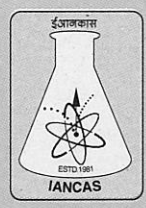


INDIAN ASSOCIATION OF NUCLEAR CHEMISTS
AND ALLIED SCIENTISTS

# Nuclear Fuel Reprocessing

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## Editorial

*A candle burns leaving nothing for reuse, so is the case with coal or oil when used in a thermal power plant to generate electricity. The rapid industrialisation in the 20th Century has resulted in significant depletion in the coal and oil resources. These invaluable resources which were left untouched for millions of years will be wiped out in a couple of centuries if the present utilisation rate continues. The future generations could be in dark. May be the answer lies with the nuclear energy.*

*In the mind of a common man, nuclear energy is associated with a stigma created from the unpardonable use of atomic bombs against civilian population in Nagasaki and Hiroshima. The 'anti Nukes' either forget or are unaware of the unique potential of nuclear energy i.e. it can make more fuel than it burns. It sounds strange, but it is true. When uranium burns in a nuclear reactor, it also results in the formation of fissionable $^{239}Pu$. The $^{239}Pu$ produced can be used in a fast breeder reactor to generate electricity and also simultaneously convert $^{232}Th$ to fissionable $^{233}U$. $^{233}U$ is the fuel for the 'third generation' nuclear reactors. However, $^{239}Pu$ and $^{233}U$ need to be separated from the spent fuel elements. The challenges in achieving this task are many but realised to a large extent thanks to the vision of Homi Jehangir Bhabha, the father of the Indian Atomic Energy programme coupled with the dedication of his handpicked scientists and technocrats. India is one among the few countries which has perfected the 'nuclear fuel reprocessing' technology.*

*The current issue of the IANCAS Bulletin is on 'Nuclear Fuel Reprocessing'. The issue is Guest-Edited by Dr. P.R. Vasudeva Rao. Dr. Rao has done an excellent job in identifying appropriate authors, relevant topics and editing the articles. I am thankful to Dr. Rao and all the authors who have contributed to this issue.*

*Before signing off, I request the readers to send their views and comments about the thematic Bulletins to improve the future issues. Our efforts are towards making IANCAS Bulletin a high quality and authentic reading material.*

**M.R.A. Pillai**

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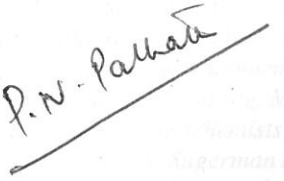

# Fuel Reprocessing - The Initial Years

***Shri N. Srinivasan*** *pioneered the development of the reprocessing programme in our country. He was responsible for the design and construction as well as commissioning of the Plutonium Plant at Trombay. He was also the Project Engineer of the Reprocessing Plant PREFRE, at Tarapur. He took charge as the Project Director of Indira Gandhi Centre for Atomic Research (then Reactor Research Centre [RRC]), in 1971 and was responsible for initiating the fast reactor programme in our country. He was the Director of RRC till 1982. Subsequently, he held the positions of the Chief Executive of the Heavy Water Board and member of the Atomic Energy Commission. Shri Srinivasan presently lives at Chennai and he continues to follow and actively support the nuclear pgorammes in our country. Shri Srinivasan is a Fellow of the Indian National Academy of Engineering, Indian Institute of Chemical Engineers and Institution of Engineers.*

The only naturally occurring source of nuclear energy is $^{235}U$, accounting for less than one percent of the natural uranium. Thus the extent of occurrence of uranium in nature would have set the limit for growth of this source of energy as is the case with the other natural fuel materials like coal and oil. It is the formation of plutonium and $^{233}U$ that practically removes the limitation. These manmade fissile materials are produced in fuel irradiated in nuclear reactors. Plutonium recovered from reprocessing of irradiated fuel from thermal reactors can be used in thermal or fast reactors. Reprocessing is of relevance even to systems using enriched uranium since the fuel discharged contains more fissile isotope than natural uranium. Thus reprocessing of irradiated fuel is an important element of any long term nuclear power programme.

Historically, nuclear power exploded into human consciousness with Hiroshima and Nagasaki. Hence discussions on nuclear power have transcended pure techno-economic considerations. Proliferation aspects have clouded the issue. It is also relevant to remember that the few countries who had reprocessing capabilities had established them for military purposes in the first instance. It is however clear that reprocessing irradiated fuel for recovery of plutonium and utilisation of plutonium in second generation reactors are inescapable, if nuclear power programmes have to be meaningful in the long term perspective. For countries like India and Brazil the scope for utilisation of the vast resources of thorium makes reprocessing even more imperative.

