affect casting behavior most and therefore require more characterization.

Introduction

The casting process is a key component of the metallic fuel cycle. The metallic fuels in the past were fabricated in a variety of ways including swaging, extrusion, and casting. The most successful process, and most recently used on a larger scale, is counter gravity injection casting, which was used to fabricate all of the fuel for the EBR II. Although this process proved reliable and robust, there remained concerns with 1) volatile element retention due to the vacuum or reduced pressures employed, 2) waste issues caused by the one time use of quartz molds, and 3) low melt utilization caused by the necessary large heel which must be recycled. To address these problems, gravity casting has been proposed as an alternative casting approach. Gravity casting would allow higher melt utilization because no large heel is required. Element volatilization can be controlled through the use of over pressure and covered crucibles and waste can be reduced by the application of a permanent mold that can be re used for several casting runs. To demonstrate the feasibility of gravity casting, a bench scale casting system (BCS) was designed, fabricated, and installed into a radiological fume hood. The BCS, shown schematically in Figure 1, is designed to simultaneously cast three pins with a total mass of up to 300 grams. The crucible and mold are independently inductively heated. The current mold is a graphite "cup and cone" design, which allows for re-use. A similar furnace, designated as the Glovebox Advanced Casting System (GACS), has been designed for glovebox use and has also been fabricated and is slated for use in minor actinide bearing alloy casting development. A schematic of this furnace is also shown in Figure 1.

Despite the long history of fuel casting very little data has survived as to the liquid metal and alloy properties. Much of the casting was done based on operator experience with respect to the appearance of the melt. As new casting processes are developed and new operators begin working in the field this experience base is becoming less and less available. In order to reduce development time, computer simulations can be used to determine if proposed designs are feasible or not. An effort was undertaken to construct computer models of the casting processes using the BCS or BCS type furnaces where fluid flow can be modelled. This can help determine which parameters are important and need further

research. A parameter that was identified early on was gas compressibility. Since earlier models were not able to include this parameter, the modelling software was switch to Flow 3D. Several simulations have been run to determine the importantance of gas compressibility and surface tension. Results from these simulations have then been used to guide fluid property characterization and to improve casting equipment design.
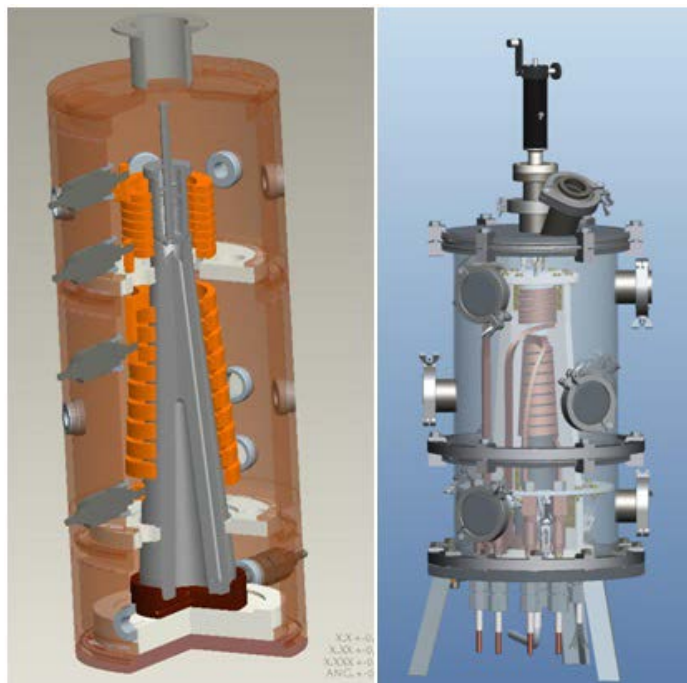

FIG. 1. Schematic view of two bench scale casting system. Left)Bench-scale casting system, note stopper rod mechanism is not shown. Right) Glovebox Advanced Casting System.

Casting Development Work

The results discussed in this paper will focus on the BCS experience because at the time of writing the GACS has not yet been used for casting of actinide material.

The nominal dimensions of the BCS cast pins were designed to be 4.3 mm diameter × 250 mm length (0.170 in. × 10 in.) which is similar to the EBR-II Mark III and Mark-IV fuel slugs (although shorter). It was also thought that this would be a conservative design because, in general, the larger the length to diameter ratio, the more difficult the casting becomes because the melt will solidify before reaching the full length. Because of this high aspect ratio, it was thought that a pressure differential would be needed to assist the melt in reaching the full length of the pin. The pressure differential is created between the vessel (crucible) pressure and the mold cavities. The differential is produced by resting the mold on a vacuum feedthrough allowing the interior of the mold to be at a reduced pressure. The mold cavities are connected to the mold interior through small holes or channels. Because the mold is not actively sealed against the vacuum fitting it was not a true vacuum, but rather a reduced pressure when compared to the crucible and vessel. The pressure differential is between 0.5 and -1.0 atmosphere (relative to the chamber), system limitations preclude making a more definite measurement.

Initial casting attempts were performed using depleted uranium although results were similar for 90wt% uranium 10wt% zirconium charges (U-10Zr). The charges were heated and held at the casting temperature for some period of time until the charge was fully melted. One second before the stopper rod was lifted, the pressure differential was applied to the mold and the stopper rod lifted. The resulting pins were typically segmented Figure 2 shows an example of the typical resulting segmented

pins. To improve pin quality a variation on this approach was also attempted, using U-10Zr instead of pure uranium. Here, the pressure differential was applied 0.5 seconds after the stopper rod was lifted, in order to give the melt time to fully fill the volume above the mold cavities before the differential drew the melt into the mold cavities. This run also resulted in segmented pins. Inspection of the cast pins did show mold features from the bottom of the mold so it was concluded that the fluid was readily flowing to the bottom of the mold.

FIG. 2. Segmented depleted uranium pins cast using the BCS under a pressure differential. Note the scale shown is in inches.

During an early fabrication campaign of the AFC-1 metallic fuel irradiation test series, a lab scale arc-casting technique was used to cast the fuel slugs. It was discovered that a certain amount of back pressure was needed to cast solid samples. In these arc-casting processes the back pressure is obtaining by inserting loose plugs into the bottom ends of the quartz molds in order to obtain different levels of back pressure. When too much back pressure was present, i.e. the plugs are too tight, the material would not drop into the mold. If insufficient back pressure was present, i.e. plugs are too loose , the material would drop but not produce a solid rod, forming either small pellets (segmented slug) or, more often, a hollow straw. As the casting results were discussed and compared to previous arc-casting experiences, it was decided to attempt casting without a pressure differential and allow the channels to provide some amount of back pressure. When this was attempted, the resulting rods were solid with only a few thinned cross sections. Of the 250 mm mold length, solid rods of approximately 178 mm (7 in.) were produced. The resulting rods are shown in Figure 3.
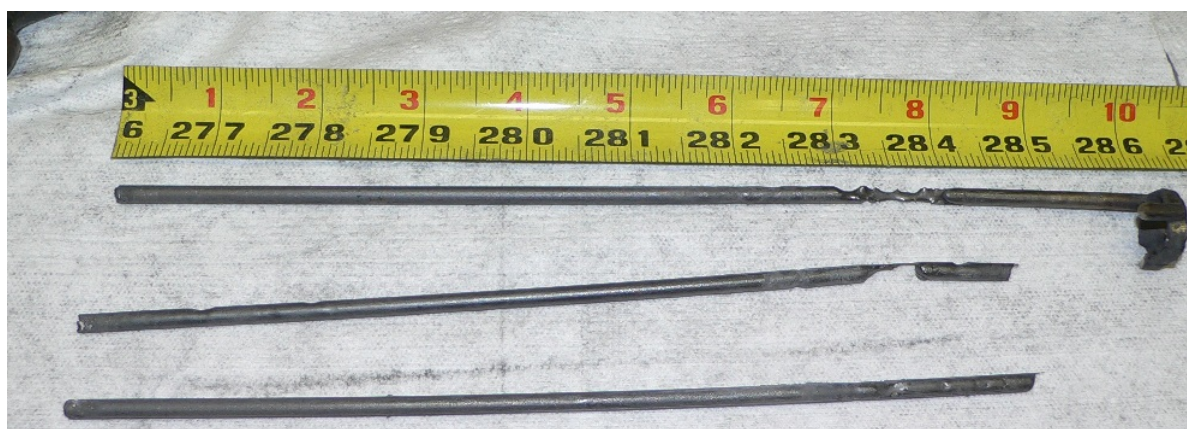

FIG. 3. U-10Zr pins cast at approximately 140 kPa (1050 Torr). Note scale shown is in inches.

From these experiments it was concluded that back pressure or gas compressibility was important and needed to be incorporated into the computer simulation. It is assumed that under a large pressure differential the material flow is very turbulent and breaks into smaller pieces which then solidify before they can be joined together again. When the differential was applied, the rod length decreased, which resulted in segmented rods. Modeling results conducted without the capability of gas compressibility support this conclusion.

In a typical casting run, the mold is inductively heated to a pre-heat temperature either under pressure or dynamic vacuum. At this point, the mold inductive power supply is shut down and the crucible is heated and held at casting temperature. During this time the mold begins to cool, except for the upper most portion, which is heated by the crucible. Because of facility power limitations at the time of design and fabrication, only one power supply could be utilized at one time. For the purposes of this report, the mold pre-heat temperature will be the temperature at which the power supply was turned off, not the temperature at casting time since this temperature is monitored but not controlled. Two levels of mold pre heat were investigated: 800°C and 1000°C. In both cases the castings were performed with molds that had not been coated.The resulting pins from either pre-heating temperature were not full length, froze before reaching the bottom of the mold, and were similar in length.

FIG. 4. Comparison of pins cast at either 1000° or 800°C mold preheat.

Most uranium cast throughout the nuclear industry is cast into coated graphite molds. The coatings are usually yttria, although other materials such as erbia have been used. Casting in the BCS typically use a yttria coating. The main purpose of the coating is to limit melt/mold interactions, which may contaminate the uranium and hinder pin removal. The coating application can be a laborious process, is often operator dependent and even small defects can lead to flaws or contamination in the cast part. The coating can also lead to production of additional waste and may necessitate a secondary cleaning operation of the cast part. Although it is standard practice to use a coating, casting without a coating would be preferable. Neither the 800° nor the 1000°C castings reached full length which shows the importance of the yttria mold coating functioning as a thermal barrier. Without the coating, even at 1000°C, the material solidified before reaching the bottom of the mold. In neither case was there any discernable reaction with the graphite mold. A general difference between most of the casting in the uranium industry and the casting research described in these studies is the scale of operation. In the BCS, the amount of graphite in the mold is much larger than the amount of uranium being poured into it. This situation is reversed in most industrial casting operations. Thus, although there was no reaction between the mold and melt in the BCS, this may not translate to an industrial scale because the amount of uranium would be increased more than the amount of graphite. On the other hand, this may indicate a chill casting type arrangement would be successful. Because of the relative thermal masses of the graphite and melt in the BCS and, despite the mold active heating, the mold essentially acts as a form

of chill casting, which causes solidification to occur too quickly for any interaction with the mold to occur. This phenomenon may be useful in other casting techniques such as a continuous casting process. These casting results indicate that the presence of a thermal barrier between the mold and the molten material is more important than the mold temperature. On close examination of the pin castins in Figure 4 it can be seen that, despite the 200° difference in pre heat temperature of the mold, the final pin lengths are very similar. A mold pre-heat temperature of 800°C appears to be adequate, but additional experiments and/or simulations are necessary to confirm the lowest temperature at which fuel could be cast and flow the length of the mold.

Another parameter considered was the casting temperature. In the BCS, the casting temperature or amount of superheat is measured by a thermocouple placed between the crucible and the refractory surrounding the crucible. The term superheat refers to the number of degrees above the melting point of a material at the time of casting. Since the melt point of U-10Zr is approximately1380°C, there is a 70° superheat when casting at 1450°C. Although the results have varied somewhat at 1450°C, it has been demonstrated that this temperature is adequate for the melt will drop into the molds and form continuous pins. However, there has consistently been a large amount of the melt that does not drop into the mold cavities, as can be seen in Figures 3-4. In order to reduce this residual material the casting temperature was increased an additional 100° to 1550°C in order to allow the melt more time to drop into the mold cavities before solidification. The resulting pins were composed of many segments (none longer than 64 mm), with many of them to be considered only short pellets (5-10 mm in length). Clearly, increasing the superheat by 100°C caused the casting quality to drop dramatically. This underscores the need for experimentation and modelling to be well coupled so as to not only decrease the number of experiments but also to guide which material parameters need to be better characterized.