To reprocess or not to reprocess irradiated fuel has often been debated on economic as well as safety considerations. The value of recovered plutonium depends on the use it is put to whether within a system or traded to another system. There could be a situation when even recycle in thermal reactors could be worthwhile. Economic and other pressures on the availability of natural uranium would be a major factor influencing decisions regarding reprocessing.

Right in the beginning of the Indian nuclear programme it was realised that indigenous resources of uranium would be limited and there was a need for India to establish capability to be self-sufficient in fuel sources if nuclear power was to make any contribution to the country's economic development. It is a tribute to the foresightedness of the Father of the programme Dr. Homi Bhabha that he decided that India will embark on a reprocessing programme as one of its first major activities.

While Canada India Reactor (CIR) was still under construction the formal order regarding the decision to set up a plant to reprocess irradiated fuel from it was issued. This was dated December 31, 1958. Apart from the historic nature of the decision it conveyed, the modalities set out for the implementation detailed in it were a veritable model for implementation of such path-breaking, scientifically challenging projects in a country which

had been independent for only a decade. The freedom and flexibility in action allowed to the project management ultimately made it possible to complete the project within the sanctioned cost and the committed time schedule.

There was not much detailed information available on the design of such a plant nor was there any experience in the country in handling systems with lot of radioactive material in a loose fluid form. The team was assembled out of very young engineers the oldest of them being twenty five. All the background they had was the course in the (BARC) Training School, which itself was in the formative stage. The plant was designed literally from the first principles of chemistry and chemical engineering. In the absence of experience in the industry for the specifications called for, fabrication of equipment was taken up in-house to ensure effective quality control and also to improvise as it progressed. The availability of engineers and craftsman trained in the construction of CIR was a useful input. As the design phase was nearing completion, some of the design engineers took up supervision of installation literally learning on the job as it went along. Ultimately the plant went 'hot' in August 1964. Help from the Radiochemistry Division, BARC was valuable in establishing the analytical procedures for this plant.

Many were the mistakes and mishaps that occurred during the earlier days, fortunately none resulting in any health hazard to personnel or environment, thanks to the commitment and devotion to the cause on the part of all personnel. The first grammes of plutonium oxide had been produced when the plant was formally inaugurated in Jan. 65. It was the first such facility outside the nuclear club set up under civilian aegis.

Neutron sources based on plutonium-beryllium, until then, were being imported involving agreements through IAEA regarding peaceful use. With the availability of plutonium, production of these sources by personnel of the Isotope Division was the first application-oriented activity. The first button of plutonium metal was produced in August 65. There was a sense of fulfillment among the personnel involved, little realising at that time that this would pave the way for the later "experiment" at Pokhran.

With a few years of experience of reprocessing CIRUS fuel the next logical step was taken, namely the setting up of a plant for reprocessing Tarapur and Rajasthan reactor fuels. This was a big step not only technologically but due to the non-technoeconomic considerations involved. It must however be conceded that at that point of time, the countries involved were not too fussy about safeguards procedures; learning along the way was an acceptable approach.

Now it is history that reprocessing has come of age in this country and experience has been gained in the fabrication of different types of fuel containing plutonium. When FBTR needed carbide fuel it was just one more challenge to be met and it was met successfully.

The really long term prospect of utilising thorium had also been provided for when in 1968 $^{233}U$ was successfully separated from thorium irradiated in CIRUS and $^{233}U$ was used in reactor systems.

When the nuclear power programme gets back on its feet, availability of reprocessing capability will not be a constraint. This was indeed the dream of the founders of the programme.

# Reprocessing to Recycle - an Option for Better Resource Utilisation in Nuclear Fuel Cycle

***Shri K. Balu*** *graduated in Chemical Engineering from Annamalai University and joined BARC in 1960 through 4th Batch of Training School. He also did an Advanced Course in Nuclear engineering from Argonne National Laboratory, USA. He is presently Director of Fuel Reprocessing and Nuclear Waste Management Group, BARC. His vast and multifaceted experience in all the domains of back-end activities of the Nuclear Fuel Cycle includes planning, erection, commissioning and operation of fuel reprocessing and nuclear waste management facilities and R&D activities related to technology development. His current efforts are directed towards commissioning of project KARP, a reprocessing facility meant to treat spent fuels from PHWRs. He has been a consultant to the IAEA on a number of occasions and was associated with many of their activities including preparation of safety and other technical documents in this field. During 1986-1995 as Director of the Directorate of Purchase and Stores, he shouldered the responsibility of materials management for the various units and technology development efforts of the DAE in the face of stiff export restriction and technology control regimes imposed by several developed countries.*

## The Need for Nuclear Power

An analysis of the world wide energy demand would reveal that in comparison to the practically saturated growth in energy demand in the developed nations, there is a growing demand for power in the developing ones. The onus of chalking out a long term strategy for power generation rests with the individual nations, which should plan their strategy based on the energy resources and technology available at their command. The developing nations have only limited options at their disposal to meet the steep increase in energy requirement and can not ignore the role of nuclear power as an alternate energy source with the potential to meet the energy demand at the projected rates. Further, from the environmental point of view, there is a global need to deploy non-fossil sources to limit the carbon dioxide liberation to the atmosphere.

India has substantial coal reserves, but to meet the energy requirements at the projected growth rates on a sustainable basis, it should go in for nuclear power especially since nuclear power production has been perfected as a technology and demonstrated as a viable process by many countries in the world. India has made steady and substantial progress in all aspects of nuclear power generation following a well planned out strategy and has acquired a sound technological base in nuclear power generation and related areas of nuclear fuel cycle activity. Given this advantage, it is imperative that India should further develop and deploy nuclear power to its full potential.

## Sustainability of Nuclear Energy by Reprocessing and Recycle

For long-term nuclear power production, there are two fuel cycle options that are of relevance and under consideration at the present juncture, viz. the once-through cycle with permanent disposal of spent fuel and the closed fuel cycle with reprocessing and recycle of uranium and plutonium. Both the options require efficient and safe waste management strategies.

As of today, the proven resources of low priced uranium are insufficient to support a long-term and meaningful contribution to India's energy demand by way of nuclear energy. Closing the nuclear fuel cycle by reprocessing the spent fuel and recycle of uranium and plutonium back into reactor systems helps in exploiting the full potential of nuclear power and maximises the resource utilisation. The Indian nuclear resources have been estimated to be around 60000 tons of uranium and around 360000 tons of thorium. In terms of fossil fuel, this is equal to around

1.2 billion tons of coal equivalent through pressurised heavy water reactor (PHWR) and around 800 billion tons of coal equivalent through fast breeder reactor (FBR) and other reactor systems using thorium. Clearly by opting for a closed fuel cycle with reprocessing and plutonium recycle, this constitutes a resource several times larger than any other resource that we have in our country for bulk electricity production.

The success of the closed fuel cycle would depend on the efficient utilisation of plutonium for power generation as it can increase the quantum of energy derived from a given amount of uranium which varies depending on the reactor systems used.

The nuclear energy program in India envisages three stages of implementation involving installation of uranium fueled thermal reactors in the first phase followed by utilisation of plutonium in fast breeder and other types of reactors and in the third phase, utilisation of reactor systems based on $^{233}$U-Th cycle. The first phase of the program is essentially based on the utilisation of PHWRs for power generation with fuel reprocessing, plutonium recycle and efficient waste management as the strategies for the back end of the Fuel Cycle.

**Advantages of Reprocessing and Recycle Option**

***Efficient Resource Utilisation***

Plutonium is an energy source and not a waste to be buried. The use of plutonium makes nuclear energy by far the largest energy resource available to human kind as it permits the burning of a significant fraction of the available natural uranium (in fast reactors) rather than just 1% as we do at present (in thermal reactors). Disposal of a fossil fuel after such a low level of utilisation of its potential would be unheard of.

The choice of the Reprocessing and Plutonium Recycle option can endow the nuclear power program with a variety of midcourse options in both uranium and thorium fuel cycle with plutonium forming the vital link between the two. As plutonium is an energy source with a long half life, its utilisation for power generation can be in 'reprocess to recycle' mode at any given point of time. With a good inventory of spent fuel, this 'reprocess to recycle' approach after extended periods of fuel storage, to meet the plutonium demand as and when it occurs has several advantages and renders reprocessing and nuclear waste management a more viable and safer technology along with reduced man-rem expenditures. Further, with the depletion of the natural uranium and fossil resources, the recycle of reprocessed uranium with an altered isotopic content of $^{235}$U would become economically viable. For example, about 30% of the fueling requirement of a LWR can be met by reprocessing and recycle of plutonium thus reducing the fresh uranium input. The increase in the overall electricity costs due to reprocessing and recycle of plutonium is very marginal over once-through fuel cycle.