Casting Modelling

Flow3D is being used to investigate the importance of surface tension and gas compressibility. A model incorporating the charge, outer and inner mold coponents, crucible, and stopper rod was input into the software based on actual BCS component dimensions and charge sizes. Modeling in Flow3D involves activation or deactivation of different models to consider the desired physics. The baseline Flow3D model considers gravity, heat transfer, and solidification. Surface tension and compressibility will be investigated separately.

Table 1 presents the fluid properties used in this model. Properties of either pure uranium or U-6Nb were employed and assumed to be near those of U-10Zr when its properties were not available. Fluid density was based on the U-6Nb density work done in [1]. Specific heat, thermal conductivities of liquid and solid uranium, and the latent heat of fusion are taken from [2]. Liquidus and solidus temperatures were estimated for U-10Zr based on phase diagrams [3-6].

Table 1. U-10Zr properties used n Flow3D model.

Density (kg/m^3)	Specific Heat (J/kg*K)	Thermal Conductivity (W/m*K)	Liquidus (°C)	Solidus (°C)	Latent Heat of Fusion (J/kg)
17,400	201.3	26	1340	1240	38,720

The initial mold temperature was taken as a gradient from 257°C K at the bottom to 851°C at the top. The crucible and molten charge are at an initial temperature of 1500°C. The initial temperature of the void inside the mold is 327°C. The first order heat transfer model considering the full energy equation is activated within Flow3D. Heat transfer occurs between the melt and the mold, the melt and the argon cover gas, and between the different mold components. A heat transfer coefficient of 100 W/m^2*K was defined for interface heat transfer between the outer and inner mold components and the inner mold and the chill plate.

Modeling Compressible Argon

Flow3D's adiabatic bubble model was used to simulate compressibility of the Argon gas filling the mold. The adiabatic bubble model simulates argon as an ideal gas and is advantageous because it idealizes the argon as a "free-surface" flow. The gas is treated as a region of uniform pressure and temperature taking away the need to determine the dynamics of the gas. This is an excellent approximation for situations such as this because the U-10Zr is approximately 10,600 times more dense than the argon, making the inertia of the argon negligible. The adiabatic bubble model requires the ratio of specific heats (Cp/Cv) and the void pressure as inputs. For argon, the ratio of specific heats is 1.667, taken from the open literature. The void pressure was taken as atmospheric pressure (1.013x105 Pa). Figure 5 illustrates an adiabatic bubble coming up through the melt during filling due to insufficient venting.

FIG. 5. Argon simulation as an adiabatic bubble passing through the melt during mold filling due to insufficient venting of the mold.

When using the adiabatic bubble model to model a second fluid, venting can be achieved by using valves. To define a valve, only the location of the valve and a loss coefficient based on the cross sectional area of the vent and the discharge coefficient are necessary. To define the loss coefficient, vent holes of diameter 0.762 mm were used. The Flow3D manual states that the discharge coefficient typically has a value of 0.5 for sharp entrances so this value was used. Vents were placed at four locations: bottom of the mold, midway up the mold, near the top of the mold, and at the bottom of the crucible. Figure 6 shows the results of the casting simulations using each pone of these valve locations. Table 2 shows the total time to fill for each condition.
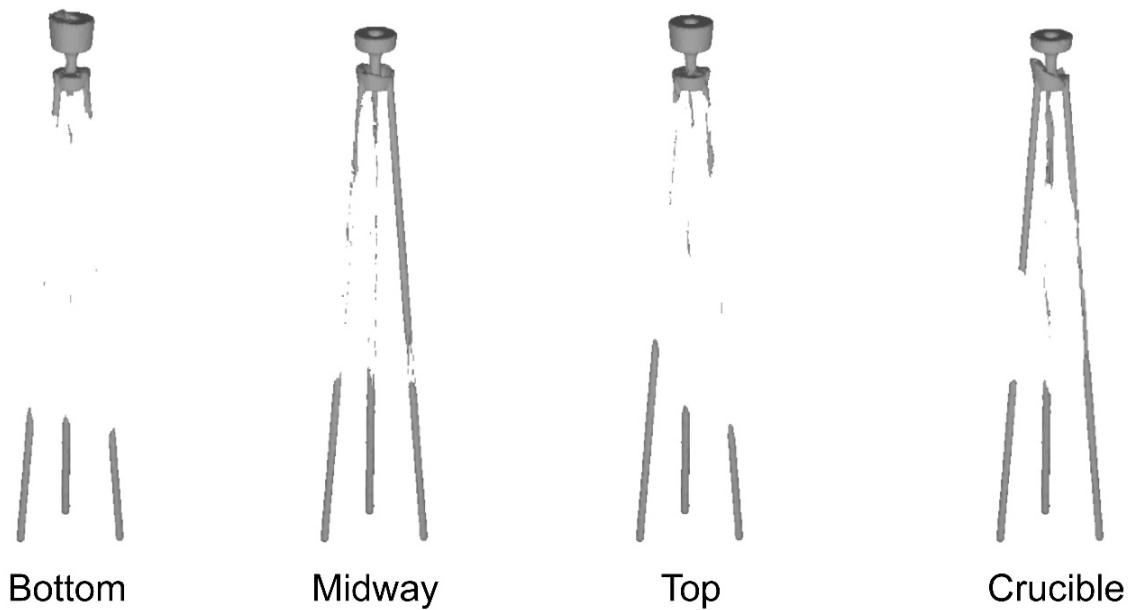
FIG. 6. Simulation results for venting of the assembly at the bottom, midway, or top of the mold or bottom of the crucible.

Table 2. Filling time for each vent location.

Bottom	Midway	Top	Crucible Bottom
1.7 sec.	1.7 sec.	2.1 sec.	1.5 sec.

Surface tension is a property of a liquid that allows it to resist an external force. It has the units of force per unit length. Flow3D's surface tension model accepts a surface tension coefficient which was estimated for U-10Zr to be 1.55 N/m. Greater surface tension causes the fluid to splatter less and break up less when filling the mold, as can be seen in Figure 7. In Figure 7, the left side of each image represents the simulation without surface tension while the right side represents the simulation considering surface tension. For an evacuated mold, inclusion of surface tension effects do not affect the fill time. Figure 8 shows that while surface tension does not appear to have an appreciable effect on the simulation results when filling an evacuated mold, it does affect the simulation results when the adiabatic bubble model is used to simulate a mold initially occupied with compressible argon. Figure 8 considers the four venting scenarios discussed above. In Figure 8, the left image for each scenario represents the final state of the simulation without surface tension while the right image represents the final state of the simulation including surface tension. Inclusion of surface tension in the model causes argon to become potentially trapped between different sections of the casting, a very undesirable situation. The best way to remedy this problem is to vent the mold at multiple locations. Perhaps at the bottom, midway up, and at the base of the crucible.
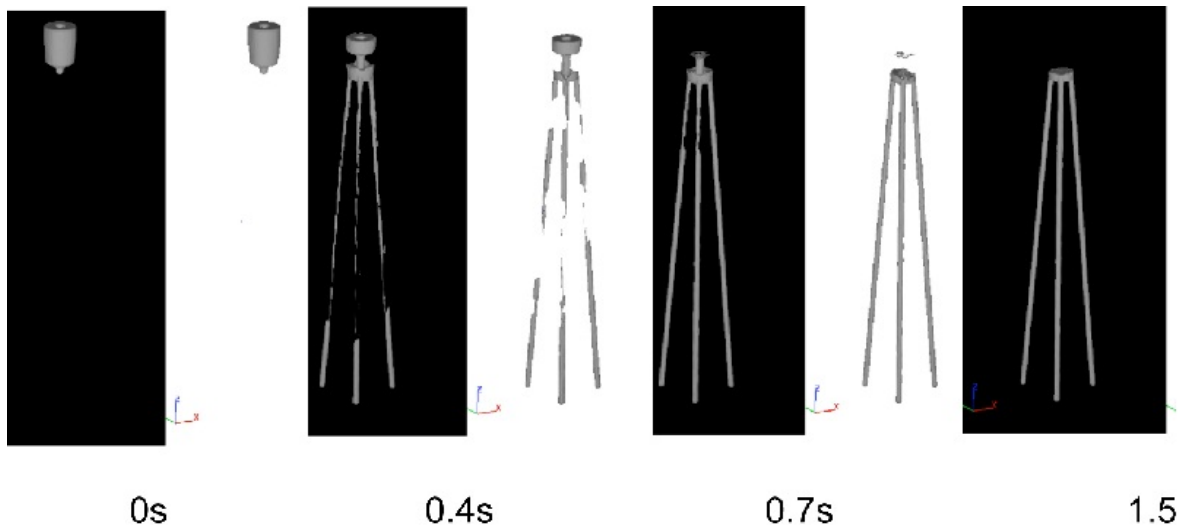
FIG. 7. Effects of surface tension on an evacuated mold. The left side graphic does not take into account surface tension while the right graphic does.
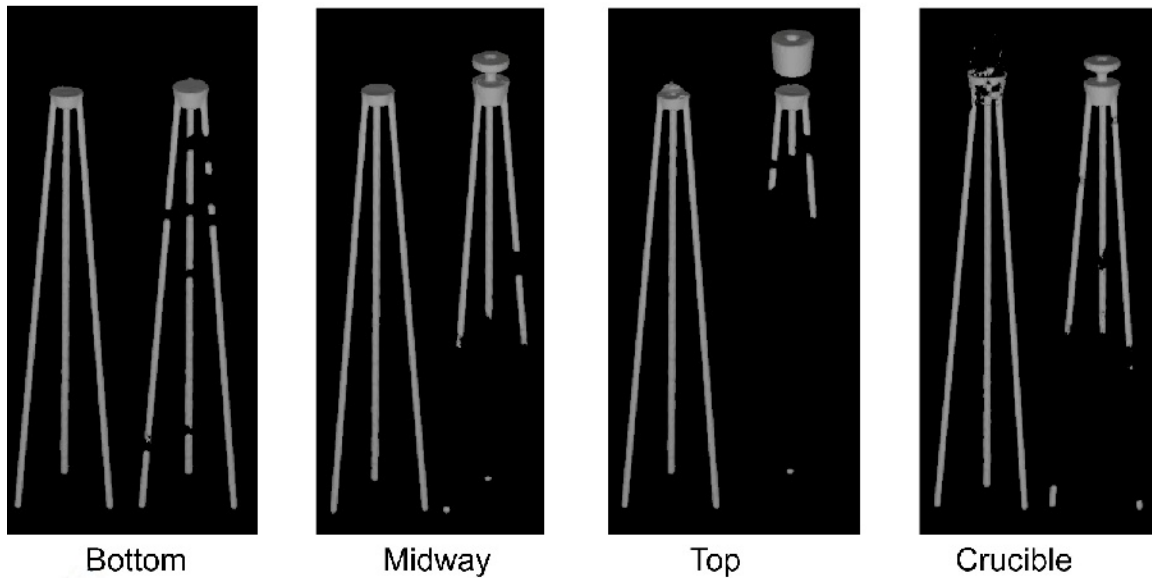
FIG. 8. Shows the results of surface tension when the mold is initially filled with argon. The left image shows filling without surface tension and the right image shows the filling with surface tension.

From these modelling results it can be seen that the initial argon gas filling the mold plays a significant role in how the molds will fill. If no vents are included in the mold design, argon will vent through the molten alloy if solidification does not occur first. It appears that no single vent location can be described as best, a combination of multiple vents are likely needed to ensure smooth filling. A surface tension value was assigned U-10Zr. Results show that when the mold is not evacuated the surface tension significantly affects the flow and quality of the cast pins. Additional work has shown that not only does surface tension play an important role in mold filling but viscosity and wetting angle interaction with surface tension are also important.

Conclusions

In conclusion, casting temperature, mold temperature, mold coating application, and pressure differential have been examined for the effects on casting in the BCS. It was found that too high a temperature led to smaller pin segments as seen in the 1450° and 1550°C castings.This may be due to a lower viscosity of the melt although the liquid properties of uranium and its alloys are genreally not known for better quantification. Also, it was discovered that the pin length increased when a pressure differential assist was not used. This was a surprising result based on initial expectations, but is supported by fuel alloy arc-casting experience. It appears that mold pre heat temperatures are not as critical as the other parameters as there was little difference between casting with 800° and 1000° mold preheat, but it was found that a mold coating is necessary. In the case of the BCS, the coating provides a necessary thermal barrier although, no chemical interaction was seen when no coating was used. This raises the possibility of using less exotic materials and coatings if a chill casting technique could be developed. This may be of use if a continuous casting method is developed because in this case the mold must remain at a lower temperature thereby limiting chemical interaction. In summary, it appears that a casting temperature of 1450°C, with a mold pre heat temperature of 800°C and no pressure differential assist are the best parameters for casting of pins in the BCS. This research has highlighted the need for better characterized liquid alloy properties. The thermal properties and viscosity of the liquid alloy are often estimated based on reference hand book and similar alloys or pure material. This hampers attempts to produce predictive models.

Modelling results support much of this work. The results of the modeling support the need to further characterize alloy surface tension and wetting angle. Through modelling it was seen that these parameters are important and affect the amount of mold filling. Also shown through modelling is the importance of venting of the molds if they are not evacuated. Results show that vent location is very important. It appears that vents incorporated at the crucible mold interface may produce the best filling results but a multiple vent design may be better. These results will be incorproated in the design and casting activities of the GACS furnace, likely saving time and material in development of casting minor actinide bearing materials.

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Combined (Pyro+Hydro) technology for FR SNF reprocessing

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Abstract. The combined technology could be used for reprocessing of the oxide, nitride, carbonitride and metallic spent nuclear fuel (SNF) of fast reactors (FR). Combined (Pyro + Hydro) uses the pyroelectrochemical operations for head-end and main product recovery. The pyroelectrochemical operations allow to reprocess FR SNF with short cooling time (up to half a year) for separating of the main part (up to 99 %) of highly active fission products (FP) from uranium, plutonium and neptunium that are recovered from SNF for the fuel refabrication. The pyroelectrochemical operation also to significantly reduce the required level of engineering environmental protection. The pyrochemical operation also allows to remove the basic amount of the FP which leads to sedimentation (molybdenum, zirconium, barium) and to problems with U-Pu-Np purification (ruthenium, technetium and etc.). The proposed combined scheme is an example of the positive synergistic effect when the combination of two methods leads to their beneficial properties combination and allows to treat FR SNF with high burn-up level and low cooling time, which allows to reduce the volume of SNF stored and plutonium amount in closed nuclear cycle; to obtain of uranium-plutonium-neptunium product of any purification class allowing the use of any fabrication technology and to process any type of FR SNF.

Introduction

As of now, the generally recognized trend in the discussion of perspective fuel for fast neutron reactors (FR) is the choice of dense fuel. Specifically, such fuel can be based on metallic composites or mixed uranium-plutonium nitrides or oxides [1, 2]. It is obvious that the closed nuclear fuel cycle of fast neutrons reactors requires that the reprocessing of dense fuel be provided for. This work considers the version of reprocessing nitride mixed uranium-plutonium fuel being considered for use in the BREST-1200 and BN-1200 reactors, permitting the reprocessing of both metallic and oxide mixed uranium-plutonium fuel.

Intense competition in the area of energy production, the constantly rising requirements for safety and low environmental impact force the developers of technology of the processing of spent nuclear fuel (SNF) to formulate (concretize and strengthen) requirements for processing technologies. At present, these requirements may be formulated as

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- Closing the cycle for uranium, plutonium and minor actinides (MA) with actinides loses in radioactive waste (RAW) of no more than 0.1%
- Reprocessing of FR SNF after 1 year of cooling
- Reprocessing various types of oxide, nitride and metallic FR SNF
- Excluding operations for the separation of plutonium in pure form
- Producing products of the necessary quality for the refabrication of nuclear fuel
- Separation fractions of minor actinides for transmutation in FRs.

Combined (Pyro+Hydro) technology for FR SNF reprocessing

It is obvious that all of the dry technologies that are presently under development (pyroelectrochemical, gas fluoride, plasma etc.) for processing of FR SNF make it possible to process SNF with cooling of even less than 1 year, but at present none of them can guarantee the production of a uranium-plutonium product suitable for the fabrication of pellets of nitrides or carbide and cannot guarantee the return to the fuel cycle of 99.9% of actinides (see Table 1). It must be noted the primary advantage of gas fluoride technology for the processing of FNR of thermal reactors, and particularly the simplicity of separation of the primary mass of uranium, does not have significance for hydrometallurgical reprocessing of FR SNF that does not envisage the separation of uranium and plutonium. On the other hand, during hydrometallurgical reprocessing of FR SNF, it is easy to reach high purification of uranium-plutonium product, ensure the separation from radwaste of 99.9% of actinides, including minor ones, but it is practically impossible to ensure a low cooling time (1 year) of the RNF due to the low radiological durability not only of the extractant, but of the water itself. As such, as of today there is not a single technology that would fully satisfy all of the requirements. However, in our opinion, combined pyroelectrochemical and hydrometallurgical technology which is based on a combination of pyroelectrochemical separation of fraction of the uranium-plutonium-neptunium and hydrometallurgical refining of that fraction can satisfy all of the aforementioned requirements.

Table 1 – Several characteristics of technologies suitable for processing of FR SNF

Indicator	Coefficient of purification of U-Pu (Np) fractions from fission products		Recovery of actinides Pu (Am)		Cooling of SNF before reprocessing	
	Achieved	Potential	Achieved	Potential	Achieved	Potential
Pyroelectrochemical	10^3	10^7	97 %	99.9%	<1 year	<1 year
Gas-fluoride	10^{4-6}	10^7	-	99.9%	-	1 year
Hydrometallurgical	10^7	10^7	99.9%	99.9%	4 years	3 years
Combined (pyro+hydro)	-	10^7	-	99.9%	-	<1 year
Combined (gas-fluoride+hydro)	-	10^7	-	99.9%	-	1 year

Combined processing technology has been applied to oxide, nitride, carbonitride and metallic SNF of fast reactors. Combined (pyro+hydro) technology envisages the use of primary

pyroelectrochemical operations that make it possible to reprocess FR SNF low cooling time (up to 0.5 years) and separate the bulk (up to 99%) of highly radioactive fission products (FP) from uranium, plutonium and neptunium separated from SNF for the refabrication of fuel. Hydrometallurgical operations of combined technology are intended for refining recycled component (U, Pu and Np) and for the separation of americium and curium. The use of pyrochemical process makes it possible not only the handle SNF with low cooling time, but also to reduce the engineering bioprotection necessary for the hydrometallurgical process and remove from the SNF the bulk of oxide forming FP that are technologically problematic for the hydrometallurgy, such as molybdenum, zirconium, barium, ruthenium, technetium, etc.

The task of the foolowing hydrometallurgical process includes refining of uranium, plutonium and neptunium from remaining FP to the level established by the requirements set for recycled component of SNF for the production of fresh fuel for FR and the separation of americium and curium for transmutation.

The separation of the bulk of FPs at the primary pyrochemical process makes it possible to minimize the number of operations (in particular, to remove the technically difficult operation of clarification of the initial solution) as well as the volumes and the specific radioactivity of the utilizable liquid radioactive waste (intermediate form of radwaste) of the hydrometallurgical process.

In the proposed technology, a diagram of which is presented in Figure 1, the following primary operations are completed:
– Removal of the carrier and fuel element disassembly
– Removal of the claddings in zinc
– Metallization of oxide SNF
– Pyrochemical recovery of fissile materials from metallic or nitride SNF
– Dissolution of cathode product
– Electrolyte purification
– Dissolution of the products of electrolyte purification
– Extraction-crystallization refining of non-divided uranium-plutonium(neptunium) pair
– Separation of fractions of rare earth (REE) and transplutonium elements (TPE)
– Separation of Am and Cm
– Evaporation processes
– Producing oxides of uranium and plutonium
– Treatment of intermediate level radioactive waste (ILW)
– Solidification of high level radioactive waste (HLW).

The pyrochemical process of the combined technology for the processing of nitride SNF is intended for:

- The processing of mixed U-Pu nitride or metallic SNF with the production of a cathode product with U, Np, Pu, Am, Cm;
- Separation of oxides of U-Pu-Np with subsequent hydrometallurgical refining from traces of REE
- The production of Am-Cm-U-REE oxides with the product being directed to the separation of Am, Cm via the hydrometallurgical method
- The production of an anode residue for the removal of remnants of Pu
- Conditioning of alkaline earth and alkaline metals.

The developed technological flowsheet envisages the use of equipment for dissembling fuel rod arrays and fuel element disassembly for the formation of SNF shipment, regeneration of the argon, circulating in the interiors of the protected cells.

The operations of the pyrochemical part of the combined process for the reprocessing of the nitride FR SNF include:

− Disassembly of the fuel rod array and the formation of fuel element shipment with nitride SNF

− Removal of the cladding of the fuel elements with fluid zinc

− Regeneration of the zinc

− Reprocessing of SNF with the production of the anode deposit with salt and Cd

− Local off-gas cleaning of the volatile fission products separated in various operations in the gas phase, Cs, Sb, Te, Se, radioactive noble gases, tritium

− Recovery of salt and cadmium from various products

− Cleaning (No.1) of salt from plutonium producing PuO_2

− Cleaning (No. 2) of salt of REE, Am, Cm, U with the production of Am, Cm, U, REE oxides

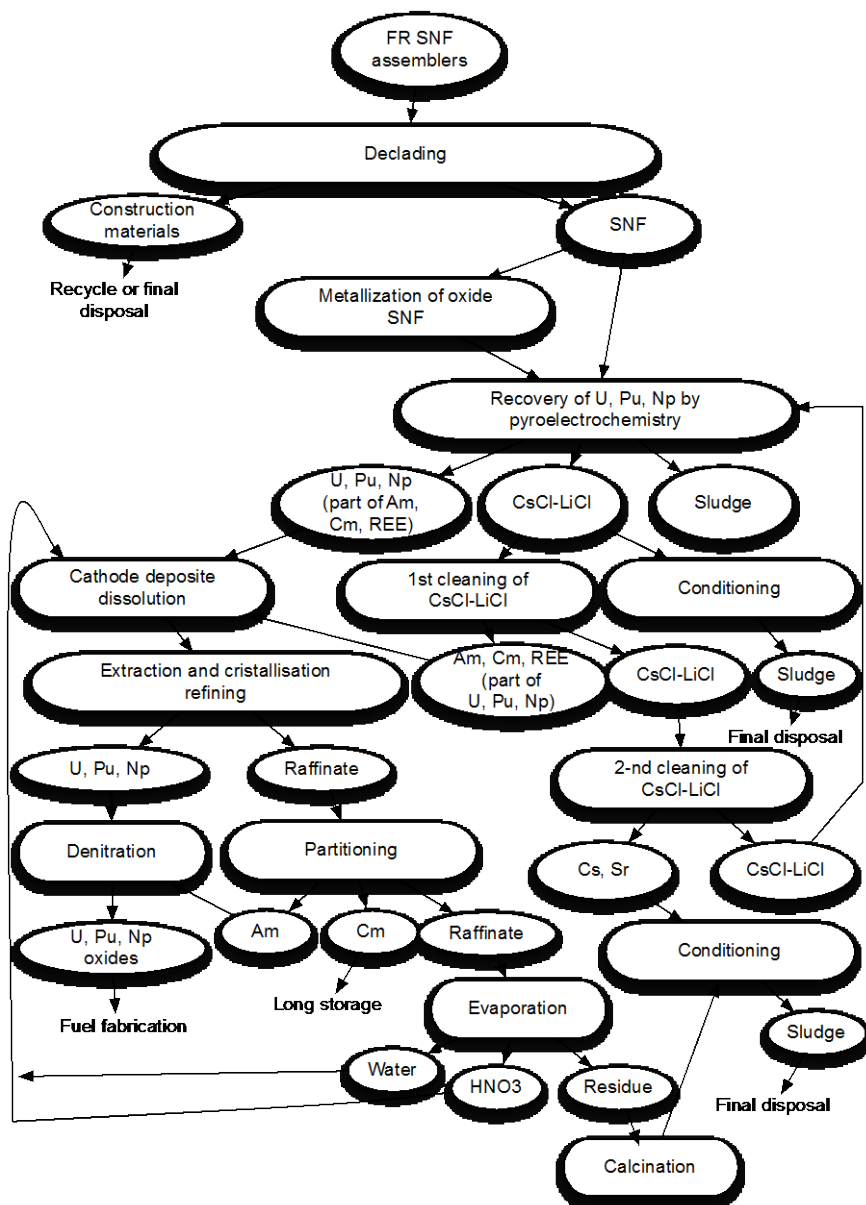− Cleaning (No. 3) of salt with production of salt ingot for HLW solidification and recycle of purified salt.