***Safe Spent Fuel and Waste Management Option***

From the safety point of view, the reprocessing technology has made vast improvements by complying with the national and international regulatory requirements and its annual radioactivity releases through various forms of effluents have steadily decreased over the years. As of today, these releases are very small in comparison to the present environmental burden of plutonium and other radioactive elements released through atmospheric testing of nuclear weapons.

In comparison to the waste from reprocessing and recycle, the disposal of spent fuel on once-through basis does not eliminate the plutonium inventory that would keep escalating with the increased nuclear power generation and spent fuel storage sites. It can be reduced only by its sustained irradiation in reactors. The comparison of hazards over extended time scale clearly indicates that reprocessing and Pu recycle is a safer option.

The aim of reprocessing is to recover uranium and plutonium which form the bulk of the spent fuel for recycle in reactors. The reprocessing waste would contain mainly fission products and small amounts of transuranium elements immobilized in specially formulated glass matrix and sealed in metal canisters designed for long-term storage.

In comparison to once-through spent fuel, the vitrified mass of fission product waste would occupy lesser space in the repository. The heat generation in the wastes is mainly from $^{137}$Cs and $^{90}$Sr and it is less than that from spent fuel stored as such. Further the

waste matrix made with unprocessed spent fuel should take into consideration the heat and helium gas generation due to the presence of macro amounts of actinides during long term storage.

In case of breach of containment and leaching by water, the vitrified glass matrix releases radionuclides only slowly over an extended period of time. The $^{237}Np$, $^{129}I$ and $^{99}Tc$ are the dominant isotopes to be considered under these conditions and with advancements in reprocessing, these isotopes can be managed satisfactorily.

The breach of repository containing spent fuel would pose more risks to the public at large than the compact reprocessed wastes. The increasing amount of uranium and plutonium and other fissile nuclides, some of which have lesser critical mass than plutonium at the unprocessed spent fuel storage repository may pose criticality hazards under accidental conditions like leaching/ water flooding over extended period of time.

The spent fuel with fission products stored over several decades would result in the decay of most of the fission products and radiation would no longer be a deterrent for accessing the fuel, but the inventory of plutonium would increase. With increasing nuclear power generation, the spent fuel management under once-through option may warrant large number of storage sites.

Though the overall risk perceptions for nuclear fuel cycle activities are small and compare well with other industrial activities, reprocessing and recycle of uranium and plutonium would reduce these risks further, as maximum risk in the nuclear fuel cycle is associated with uranium mining and recovery activities.

**Evolving Global Perceptions on Reprocessing**

The light water reactors (LWR) have been the mainstay of nuclear power program in many parts of the world, with PHWRs and FBRs contributing significantly to this effort in a few countries. Over the past few decades, the operation of the uranium based power reactors and the various research reactor systems have led to increased fissile inventories of plutonium in the spent fuel. During the first generation nuclear fuel cycle activities, reprocessing and recycle of uranium and plutonium for power generation was perceived by many countries to be among the best of long term strategies for the management of spent fuel. For several reasons, this perception has changed gradually over the years in some of the countries which now consider that once-through fuel option as the economical and proliferation resistant approach that should be accepted globally. However, these two criteria may differ from country to country and their perceptions would also differ accordingly.

Several nuclear energy countries like France, India, Japan, Russia and the United Kingdom have used reprocessing as part of their strategy for spent fuel management whereas a few countries like Canada, Sweden and USA have opted to use the uranium once-through cycle option. USA has abundant reserves of coal, natural gas and oil. Canada has abundant natural uranium reserves and has no need to reprocess and recycle Pu. Among the European countries, France has pursued a very active program on reprocessing and recycle of plutonium as MOX fuel. The technologically advanced Japan with poor energy resources has an active programme on Pu recycle. Uranium enrichment activities for fueling LWR leads to a significant build up of depleted uranium as waste which can be reused after mixing with plutonium. There is also a possibility that Pu in MOX form may eliminate the need for uranium enrichment. Thus for any country, the choice of its fuel cycle options with its minor variations should rightly be governed by its own assessment of its energy requirements on a long-term perspective, the alternate energy resources available at its command with their cost and its technological infrastructure capabilities to support and sustain modern sophisticated technologies such as nuclear power and subsequent spent fuel management.