Figure 1 – Principle flowsheet of the combined (pyro+hydro) technology for FR SNF reprocessing

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The operations for hydrometallurgical procedure of the combined technology for the processing of FNR RNF include:
- Dissolution of cathode oxide
- Dissolution of deposits of dioxide plutonium
- Dissolution of deposits
- Off-gas cleaning
- Solutions clarification
- Extraction crystallization refining of non-separated uranium-plutonium-neptunium
- Separation of fractions of TPE from raffinate of the extraction-crystallization refining of U, Pu and Np
- Separation of Am-Cm
- Evaporation processes
- Producing oxides of U, Pu and Np
- Producing oxides of americium (option, it is possible to return the solution of nitrate solution to the operation for the production of U, Pu and Np) oxides
- Producing oxides of curium for long-term storage
- Treatment of ILW
- Solidification of HLW.

Conclusion

The proposed combined technology is an example of a positive synergistic effect when the combination of two methods leads to a combination of their positive characteristics and makes it possible to:
- |Reprocess FR SNF with high burn and low cooling time, which makes it possible reduce the volume of stored SNF and the quantity of plutonium in the FR closed nuclear fuel cycle (reducing the volume of stored Pu)
- Reprocess any type of FR SNF
- Produce uranium-plutonium-neptunium product of any level of purity, which makes it possible to use pellets technology for refabrication of fuel.

ACKNOWLEDGEMENTS

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The Molten Salt Fast Reactor as Highly Efficient Transmutation System

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Abstract. The basic development and design of a molten salt reactor with fast neutron spectrum (Molten Salt Fast Reactor – MSFR) is the target of the EVOL project in FP7. The MSFR offers certain advantages in the view of transmutation compared to solid fuelled reactor types. In the first part, these advantages will be discussed in a comparison with the sodium cooled fast reactor technology and the research challenges will be analyzed. In the second part, cycle studies for the MSFR, based on the EVOL benchmark design, will be given for different configurations – core with U-238 fertile, a fertile free core and a core with Th-232 as fertile material. For all cases, the transmutation potential will be determined and a significant improvement in the transmutation performance for the case with Th as fertile will be demonstrated. The time evolution of different important isotopes will be analyzed. Additionally, the used tool HELIOS 1.10 and the adaptations needed for the simulation of a MSFR will be described.

1. Introduction

Molten salt reactors have a long history. "The idea of using molten fluoride salts and thus liquid nuclear fuel in a reactor is rather old. Molten salt reactors were already proposed during the post-World War II attempt to design the nuclear powered aircraft. The Aircraft Reactor Experiment, a small thermal reactor (2.5MW) using circulating molten salt, operated for several days in 1953" [1]. This first experiment was followed by a larger scale experiment with 8 MW thermal, the Molten Salt Reactor Experiment (MSRE)."Design of the MSRE started in the summer of 1960 and construction started 18 month later, at the beginning of 1962. The reactor went critical in June 1965, and was briefly at full power a year later "[1]. A major step in the MSRE was the demonstration of the uses of thorium as fertile material and U-233 as fissile material. The reactor was operated until December 1969 and the U-235 fuel salt was successively replaced with U-233. Finally, the reactor was operated with U-233 fuel for several months. It was the first time U-233 has been used as reactor fuel [1].

The molten salt reactor technology has gained some new interest which was focused in the EURATIOM project MOST – Review on Molten Salt reactor Technology [2], [3]. Another two current important projects are EVOL [4], [5] and MOSART [6], [7]. This new interest can be explained by some really interesting features of molten fluoride salts. "Molten fluoride salts have some beneficial characteristics, like the wide range of solubility of uranium and thorium, the thermodynamic stability and the resistance against radiologic decomposition, the low vapor pressure at operation temperature and the compatibility with nickel based alloys which are traditionally used as construction material" [1]. Most of these features described for the fluoride salt in the thermal molten salt reactor comply with the Gen-IV requirements [9]. Nevertheless, the thermal molten salt reactor is not attractive for transmutation due to the soft neutron spectrum which leads to an accumulation of trans uranium elements (TRUs) instead of burning these isotopes. This limitation led to the change in focus from the thermal system to designs using a fast neutron spectrum.In addition, MSFRs exhibit large negative temperature and void reactivity coefficients, a unique safety characteristic not found in solid-fuel fast reactors [8]. MSFR systems have been recognized as a long term alternative to solid-

fuelled fast-neutron systems with unique favorable features (negative feedback coefficients, smaller fissile inventory, easy in-service inspection, simplified fuel cycle, etc.) [9].

In the frame of the development of future energy resources and an improved nuclear waste management, the specifics of the fast molten salt reactor concept offer a large capability of operation. Previous studies led to the definition of the Molten Salt Fast Reactor (MSFR) concept, which is now one of the six concepts selected by the Generation IV International Forum (GIF) [9], for further study. In contrast to molten salt reactors previously studied, the specificity of the MSFR is the removal of any solid moderatorin the core. This choice is motivated by the study of parameters such as feedback coefficient, breeding ratio, graphite lifespan, and U-233 initial inventory [8]. The changes result immediately in a fast neutron spectrum molten salt reactor [10].

The MSFR proposed in the EVOL project is foreseen to operat in the Th/U-233 fuel cycle with fluoride salts. Since U-233 does not exist in nature, the will be started with the Plutonium and Minor Actinides produced in today's LWRs as fissile material [11].

The focus of this study is the discussion of the specific differences and advances of the molten salt fast reactor for the use as transmutation system. The MSFR is compared with the most advanced fast reactor concept, the sodium cooled fast reactor. Further on, different operational modes of a MSFR are analyzed. The effect of different fertile materials, Th-232, depleted Uranium on the evolution of the TRU inventories is investigated and compared to the limit case of the fertile free core. The calculations for all cases are based of the neutronic benchmark case defined in the EVOL project. Finally, the transmutation efficiency of all three cases is compared based on the calculations for evolution of the inventories for the three studied cases.

2.   Special MSFR Features for Transmutation

There is a wide range of operational experience available for sodium cooled fast reactors (SFRs). Thus, this reactor concept is the most mature fast reactor concept with a wide range of experience in design, construction, and operation. Most advanced development status is reflected in the in the current construction of two new SFRs and the fast progressing design of the first industrial size Gen-IV reactor in the French ASTRID project [12]. Additionally, the existing operating sodium cooled fast reactors have shown excellent operational behaviour within the last 10 years and new designs and methods are available to improve safety significantly. These features make SFRs like already mentioned the most mature choice in fast reactor technology [18]. Additionally, the technical possibility for transmutation of plutonium and minor actinides has been demonstrated in the PHENIX reactor [19], a SFR. Nevertheless, it has to be recognized that the early SFRs, designed in the 1970s, have been designed with the target of efficient breeding of new fissile materials and not for transmutation.

The new SFR designs which are currently under development follow other design criteria than those used for systems dating from the 1970s. Fuel breeding is not the major task anymore; thus, well-balanced systems are designed with optimized feedback effects, which result in excellent safety behavior. Additionally, the recently investigated use of fine distributed moderating material offers the possibility of designable feedback effects, since the most important feedbacks, the Doppler and the coolant effect, can be influenced significantly without negative implications on the other safety and operationally relevant system parameters [17], [20], [21], . Thus for the point of view of safety, new additional possibilities are given to counteract the influences of high amounts of transmutation fuel on the system safety. Nevertheless, not only the consequences of TRU fuel on safety, but also some technological issues limit the use of SFRs for highly efficient transmutation. From the transmutation point of view, conflicting targets always exist, when high transmutation rates are requested::

- a high TRU content is required for efficient transmutation
- no breeding is desired to avoid the built up of new TRU isotopes, thus a fertile free core seems to be optimal

- long cycle time is required for efficient transmutation, since TRUs are burnt only when the reactor operates
- long cycle time requires a small reactivity loss over cycle as design target for the core or a core design with high excess reactivity
- small reactivity loss over cycle requires breeding of new fissile material, thus fertile material is essential
- high excess reactivity has negative safety consequences, therefore a strong control system is needed
- a high burnup is required for an efficient transmutation
- very high Pu content tends to degrade the Pu vector; this has already been discovered in the CAPRA project [23]
- short out of core period and long in core residence time of the TRU fuel is required

High reactivity loss over cycle like it appears in the case of absence of a fertile material is no problem in MSRs since the reactivity loss can be compensated by an online re-feeding of fissile materials. Thus no excess reactivity is required. In contrast in solid fuelled fast reactors, fertile free fuel causes problems due to the required high excess reactivity needed to allow an acceptable long cycle time. Reduced cycle time results in reduced operational performance and thus limited transmutation time. Especially in a fast reactor, where traditionally the outage time is longer than in LWR, this option is not attractive. High excess reactivity requires strong control and shut down systems. This counteracts the efforts to reduce the reactivity loss over cycle as one of the main design criteria to reduce the consequences of unprotected transient over power events. The effectiveness of a single control or shut down assembly has to be limited. This is required to limit the reactivity insertion caused by a mis movement of a control or shut down assembly. This fact leads directly to the safety of the system itself. On the one hand, the amount of minor actinides in a classical fast reactor core is limited, since minor actinides reduce the negative Doppler feedback, increase the positive coolant feedback and the sodium void worth. The the control rod efficiency [17] will be decreased as well as the delayed neutron production in the case of absence of fertile materials. On the other hand the MA transmutation efficiency increases with increasing MA content [17]. In contrast to solid fuelled fast reactors, a major advantage in the MSFR is the structure of the feedback effect due to the conjunction of fuel and coolant. What is called coolant effect in the SFRs, is in the MSFR the density effect of the salt. This effect is in all cases strongly negative due to the coincidence of coolant and fuel in a molten salt reactor. The problem of the reduced delayed neutron production has been dealt with in the fertile free core of the CAPRA concept [22], thus it should be possible in a MSFR too. A long in core residence time can be assured in the MSR, since the salt cleanup will be performed on hot fuel, thus no extra cooling time of fuel assemblies, no transport to the reprocessing and no solid fuel pellet production is required. Online reprocessing or salt cleanup has to be designed as one of the special challenges of MSRs, but losses in the process do not lead to an accumulation of MA in the final disposal stream. In MSR losses due to insufficient separation of fission products lead to an accumulation of lanthanides in the core. Additionally, another major hurdle in the industrial implementation of a transmutation cycle besides the partitioning of the MA is the production of the solid fuel pellets with high MA content. This problem is eliminated completely in MSRs. Here it is only essential to limit the MA content to avoid segregation of the MA salts.

Finally, the neutron spectrum has to be discussed. The neutron spectrum in a MSFR is slightly softer than in other fast reactors like it is shown in the comparison with an oxide fuelled SFR and the metal fuelled GUINEVERE experiment with a lead matrix (see Figure 1). The reason for the softer spectrum is the high amount of light materials (Li, F) in the core. Nevertheless, it has already been shown that this does not lead to a high accumulation of higher actinides [11] and that the transmutation efficiency is not always directly related to the hardness of the neutron spectrum [17].
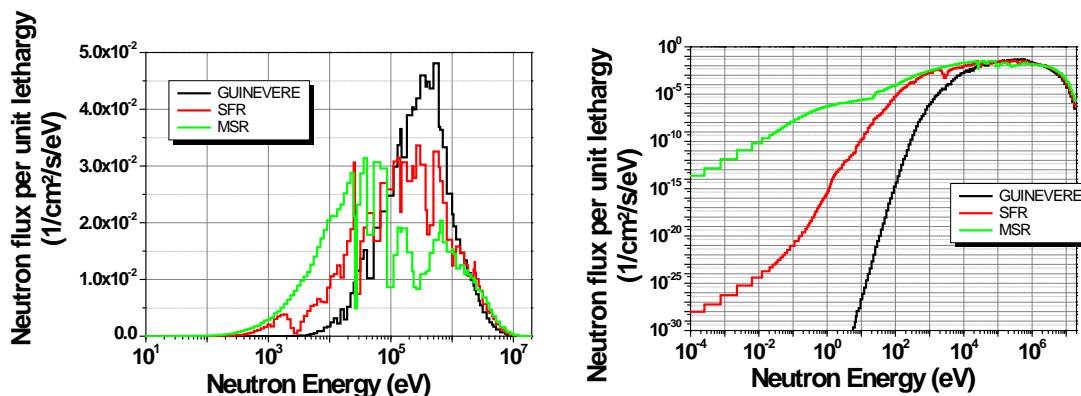
Figure 1: Comparison of the neutron spectrum in different fast reactor systems

3. Code and Data

The test calculations for the investigation of the influence of different fertile material configurations are based on the material configuration, the core dimensions and the boundary conditions of the EVOL benchmark definition. The geometric arrangement of the benchmark core for a 3000 MW thermal molten salt reactor is given in Figure 2.
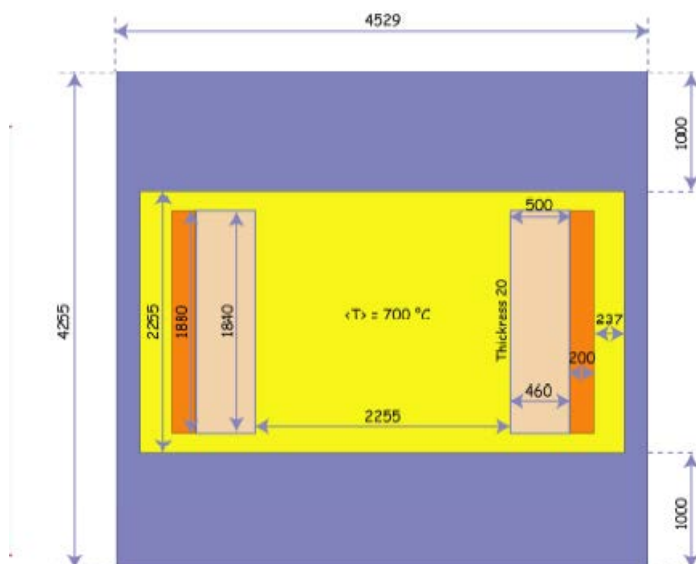
Figure 2: Geometric arrangement of the benchmark core defined in EVOL

The salt configuration consists of 77.5 % LiF with ThF_4-(Pu-MA)F_3 in the core and of pure ThF_4 in the blanket. The over all fuel salt volume is 18 m³ containing 30619 kg Th, and 12661 kg TRU following the the TRU vector given in Table 1 [14].

Table 1: TRU vector from PWR fuel (burnup of 60 GWd/tHM) and after five years of storage

Np 237	6.30%
Pu 238	2.70%
Pu 239	45.90%
Pu 240	21.50%
Pu 241	10.70%
Pu 242	6.70%
Am 241	3.40%

Am 243	1.90%
Cm 244	0.80%
Cm 245	0.10%

For the simulations, the HELIOS 1.10 code system with the internal 47 energy group library is used [16]. The code is a 2D spectral code with wide unstructured mesh capabilities and a transport solver based on the collision probability method [15]. It is written for the simulation of solid structure fuel assemblies. The possibility of online refueling and online reprocessing is not foreseen. To deal with these very special features of molten salt reactors a python script has been developed. The script is based on the special features of HELIOS. All important information which is not changed during the whole reactor operation is stored in the expert input, while the changing material configuration is given in the user input. Both inputs are merged in the pre-processor AURORA, which creates the input for the HELIOS run for the determination of the neutron flux distribution and the burnup. The results are evaluated in the post-processor ZENITH. Here it is decided which isotopes will be fed back into the next user input which is created in the script (see Figure 3). With this calculation loop it is theoretically possible to precisely simulate a molten salt reactor by using small time steps. In a real MSR two different time scales for the salt cleanup are used, due to the different extraction methods for the fission products. The helium bubbling, which has an halving time of ~ 30s for gaseous fission products and the salt cleanup, which takes 450 days to have a throughput of 100% of the fuel salt volume. For envisaged long time investigation only the second process is simulated. All fission products are extracted after an operation time of 450 days. The salt cleanup is established inside the post-processor, only the isotopes which remain in the salt are forwarded to the script. Additionally, a defined amount of material with a given isotope vector, e. g. refill of thorium to the initial amount at each cycle or refill of a certain amount of fissile material, can be added to the individual isotopes and will be rewritten in the script to the new user input.
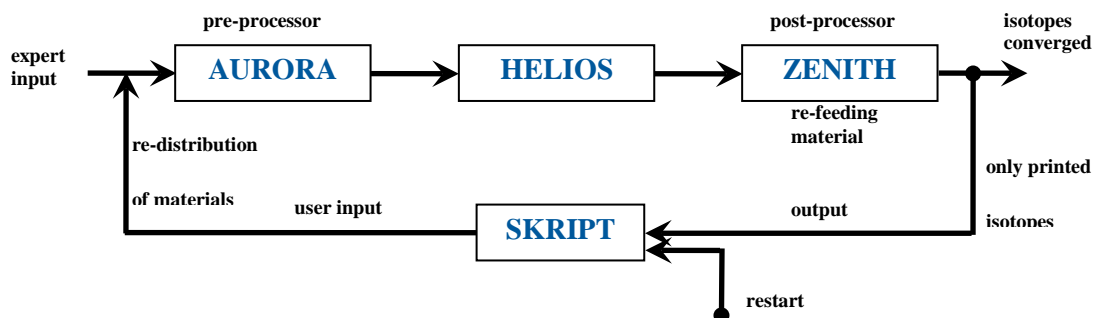
Figure 3: Description of the calculation cycle for the simulation of a MSR

Due to the characteristics of HELIOS, some approximations have to be accepted. There is no fuel salt movement in the 2D system, thus a burnup distribution will arise during the 450 day cycle. The materials are only re-distributed when a new user input is defined. The effect could be reduced by reducing the cycle time and a re-feed of a part of the fission products. HELIOS is a LWR code and a LWR spectrum is used for the weighting of the master library. Nevertheless, comparisons to SERPENT on the isotope accumulation during burnup have shown good agreement for the major isotopes. The approximations and the use of HELIOS seem to be adequate for the approximation level required for this kind of long term study.

4. Different Operation Options for the MSFR

A comparison of different operational options is given in the chapter below. The system is fed with the identical TRU vector during the whole operation time in all cases, but the fertile part is different. One system is based on thorium as fertile material, another is based on depleted uranium as fertile material

and the third system is fertile free. In the system with fertile, the fertile material is refilled at begin of each cycle. The bred fissile material from the blanket is taken out of the reactor, thus real breeding of fissile material takes place.

The reactor is operated for 40 cycles with a cycle time strongly dependent on the initial heavy metal load and the k_{eff} in core inventories of the major TRU isotopes are discussed. Figure 4 shows the keff evolution over burnup for the period of 40 cycles. The initial burnup step in all three cases is configured that the average k_{eff} is 1.011181. This value is taken from the critical configuration of the EVOL benchmark and is based on the criticality of the 3D system. The criticality drops during the 450 day cycle, on the one hand due to the burning of fissile material, on the other hand due to the accumulation of fission products. This behavior is a consequence of the approximation on the refill only at the beginning of cycle and on the simulated batch salt clean-up instead of the continuous process. Both processes refill and clean-up would be continuous in a real reactor. The criticality loss per cycle caused by the approximation depends on the breeding capabilities of the fertile component in the fuel, thus the loss is much stronger for the fertile free case.
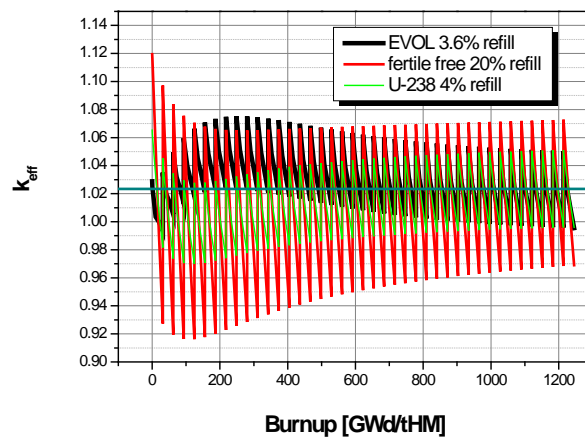

Figure 4: Comparison of the k_{eff} evolution over the whole operation period

In the following, the evolution of different isotopes will be analyzed. The evolution of the isotopic content in the core of the original EVOL benchmark case using Th-232 with 3.6% of the initial TRU load re-filled at begin of each cycle is given in Figure 5. The most interesting changes during the operation time are the built up of the U-233 due to breeding processes form Th-232 (black curve). The U-233 concentration reaches an asymptotic value roughly after half of the operation time. The Pu-239 is reduced from the initial value by roughly two third (red curve). The appearing steps are caused by the re-feeding of fissile material in each cycle. The other fissile Pu isotope Pu-241 is reduced rapidly from the BOL configuration too and it reaches already after short time an asymptotic value. The material which is added at each cycle is than burnt during the cycle. The Pu-240 content (blue curve) is rising slightly at the beginning of operation to a maximum level at ~180 GWd/tHM and reduces than to a nearly asymptotic value at the end of operation. The other even Pu isotope Pu-242 is nearly constant over the complete operation period, thus the added material is burnt. The americium isotopes Am-241 and Am-243 end with an asymptotic level. The amount of Am-241 is slightly reduced from the BOL amount, while the Am-243 amount rises to the asymptotic level. Cm-244 and Cm-245 rise slightly over the operation period, but both isotopes approach an asymptotic level. Only marginal amounts of californium are produced during the lifetime of nearly 50 years.
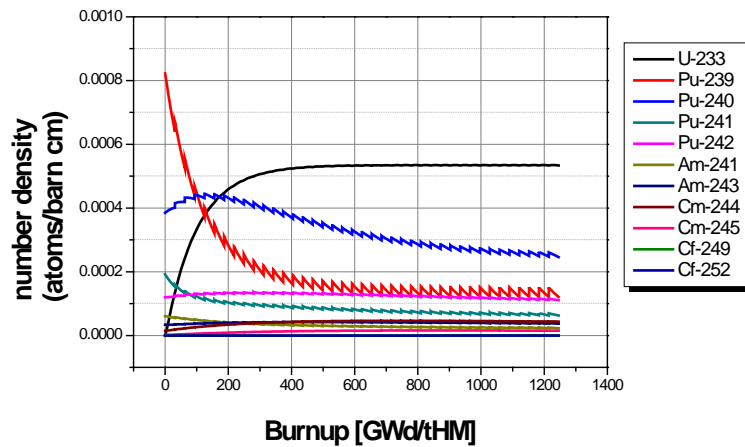
Figure 5: Evolution of the isotope inventory for the case based on Th-232 fertile material

The evolution of the isotopic content in the core of the fertile free system with 20% of the initial TRU load re-filled at begin of each cycle is given in Figure 6. Already a first glance indicates some important differences between the fertile free system and the thorium based system No significant built up of fissile material occurs during the operation of the fertile free system. The amount of fissile isotopes Pu-239 stays nearly constant and Pu-241 rises slightly compared to the initial value, but most of the re-fed material is bunt during operation. The final inventory of Pu-239 is nearly the initial one and the Pu-241 content is about two times higher compared to the thorium based system. The Pu-240 as well as the Pu-242 content is rising strongly over the whole operation time, thus the even isotopes are accumulated and only a small part is burnt. The observed americium and curium isotopes are accumulated in the core too..