The successful and safe implementation of nuclear power programme and the associated fuel cycle activities would contribute greatly towards a positive public acceptance of nuclear power as a promising approach for meeting the energy demands on a long term perspective. The Purex process for the reprocessing of spent nuclear fuel and the practices followed for the safe management of the nuclear waste arising out of theses operations are viable and safe back end fuel cycle technologies are practised in many parts of the world. Over the years, several

thousand tons of spent fuel have been processed with satisfactory management of the waste arisings.

From the Indian context, the following aspects pertaining to economy and non-proliferation concern merit attention.

The availability of uranium resources in India is limited. Other than the constraints to be overcome in meeting the energy security and non-proliferation concerns, purely from the economic considerations, uranium procurement would add substantially to the foreign exchange component of the energy bill. The Indian reprocessing and storage costs in terms of installation and operation are substantially lower in comparison to the figures reported for western countries. Larger size facilities may even cost less, with the full technology being mostly indigenous.

From the proliferation angle, we consider that reprocessing and recycling is more proliferation resistant than once-through option, because recycling consumes plutonium while once-through leaves behind huge stocks of spent fuels which contain recoverable plutonium that may prove to be a rich and easy source for plutonium after several hundred years of cooling. Further, its utilisation for power generation in 'reprocess to recycle' mode, to meet the plutonium demand avoids the long term build up and storage of reprocessed plutonium stocks and inventory.

Thus from the Indian stand point, the reprocessing and plutonium recycle option is not only considered to be a superior option but also to be an inevitable one. This perception had emerged some four decades ago and has since remained unaltered.

## The Indian Nuclear Energy Program

### *Nuclear Reactor and Power Generation*

Besides the two BWRs at Tarapur, there are several operating PHWRs with a design capacity of 220 MWe each. A few more reactors of similar type including two reactors each of 500MWe are under different stages of planning, construction and commissioning. Under Fast Breeder Reactor (FBR) technology development programme, a 40 MWt Fast Breeder Test Reactor (FBTR) is operational at Kalpakkam and the design of a 500 MWe Prototype Fast Breeder Reactor (PFBR) is in progress. In addition to PHWRs and FBRs, it is proposed to include LWRs and Advanced Heavy Water Reactors (AHWR) in the power programme.

These activities call for extensive recycling of Pu generated from PHWR's in FBR's or in the existing PHWRs or in newly conceived reactors of the AHWR type. These concepts are evolved to maximize the use of available resources and are heavily dependent on successful reprocessing and recycle of Pu.

### *Reprocessing and Fuel Fabrication*

Over the years, in tandem with the increase in spent fuel arisings from the growth of nuclear power, the reprocessing and nuclear waste management capabilities have been augmented to keep pace with the plutonium demands. There are now two reprocessing facilities to treat spent fuels from PHWRs.

Based on the plutonium fuel fabrication experience on a pilot plant scale at Trombay, a sophisticated industrial scale Advanced Fuel Fabrication Facility (AFFF) has been setup at Tarapur to meet the MOX fuel fabrication requirements of thermal reactors, FBTR and the initial startup requirements of FBR. A larger facility to cater to the fuel requirements for FBR is planned at Kalpakkam.

### *Thorium / Uranium-233 Fuel Cycle*

To meet the challenges of thorium based fuel cycle which is the nuclear fuel cycle of the future for India, R&D efforts are directed towards extractive metallurgy of thorium, fuel fabrication and its utilisation in reactors, reprocessing of irradiated throium for $^{233}U$ recovery and studies on $^{233}U$ based reactor systems. Demonstration facilities have been operated in all these domains. For the separation of $^{233}U$ from thorium irradiated in different reactors, an engineering scale facility is coming up at Trombay. With $^{233}U$ as fuel, India has operated three reactors, PURNIMA-II & III and the latest one being KAMINI, a 30kW research reactor with $^{233}U$-Al alloy as fuel, commissioned in 1996 at Kalpakkam. Thus India is one among the few countries which have developed all-round capabilities in thorium based fuel cycle.