The differences between the two cases can be explained with the lack of fertile material. The fissile content has to be approximately the same in both cases, but in the thorium based case a significant amount of fissile material is replaced by the bred U-233. To compensate for the absence of significant breeding of fissile material, the amount of fissile material which has to be added has to be increased. Due to the high plutonium amount in the core a competition between fission and capture events takes place. Even in the very efficient fissile odd plutonium isotopes the capture leads to higher, even isotopes which have than to undergo more capture events to create new fissile material. This processes and effects have already been discovered during the cycle analysis of the CAPRA project [22] and the effect rises the more plutonium is inserted.
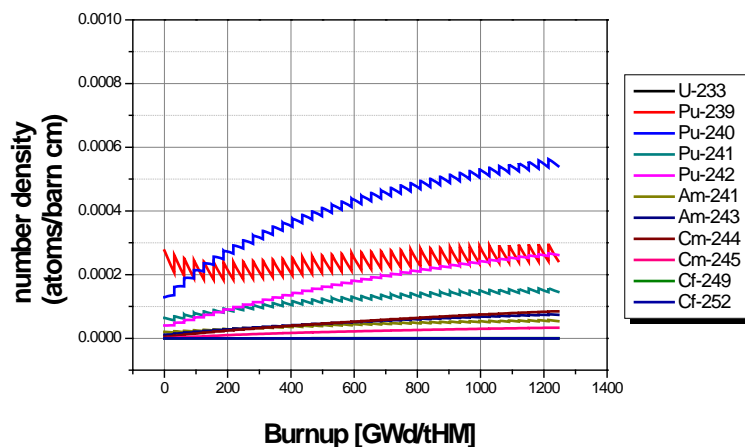

Figure 6: Evolution of the isotope inventory for the case of a fertile free core

The evolution of the isotopic content in the core for the case of the use of U-238 as fertile material is given in Figure 7. Due to the use of U-238 as fertile material, the Pu-239 content does not change by a significant amount. The burnt Pu-239 is nearly one by one replaced by new bred one. The fissile material is mainly configured by Pu-239 and Pu-241 and there is no replacement like in the case for the thorium fertile material. The initial Pu-241 content is slightly reduced and reaches already after short time a steady state value. The concentration of Pu-240 rises over most of the operational period and reaches about EOL a almost asymptotic value. Pu-242 stays nearly constant over the whole operation. The same can be observed for the americium and the curium content. Only the californium content rises.
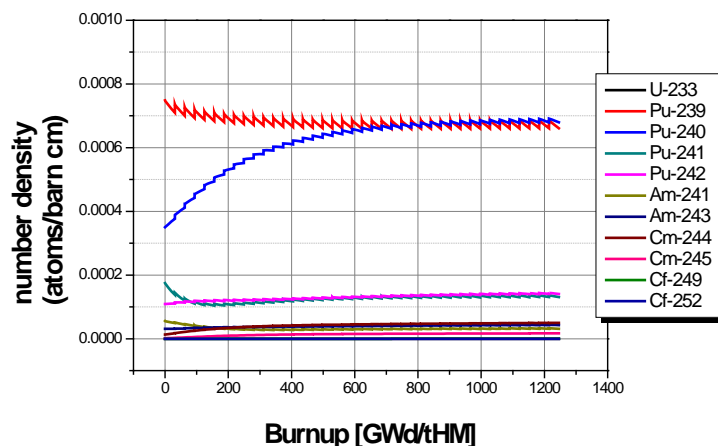
Figure 7: Evolution of the isotope inventory for the case based on U-238 fertile material

The in-core contents of the fissile isotopes are only a part of the interesting information, since different amounts of TRU are fed into the system in the initial state, as well as during the operation. The initial amount of TRU is given in Table 2. for all three observed cases. The detailed EOL amounts of new dcreated materials to be unloaded from the core are given in Table 3 .

The initial amount of TRU to make the systems critical is highest for the case using thorium as fertile material, since the absorption in Th-232 is stronger than for U-238 fertile material. The lowest initial content of TRU appears for the fertile free core, since there appears no strong absorbing material. In contrast , the feed over the 40 cycles is highest for the fertile free case (20%) and lowest for the thorium based case (3.6%). The combination of all values leads to the over all feed Table 2. The over all feed for the thorium case and for the U-238 case are nearly identical, the initial load is significantly lower for the fertile free case and the feed during operation is lower too. The over all TRU loading is by more than 60% higher for the case using Th-232 as fertile material.

Table 2: Whole feeding mass consisting of initial feed and TRUs fed over 40 cycles operation period

	Th-232 fertile (kg)	U-238 fertile (kg)	Fertile free (kg)
Pu	26634	25382	9701
Np	1897	1808	691
Am	1628	1551	593
Cm	279	266	102
Summe	30437	29007	11086
Cycle time	450	442	45

A detailed comparison of the data in Table 3 shows, that the unloading masses of higher actinides (isotope mass > 245) are slightly higher for the uranium than for the thorium case, while the absolute amounts are decreased in the fertile free case. The major part in all cases is Curium-246 and 247. The

Californium production is only in the range of grams and slightly higher in the fertile free case. Nevertheless, it is obvious that the production is 3 times higher in the fertile free case. For the observations in the fertile free case it has to be kept in mind that the inserted TRU amount is by neary a factor of three lower.

Table 3: Masses of higher isotopes bred which will be unloaded from the core after 40 cycles for the observed isotopes and for the three cases (thorium fertile, depleted uranium fertile, fertile free)

	Unloading masses (kg)		
	Th-232 fertile	U-238 fertile	Fertile free
96246	61	61	34
96247	12	13	10
96248	4.9	5.8	3.1
97249	0.17	0.23	0.22
98249	0.43	0.52	0.64
98250	0.27	0.38	0.34
98251	0.068	0.107	0.165
98252	0.0060	0.0110	0.0167
Sum	79	81	49

Figure 8 shows the transmutation efficiency for the three different cases. It is obvious, that the incineration of the major plutonium isotopes (Pu-239, Pu-240, and Pu-241) which represent 89% of the plutonium content is slightly most efficient in the case using thorium as fertile material. The transmutation efficiency of most other isotopes is slightly better in the thorium based case than in the uranium based case and the fertile free case. The use of a fertile free core configuration is in a strong contrast. Several isotopes are strongly produced (bars to the left which represent accumulation) in this case these are the fissile plutonium isotopes, especially. The over all transmutation efficiency of the thorium based case is 82% compared to 60% in the uranium based case and 71% in the fertile free case. When the long lived even uranium isotopes are taken into account the transmutation efficiency of the Th case drops only to 77%. The strongly different cycle times for the different cases has to be kept in mind.
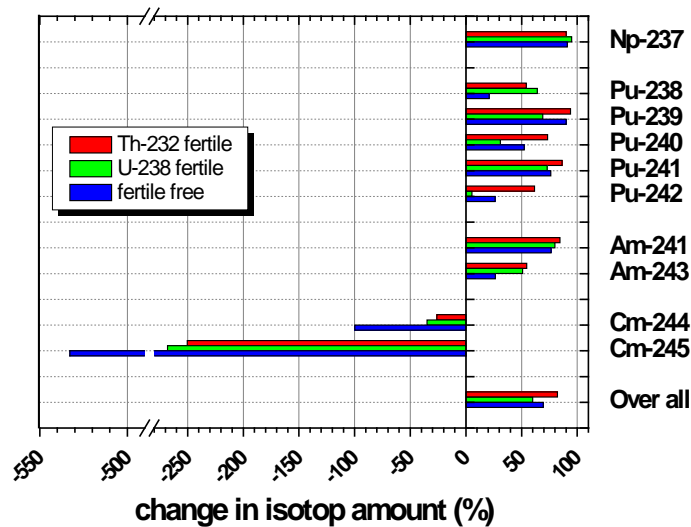

Figure 8: Comparison of the share of burnt material during the operation of 40 cycles for the different cases (thorium fertile, depleted uranium fertile, fertile free) and by a special add on time for deep burning of TRU

5.   Conclusions

The molten salt fast reactor seems to be the ideal system for transmutation, if the technological challengees can be solved to an acceptable extent. There are some specific advantages due to absence of solid fuel, solid fuel production is avoided. Due to the online salt cleanup, losses stay in the system and no transport of materials is required. Due to the continuous feeding mode, no excess reactivity is needed. From the safety point of view, the strong negative feedback in the whole operational range due to homogeneous mix of fuel and coolant is very attractive, and the possibility of draining the core opens new features for the decay heat removal.

Sure, there are several technological challenges to be solved. The main challenge is the stability of the structural materials under high temperature, high neutron irradiation, and exposition to corrosive media. Additionally, a mature design has to be defined for a molten salt reactor. A basic design will be the outcome of the EVOL project. Finally, a step by step approach has to be foreseen to gain operational experience, thus a development has to be started with a small low power experimental machine. Such a machine has to be planned, built, and financed. Finally, the required development of the salt clean-up has to be developed for the online-reprocessing

The study on the transmutation has shown that the transmutation is even more efficient (in the view of the left overs) in a system based on thorium as fertile material than in a uranium based or even in a fertile free system. Finally, not only the effiency given by a good burn out has to be kept in mind. Another inportant point is the time requested to burn the transuranium isotopes. In this case the fertile free system is much more attractive due to the significantly shorter cycle times. Thus, the decission for the ideal case is always strongly dependent on the foreseen future of nuclear energy production.

ACKNOWLEDGEMENTS

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TREATMENT OF HIGH LEVEL WASTE ARISING FROM PYROCHEMICAL PROCESSES

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Abstract. The report describes the JSC «SSC RIAR» research experience on management high-level waste (HLW) arising from pyrochemical processes. The laboratory investigations including simulated and real waste forms generated as a result of the experimental reprocessings of spent nuclear fuel (SNF) of fast reactors are summarized. Pyrochemical processes are characterized by a few types and a small volume of the waste, their high specific activity and, practically, absence of the liquid process HLW. The main types of solid process wastes are phosphate and oxide precipitates and spent electrolytes. The investigation included the chemical and radionuclide composition, gas release, chemical durability, thermal stability of the precipitates and spent electrolytes. The results of the analysis suggest that the main waste forms of the pyrochemical processes can be stored for a long time in shielded containers without any chemical conversion and immobilization. To increase the efficiency of the shielded barrier for the purposes of the long-term geological storage, the waste forms of the pyrochemical processes can be transferred into more stable chemical forms.

1. INTRODUCTION

JSC «SSC RIAR» has been performing research and development activities in support of closed fuel cycle of fast reactor since the middle of 1960s [1]. Fuel cycle involves fabrication and reprocessing of spent nuclear fuel (SNF) using pyrochemical methods of reprocessing in molten alkali metal chlorides.

At present pyrochemical methods of SNF reprocessing in molten chlorides has reached such a level in their development that makes it possible to compare their competitiveness with classic aqueous methods. Their comparative advantage lies in high inherent safety, compactness, high protectability as to nonproliferation of nuclear materials, and reduction of high level waste volume [2].

Pyrochemical process flowsheets underwent evolutionary development at a laboratory-scale level and commercialized by operating pilot MOX fuel (mixed uranium-plutonium fuel) fabrication facility as well as trial reprocessing of irradiated uranium oxide, MOX, nitride and metallic fuel. Table 1 summarizes the operating experience of the pilot MOX fuel fabrication facility as well as trial reprocessing of spent nuclear fuel and main types of radioactive waste (RW).

Considerable study has been given to release, composition and properties of high-level waste at all the stages of development and operational verification testing of production flowsheets.

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The present paper describes various reprocessing methods of recyclable products and methods of high level waste (HLW) preparation for controlled storage based on the gained experience of JSC "SSC RIAR". Considered here is HLW produced at different stages of fuel cycle.

2. SHORT SUMMARY OF PYROCHEMICAL PROCESS FLOWSHEETS AND MANAGEMENT OF RECYCLABLE PRODUCTS AND WASTE

Pyrochemical processes based on the use of molten chlorides can undergo certain changes in accordance with the goals and tasks but the main operations of the process romaine unchanged. Origin and composition of initial materials to be reprocessed have an effect on the composition and properties of the resulted waste. In terms of radiation exposure, the most challenging task is reprocessing of irradiated fuel and so the resulted waste forms are high level waste that call for development of special management methods and immobilization techniques in order to provide their long-term geological disposal. So the present paper is focused on the experience of JSC "SSC RIAR" in field of trial reprocessing of both MOX and dense fuel (table 1). It also gives specification of radioactive waste resulted from fuel reprocessing as well as describes experiments related to their immobilization.

Table 1. Experience of JSC "SSC RIAR" in field of trial reprocessing of both MOX and dense fuel

Year	Fuel description	Reprocessing output (fabrication)	Main RW types	References
1988-1990	MOX-fuel for the BOR-60 and BN-600 reactors	1500 kg	Americium-containing RW	[3]
1991-1992	The BN-350 reactor fuel with a burn-up of 4.5% h.a. and cooling time of 5 years	4.1 kg	Phosphate precipitates, spent electrolytes	[4]
1995	Vibropack MOX-fuel of the BOR-60 reactor with an ultra high burn-up of 21-24% h.a. and cooling period of 2-3 years	3.3 kg	Phosphate precipitates, spent electrolytes	[5]
1998-2002	MOX-fuel (34 fuel assemblies of the BOR-60 reactor and 6 fuel assemblies of the BN-600 reactor) made of weapon-grade plutonium alloy	435 kg	RW with plutonium	[6]
2010-2011	Dense metallic fuel U-Pu, U-Zr, U-Pu-Zt with sodium sub-layer and burn-up of 6-10 % h.a. and nitride fuel U-Pu-N with lead sub-layer and burn-up of 4.8% h.a.	0.6 kg	Oxide deposits, spent electrolytes	[7]

2.1. Summary of the MOX-fuel reprocessing process and main types of radioactive waste

The reprocessing process aims at extracting plutonium from the irradiated fuel for its reutilization and removing uranium temporarily from the cycle with the bulk of fission products for storage as uranium worthiness is much lower (because the uranium in the isotope composition occurring in nature or the uranium with lower content of the fissile isotope U-235 is used).

The MOX-fuel to be reprocessed is subjected to mechanical decladding, grinding to a powder and loaded into the head device-chlorator-electrolyser. All the operations of pyroelectrochemical reprocessing are carried out in the device. The sequence of operations is as follows:

• Fuel chlorination in molten NaCl-KCl; LiCl-NaCl-KCl-CsCl;

• Electrolysis for removal of UO_2-1 with some fission products (FPs) captured by cathodic deposit;

• Precipitative crystallization of PuO_2 decontaminated from FPs and other impurities;

• Additional electrolysis for removal of UO_2-2 with deposited FPs and other impurities;

• Molten salt purification by introduction of phosphates into the melt.

The pyrochemical reprocessing flowsheet is based on the principle of the highest possible recycling of recyclable products that will allow for obtaining a product with the PuO_2 recovery rate of 99.5-99.9% and for minimizing the production of high-level waste. Cathode deposits UO_2-1 and UO_2-2, PuO_2, and phosphate precipitate are purified from the captured salts. Aqueous solutions are evaporated, undissolved solid salts can be returned into the very beginning of the process but condensate water is reused. The PuO_2 precipitate is expected to be used for manufacturing shortened fuel rods but uranium oxides are intended for long-term storage followed by processing and uranium return into the cycle. The phosphate precipitate passes the stages of storage, immobilization and disposal. The salts can be used for several process cycles followed by their removal from the process, storage and reprocessing before disposal.

Different flammable radioactive materials can be produced when the fuel regeneration facility is under operation. Among these materials are polyethylene film, cleaning waste, overalls, filters and rubber. It was proved by experiments that all these materials can be incinerated at a regular basis in molten salts. The laboratory-scale experiments made it possible to study and specify the main parameters of incineration process for pyrographite components of the chlorator – electrolyser, which reach the end of their service life. All the equipment components including claddings of fuel rods are subjected to decontamination before they are removed from the process.

2.2. *Summary of dense SNF reprocessing process and main types of radioactive waste*

The basic processes include the following stages of the dense SNF reprocessing:
1. Regeneration through dense fuel chlorination with cadmium in molten 3LiCl-2KCl by a chemical method and electrorefining of fissile materials in a liquid cadmium cathode.
2. Elemination and condensation of liquid cadmium followed by separation fissile materials for further manufacturing of metallic and nitride fuel.
3. Partitioning of minor actinides and fission products in a liquid bismuth cathode.
4. Precipitation of fission products by introduction of carbonate followed by production, collection and removal of salts from the oxide product.
5. Immobilization of the resultant oxide product and spent electrolyte (after repeated use).

3. High level waste from pyrochemical processes and their specification

Certain weight quantities of HLW resulted from the experiments on reprocessing of irradiated fuel from the BN-350 and BOR-60 reactors. Experiments and studies were carried out in order to obtain physical and chemical characteristics of this waste and determine conditions of its long-term storage.

3.1. *Phosphate precipitates*

As a result of the BOR-60 fuel reprocessing (in 1995) phosphate precipitate was obtained. Some characteristics of this precipitate are given in Table 2. Phosphate precipitate represented itself a fine powder. It was reddish-brown in color. Nuclides $^{144}Ce + ^{144}Pr$ are responsible for 90% of the powder γ-activity but α-activity results from ^{241}Am by 92% (see Table 3). The X-ray phase analysis of the powder after annealing in air at 1000ºC revealed the presence of phase with the structure of monazite mineral i.e. (Ce, La,Y, Th…)PO_4.

Table 2. Some characteristics of phosphate precipitate

Weight, g	Bulk density, g/cm^3	Specific heat release, W/kg	Specific radioactivity, Ci/g	
			α-nuclides	γ-nuclides
442	0.6-0.7	9.5	$9.3 \cdot 10^{-2}$	1.0

Note: heat release and activity data are given as of June 01, 1997.

Table 3. Radioactivity of nuclides in phosphate precipitate

Radionuclide	Radioactivity, Bq/g (%)	Radionuclide	Radioactivity, Bq/g (%)	Radionuclide	Radioactivity, Bq/g (%)
^{106}Ru+^{106}Rh	$1.7 \cdot 10^7$	^{154}Eu	$7.8 \cdot 10^8$	^{241}Am	$3.2 \cdot 10^9 (92.5)$
^{144}Ce+^{144}Pr	$3.3 \cdot 10^{10}(90)$	^{155}Eu	$0.3 \cdot 10^{10}(9)$	^{242}Cm	$6.3 \cdot 10^7$
^{137}Cs	$1.6 \cdot 10^7$	^{54}Mn	$4.8 \cdot 10^6$	^{244}Cm	$2.1 \cdot 10^8$
^{125}Sb	$1.3 \cdot 10^7$	^{60}Co	$1 \cdot 10^6$		

Under the long-term storage of HLW, the storage conditions depend largely on such properties as release of radionuclides in the environment gas as well as leachability whenever their contact with liquid phase becomes possible (for instance, with water). The gas phase can be contaminated due to generation of radioactive aerosols and volatile chemical compounds. Leachability depends on the overall stability against solvents, especially in particular when it comes to hydrolysis. Analysis of gas phase radioactivity revealed that it depended on the ^{106}Ru+^{106}Rh release by 60-80%. Higher release of ^{137}Cs and ^{125}Sb was also observed. At the same time releases of ^{154}Eu and ^{155}Eu, ^{144}Ce+^{144}Pr, and ^{241}Am are lower by 1-3 orders as opposed to Ru (Rh). It is expected that such a release occurs due to the emitted dust (sols). Probably, higher release of ruthenium radionuclides (rhodium), antimony and cesium results from higher volatility of their compounds.

Hydrolysis tests on phosphate precipitate revealed that the ^{134}Cs and ^{137}Cs isotopes make for 55% to 88% of the solution activity, the ^{144}Ce (Pr) isotopes make for 6.8% to 21% of activity and ^{125}Sb produces from 4.5% to 16% of activity.

The temperature of waste storage depends on corrosion resistance of structural materials of the cask. Widely used carbon steel St 3 and stainless steel 12X18H10T were chosen as candidate materials for manufacturing containers. The stainless steel was proven not to undergo corrosion in the phosphate precipitate environment at a self heating temperature. As to ten point grading scale of corrosion resistance, it can be assigned to the second-the forth grade (corrosion resisting steel).

3.2. Oxide precipitate

In December 2010 26 g of oxide precipitate were obtained at JSC "SSC RIAR" as a result of dense fuel reprocessing. Its characteristics are given in Table 4.

Table 4. Characteristics of real oxide precipitate

Precipitate weight, g	Content of some components and radionuclides					
	U, mass%	Pu, mass%	^{241}Am, Bq/g	^{137}Cs, Bq/g	^{154}Eu, Bq/g	^{144}Ce, Bq/g
26	4.2	<0.001	$5.4 \cdot 10^6$	$3.1 \cdot 10^4$	$1.0 \cdot 10^7$	$8.6 \cdot 10^6$

3.3. Spent electrolytes

Spent electrolytes are generated in the course of many pyrochemical processes but they are different in radiation level depending on the type of fabricated or reprocessed fuel, fuel burnup, its cooling time, efficiency of fission products precipitation in melts and repetition in use of electrolytes.

As an example, we refer to the spent electrolyte generated after high burnup fuel reprocessing of the BOR-60 reactor (1995). As a result of reprocessing 8.1 kg of molten alkali chlorides remained. Their original composition was LiCl-4.53NaCl-4.88KCl-0.66CsCl. The specific heat release of spent electrolyte was 0.95 W/kg as of June 01 1996, a temperature of self heating was about 30°C (weight was about 2 kg). Activity of gamma nuclides depended on Cs-137 by 84% (see Table 5). The obtained alpha spectrum included 88.7% of ^{241}Am, 4.8% of ^{242}Cm and 6.5% of ^{244}Cm.

Table 5. Chemical and radionuclide composition of spent electrolyte

U weight %	Pu weight %	Activity of α-nuclides GBq/kg	Activity of γ-nuclides, GBq/kg							
			[106]Ru (Rh)	[125]Sb	[134]Cs	[137]Cs	[144]Ce(Pg)	[147]Pm	[154]Eu	[60]Co
<0.001	<0.001	0.2	1.9	0.7	151.7	2024	200	33.3	5.9	0.1

Analysis of the gas phase activity over the electrolyte (weight – 2 kg, melt, end surface-78.5 cm^2) revealed that it depended on ^{137}Cs by ~95% which was actually equivalent of its contribution to the total activity of electrolyte. As the temperature increases from 30°C up to 300°C, the rate of activity release increases four times roughly. It was observed that the values of activity release were comparable with or a little lower than the phosphate precipitate values. Probably, the reason is that the electrolyte is solid as opposed to powders and a chance of significant powdering is excluded.

Corrosion tests of steels St 3 and 12X18H10T were carried out both in "cold" solid electrolyte (20°C) and hot molten electrolyte (650°C). As investigation showed, the highest corrosion rate was observed when molten electrolyte was filled in and such an effect was produced due to a high temperature of melt. Corrosion resistance of samples corresponds to grade 4 (corrosion resisting steel) for steel St 3 and grade 2 (highly corrosion resisting steel) for steel 12X18H10T.

4. Vitrification of HLW after pyrochemical processes

4.1. Vitrification of phosphate precipitates

Since the phosphate precipitate is in the powder form and molten salt has high solubility and they have to be disposed, an additional safety barrier should be created that is embedding them into a stable matrix, e.g. glass.

A possibility is shown to embed the phosphate precipitate in the alumofluophosphate glass. The experiment on vitrification of the phosphate precipitate containing [241]Am (specific activity of the phosphate precipitate is 2.8*10^8 Bq/g) showed a high chemical resistance of the samples (2.8*10^{-8} g/cm^2*day in a week). Its deposition for 7 years did not show any structure changes.

The real phosphate precipitate generated after BOR-60 fuel reprocessing contains 22.3% of REE and 14.7% of iron; 96% of activity is given by [144]Ce(Pr), while 86% of alpha-activity is given by [241]Am. The X-ray phase analysis showed that the precipitate structure corresponded to the monazite one. A composition of glass matrix and waste was selected to carry out a real experiment: (NaPO$_3$-75 %, AlF$_3$-10%, NaF-5 %, Al$_2$O$_3$-10%)-85%, phosphate precipitation - 15%.