*Emerging Concepts in Pu Recycle:*

Though the FBRs are the best long term options for Pu recycle and burning, utilisation of plutonium in PHWR also offers considerable flexibility in terms of fuel cycle variations. Using U-Pu MOX in various combinations in PHWR, it is possible to get improved fuel utilisation and extended burn-up resulting in significant increases in the overall installed capacities. The conceptual once-through thorium fuel cycle studies reveal that thorium can be used in combination with plutonium in reactors to high discharge burn-ups. It can burn plutonium to a very significant extent. Studies on various reactor concepts indicate that heavy water reactors are second only to molten salt reactor systems as a choice for thorium utilisation. An attractive option would be the use of plutonium as a key to initiate the thorium cycle. As part of this programme, India is working on the design of AHWR. This reactor requires an initial inventory of $^{233}U$ as well as plutonium. It derives 75-80% of its power from thorium in a self-sustained mode of $^{233}U$-Th cycle. The reactor needs some initial input of Pu in the form of mixed U-Pu oxide which contributes to 20-25% of the power and the recurring need for plutonium is relatively small. $^{233}U$ in the thorium is adjusted to be at the self-sustaining level and a discharge burn-up of 20000MWD/T is attained using plutonium as additional make up in the form of U,Pu oxide pins. The Pu pins are placed where neutron spectrum is most advantageous to Pu and the thorium fuel remains uncontaminated by the long lived plutonium and transplutonium actinides.

*Radioactive Waste Management*

The Indian programme on safe management of radioactive wastes envisages two distinct modes of final disposal in respect of radioactive wastes; near-surface engineered, extended storage for low and intermediate-level active wastes and deep geological disposal for high-level and alpha bearing wastes.

A waste immobilisation plant for the treatment of HLW is operational at Tarapur. It is a semi-continuous pot glass process involving calcination followed by melting in the process vessels. Two more waste immobilisation plants are being set up at Trombay and Kalpakkam. Use of joule heated ceramic melters is under development. A solid storage and surveillance facility (SSSF) has also been set up for interim storage of vitrified HLW.

As regards ultimate disposal, the Indian choice is focused on igneous rock formations and some selected sedimentary deposits. Investigations are in progress for evaluation of candidate sites for a repository.

*Partitioning and Transmutation (P&T) Options*

Following the separation and recovery of uranium and plutonium from spent fuel by Purex process, the highly radioactive fission product wastes are concentrated and compacted into vitrified mass for long term storage in geological repositories. This waste usually contain most of the fission products, residual U & Pu and other actinides like Np, Am and Cm. Over a period of 1000 years, most of the fission products decay to negligible levels except a few like $^{129}I$, $^{99}Tc$ etc. However long lived actinides like $^{237}Np$, $^{243}Am$, $^{241}Am$ etc. remain with the waste, thus becoming the major contributors to the hazard posed by this waste on a long term perspective ie. beyond 1000 years. The removal of long-lived alpha emitting actinides from these wastes under P&T option would greatly reduce their long term radiological hazards. Removal of shorter lived fission products such as $^{90}Sr$ can reduce the heat generation from these wastes. Further, recovery of useful nuclides from this waste will make the waste management with P&T more economical and viable. Thus the main objective of partitioning high level waste is that it shall lead to a safer waste, more acceptable to the public.

From the Indian context, the present studies are limited to the partitioning of the long lived actinides from the HLW as any reduction in the alpha burden of these wastes would render them safer with respect to long term disposal. At appropriate time, a long term policy on the final utilisation / transmutation of the recovered actinides would be evolved, based on the available state-of-the-art technology at that point of time.

Studies are in progress for the quantification of the PHWR spent fuel arisings, the radiological source terms of the relevant actinides and fission products in Purex HLW after reprocessing and

evaluation of their hazard ranking. Solvent extraction and extraction chromatographic studies with HLW are in progress to propose suitable flow sheets for partitioning of the relevant actinides from these wastes and to reduce the alpha burden to very low levels.

From reprocessing angle, improvements in Purex process to reduce Pu losses to the waste, recovery of neptunium and possibly $^{99}$Tc in the process are some of the aspects receiving attention. Alkaline trapping for $^{129}$I is also envisaged.

However, an advanced fuel cycle with complete recycle of uranium and transuranium elements will have many additional steps such as efficient minor actinide separation from HLW, MOX fuels or target fabrication for fast or thermal reactors or transmutation facilities, reprocessing of spent FR/MOX fuel with quantitative and multiple recycling for transuranium elements depletion and final storage/ disposal of highly radioactive spent fuels from fast reactor. All these technologies are still to be evaluated and mastered. The disposition of surplus weapons grade plutonium by its recycle in reactors would also pose similar challenges.