At the vitrification stage (T=1000°C), the release of activity into the gas phase made up 2.8·10^{-3} and 1.0·10^{-4} % of the initial phosphate precipitate activity for γ- and α-emitters, respectively. Among the γ-emitters, [125]Sb (51.6 %) and [137]Cs (41.9 %) made the key contribution to the gas phase activity; as for the α-emitters, it was [241]Am (92 %). Thermal conductivity of the vitrified waste made up 0.8-1.1W/ (m·^{0}C) at 35-300°C that was an admissible level for the phosphate glass [8, 9].

The leaching rate for Na, Al, P, F and fission products at the 28th day did not exceed 1*10^{-6} g/(cm^2*day) and it decreased to 1*10^{-7} – 1*10^{-8} g/(cm^2*day) at the 118th day. The thermal analysis of the glass samples allowed us to define a devitrification temperature (570-580°C) and storage temperature that should not exceed 450°C. Exothermic effects occurring at 590 and 620°C correspond to the crystallization process. Endothermic effects occurring at 410, 460°C and 630, 660°C correspond to the vitrification process and glass mass melting, respectively.

4.2. Vitrification of spent electrolytes .

The pyroelectrochemical reprocessing of spent fuel uses different chloride mixtures as a salt electrolyte: NaCl·KCl, NaCl·2CsCl, (Na-Li-K-Cs)Cl [4] in different mole ratio.

It was stated that amorphous transparent glass samples can be got if the charge contains less than 8% of a chloride ion. It is partially removed when the charge is melted. Up to 5% of the chloride ion contained in the transparent samples after the treatment. Thus, depending on the atomic mass of alkali metal, the total amount of chlorides that can be introduced in the glass matrix, will make mass %: 7 - 12 % for LiCl, NaCl, KCl, up to 22 % for CsCl. To increase the mass fraction of vitrified chlorides, experiments were performed to convert chloride into metaphosphate, i.e. on of the glass charge components. This additional process allows vitrifying up to 46% of salt waste.

Four model and three radioactive samples (Table 6) were obtained. The X-ray analysis of the samples showed their high level of amorphism. As for sample P-5, an experiment was carried out to determine ^{137}Cs release into the gas phase. During the experiment, the Cs-137 release, together with off-gases, made up $1.3 \cdot 10^{-2}$ % from the initial amount.

Table 6. Composition of glass samples made from electrolytes (mass fraction of the initial components,%)

Sample	KPO$_3$·NaPO$_3$*	AlF$_3$	Al$_2$O$_3$	NaPO$_3$	LiPO$_3$·4,53 NaPO$_3$· 4,88 KPO$_3$·0,66 CsPO$_3$*	NaPO$_3$· 2CsPO$_3$*	NaCl · 2 CsCl
M-4	75	20	5	-	-	-	-
M-5	-	20	5	-	75	-	-
M-6	-	15	5	20	-	60	-
M-7	-	16	4	60	-	-	20
P-3	-	20	5		75	-	-
P-4	-	15	5	20	-	60	-
P-5	-	16	4	60	-	-	20

*After conversion of chloride into metaphosphate

The heat patterns show a similarity of the phase conversion under heating at 20-800°C. The endothermal effects at 420-460° are conditioned by the vitrification process. Exothermal effects at 450-600°C corresponded to crystallazation.

The hydrolythic tests show that inclusion of spent electrolites into the selected glass matrix allows having a glass-like materials with a high chemical stability that is one of the most important creteria of the safe HLW storage.

5. HLW CERAMIZATION

As an alternative approach to preparation of pyrochemical wastes for disposal, a possibility of their immobilization into crystal mineral-like matrices is investigated. Monazite-based matrices were investigated for embedment of phosphate precipitates while murataite-based matrices - for embedment of oxide precipitates. In case of spent electrolytes, their chemical conversion into chemically stable orthophosphate mineral-like forms with conarite mineral structures (phosphate sodium-zirconium, NZP) and langbeinite was investigated.

5.1. *Ceramization of phosphate precipitates*

Compaction of phosphate powder by compression and annealing makes it possible to produce ceramic blocks with the properties that meet the requirements of long-term storage or disposal.

A simulator of phosphate concentrate of pyroelectrochemical process is produced from NaCl-2CsCl melt [10]. The oxides chlorated with gaseous Cl$_2$ were added into the melts and precipitation of fission product simulators with the use of sodium orthophosphate was carried out. The precipitate was

washed from the captured salts with 0.1 N HNO3 solution. The procedure for precipitate production and its chemical composition (table 7) was close to technological conditions and composition of high-level radioactive product known from the previous investigations [5].

The produced powder was compacted into pellets annealed in air at 800-1400°C for 10-12 hours. Phase composition of products was analyzed by X-raying. Chemical composition was identified by the emission spectrum analysis and X-ray spectrum microanalysis with the use of a scanning electronic microscope. The ceramics included the main monazite-like phase with the lattice parameters of a=6,773±0,003 Å; b=6,987±0,002 Å; c=6,435±0,002 Å ; β = 103,68±0,02 degrees.

Leach rate values for main components of ceramics are about 10^{-6}-10^{-7} g/(cm^2·day). Taking into account the localization of the most ecologically dangerous radionuclides in the monazite phase, rather high geometrical density of ceramics (ρ = 4,35 g/cm^3, 85 % of theoretical), as well as chemical and thermal stability (up to 1400°C), the investigated ceramics can be considered as the main promising material for future technology developments.

Table 7. Calculated composition of phosphate precipitate

Element	Mass fraction, %	Element	Mass fraction, %
La	2,74	Fe	13,70
Ce	4,11	Ni	0,55
Pr	2,06	Ti	0,19
Nd	10,27	Mo	0,55
Sm	1,37	Cu	0,14
Eu	0,20	Zn	0,21
Gd	0,1	Mg	1,02
Y	0,41	Pb	0,14
Al	0,20	Ca	2,74
Cr	2,03	Sr	2,80
Mn	0,27	P+O	54,17

5.2. *Ceramization of oxide precipitates*

To carry out the experiments on ceramization of oxide precipitates, initial charge composition developed by MosNPO RADON was taken [11].

Previous simulation of various ceramic compositions was performed taking into account compositions of real precipitates produced in reprocessing of dense fuel. The murataite ceramic is concluded next oxides:

charge components (90,00 wt %) : TiO_2 (55,00 wt %), MnO_2 (10,00 wt %), CaO (10,00 wt %), Fe_2O_3 (5,00 wt %), Al_2O_3 (5,00 wt %), ZrO_2 (5,00 wt %).

high level waste simulations (10,00 wt %): SrO (0,3934 wt %), MoO_3 (2,1930 wt %), CeO_2 (2,7222 wt %), Pr_6O_{11} (2,5452 wt %), Nd_2O_3 (0,5042 wt %), Sm_2O_3 (0,7812 wt %), Eu_2O_3 (0,5265 wt %), UO_2 (0,3344 wt %).

Murataite as a dominating phase is observed for all ceramics, both fused and sintered.

In the real hot experiment in the hot cell, a real oxide precipitate was used instead of simulator components. Fusion of components was conducted at 1350°C for an hour.

5.3. *Ceramization of spent electrolytes*

Orthophosphate compositions of complicated cation structure with the cosnarite mineral structure, including cations of alkaline elements from salt mixtures simulating spent chlorides of alkaline metals were produced. Their phase structure and chemical stability was investigated.

According to the reference data, in systems of double zirconium orthophosphates and cations of alkaline metals, the crystallization of the NZP-like phases depends by the nature of cations and their

quantitative ratio [12, 13]. Various orthophosphate structures on the basis of electrolytes NaCl–KCl, NaCl–2CsCl, LiCl–4,53NaCl–4,88KCl–0,66CsCl used in pyroelectrochemical process [14] were chosen.

Conversion of chlorides to orthophosphates was carried out using various methods: phosphate precipitation from solutions, impregnation of initial reagents by orthophosphate acid, solid-phase method, precipitation from molten chlorides. The powder produced after heat treatment (800°C) was used for ceramics manufacturing (cold compaction-sintering: 200MPa, annealing within 1000-1400 ^{0}C).

The composition of ceramics on the cosnarite basis irrespective of a production method is formed by one or two main NZP phases. There are also phases of zirconium pyrophosphate (ZrP_2O_7) and monoclinic zirconium dioxide – brazilite (ZrO_2). At temperatures above 1300 ^{0}C the last two phases dominate (for structure of $Na_{1/3}Cs_{2/3}Zr_2(PO_4)_3$ higher than 1100^0C). The analysis of the crystal lattice metrics of the NZP phases showed that they represent solid solutions containing alkali cations of two or more types.

The ceramics produced from the NaCl-2CsCl melt as the most widely used was subject to a more detailed research. For this purpose, microstructure, phase and chemical elemental composition were studied by SEM and X-ray spectrum microanalysis for this type of ceramics.

The analysis of backscattered electron images with composite contrast allowed to identify three main phase components of ceramics: light particles of uncertain or oblong shape, dark particles and a grey phase. Results of the X-ray spectrum analysis of the light and dark phase for ceramics produced from the salt system NaCl-2CsCl are evident of the existence of two phases of $Na_xCs_{1-x}Zr_2(PO_4)_3$ composition with the various content of sodium and cesium.

The investigations on the conversion of mixtures of alkali metal chlorides applied as electrolytes of pyrochemical processes in nuclear fuel manufacturing and reprocessing of spent nuclear fuel (SNF) into orthophosphate ceramic materials on the basis of langbeinite mineral was carried out [15]. The results of solid-phase synthesis of phosphates were described. Optimal temperatures for the formation of the langbeinite phase range within 800-950°C.

The analysis of XRD patterns of pellet samples obtained within the range of 800-1100 ℃ showed dominating phases with the langbeinite structure.

Ceramic samples were studied for their chemical stability (MCC-1 test, distillate, 90℃). The materials produced with preliminary washing of powder (before compaction) from the captured chlorides and without it were investigated. The post-leaching analysis of solutions for the content of main cations was carried out by an emission-spectrum method. Cesium leach rates (3-14 days) were at a level of 10^{-4} g/(cm^2·day). Indicators of the chemical stability of the produced phosphates against water leaching of cations of alkali metals are by 1-2 orders higher than the required ones in accordance with GOST. These values don't correspond to permissible standards in accordance with GOST R 50926-96 for solidified waste forms yet.

A rather high leach rate is explained by a partially loose structure of ceramics and its low density (geometrical density - 1,64 g/cm^3, theoretical one - 3,57 g/cm^3).Therefore, to increase chemical stability and density, special processing methods were developed. To improve the ceramic material properties, washing of orthophosphate produced from the captured salts, as well as compaction and annealing with a binding material (addition of 3 % mass of 89 % Bi_2O_3+11 % NaF mixture to the press-powder) were carried out. As a result, the density of ceramics increased by 2 times, leach rate values for sodium and cesium decreased approximately by 10 times (down to 10^{-5} g/cm^2·day).

6. CONCLUSIONS

The report presents the RIAR research experience in management of high-level wastes of pyrochemical processes.

The data presented refer to the results of laboratory-scale investigations of dummy wastes, as well as of hot cell experiments with real wastes produced after pilot reprocessing of SNF from fast neutron research reactors.

Pyrochemical processes are characterized by a small spectrum and volume of the produced wastes, their high specific activity, absence of liquid high-level process wastes.

The main types of solid process wastes are phosphate and oxide precipitates, as well as spent electrolytes.

The main waste forms of pyrochemical processes can be stored long-term in shielding containers without using any schemes of their chemical conversion and immobilization.

If necessary, to enhance efficiency of the HLW shielding barrier for their long-term geological disposal, waste forms of pyrochemical processes can be converted into more stable chemical forms.

Alumofluophosphate glass and monazite-based matrix can be used for immobilization of phosphate precipitates.

Fuse ceramics on the basis of murataite mineral can be used for immobilization of oxide precipitates.

Alumofluophosphate glass and ceramics with the structures of cosnarite and langbeinite can be used for immobilization of salt electrolytes.

Further investigations on immobilization of salt systems can be aimed at a search of effective ways to prevent the formation of conversion and corrosion chlorine-containing gases, effective chemical bonding of chlorine-ion, research and development of hybrid glass-ceramic method of spent electrolytes fixation.

7. ACKNOWLEDGEMENTS

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