Under P&T option, repeated recycle of actinides would lead to high levels of $^{238}$Pu, $^{241}$Am, $^{243}$Cm and $^{244}$Cm in the materials to be handled. The man-rem expenditures associated with P&T tasks involving these nuclides should be compared with the dose the coming generation would be expected to receive in the distant future, in the event of leachates from geological repository reaching the biosphere without P&T. Such a comparison would be of help in reaching a decision regarding P&T option.

In the Th/$^{233}$U fuel cycle, the amount of transuranium nuclides generated is smaller by several orders of magnitude as compared to that arising from $^{235}$U/$^{238}$U fuel cycle. The minor actinide production is maximum in the LWR reactors and the minimum with the $^{232}$Th-$^{233}$U fueled PHWR type reactor. In the case of LWR, the major hazard is from Am, Np, Cm isotopes and the left out Pu and U, whereas in the $^{232}$Th-$^{233}$U fuelled reactor, the hazard is mainly from $^{231}$Pa.

**Conclusion**

The present developments indicate that by opting for a closed nuclear fuel cycle, a significant fraction of the energy input could be coming from materials being reprocessed for recycle. The closed fuel cycle option would in turn open up an ever widening spiral of back end activities that would encompass advanced reprocessing and fuel fabrication, fuel cycle with P&T options for recycling of actinides, recovery of important fission products and efficient and safe management of the waste on long-term basis. Thus the back end activities for closing such an advanced U/Pu fuel cycle promises to be an area filled with many possibilities and challenges and will open up new vistas in nuclear fuel cycle.

# An Introduction to the Purex Process

*Dr. A. Ramanujam joined BARC in 1963 after his post graduation in Chemistry from the University of Bombay and has been associated with the Trombay Plutonium Plant since its inception. In 1970, as an ASTEF scholar, he specialised in reprocessing of high burn up fuels at CEA, France. He obtained Ph.D. (1980) in the field of solvent extraction and process chemistry of actinides. As Head of the Laboratory Section of the Fuel Reprocessing Division, he is responsible for plutonium product processing and process control analytical operations at the Trombay Plant and for setting up the laboratory systems in the new repocessing projects like KARP, FUS etc. He was responsible for the management of $^{233}U$ fuel in Purnima II Reactor and for the supply of $^{233}U$ during the fabrication of U-Al alloy fuel for KAMINI Reactor. His R&D interests include Purex and Thorex process development, automation in Pu and $^{233}U$ product processing, partitioning and recovery of minor actinides and important fission products under P&T programme. He is the chief investigator for an IAEA-BARC Coordinated Research Programme on P&T. He was a member of the IAEA-TCM for reviewing the Safety Series book on 'Safe Handling of Plutonium'. He was the Treasurer of IANCAS during 1985-88.*

**Introduction**

During the operation of nuclear reactors, $^{235}U$ component of the natural uranium fuel is fissioned, generating neutrons and a host of highly radioactive fission products. Simultaneously, the fertile $^{238}U$ captures some of the neutrons and yields $^{239}Pu$, a new and useful fissile nuclide.

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow \text{Fission products} + 2.5\ {}^{1}_{0}n + 194\ \text{MeV}$$

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U \xrightarrow[23.5\ \text{min.}]{\beta^-} {}^{239}_{93}Np \xrightarrow[2.3\ \text{day}]{\beta^-} {}^{239}_{94}Pu$$

The accumulated fission products in the fuel hinder the operation of the reactor system from radiation and neutron economy points of view. Because of this, as the burn up (expressed as MWD/tonne) of the fuel goes high, the spent fuel has to be replaced with fresh fuel in the reactor to continue its operation.

The spent fuel discharged from reactors contains significant quantities of fissile nuclides, mainly the unutilized $^{235}U$ and the newly formed $^{239}Pu$ which can be re-used. The process of separating the fissile and fertile materials (Pu and U) from the fission products in the spent fuel after allowing for the decay of short-lived fission products is termed as spent fuel reprocessing.

**Process Requirements**

Fuel reprocessing differs from conventional chemical processing due to the radioactive nature of the materials being processed. The equipment have to be installed behind massive concrete shielding (sometimes as much as 1.5 M thick) to provide built-in arrangement for separation and protection of the operating personnel from equipment with high radiation field. Stringent air ventilation and exhaust requirements are to be met in the entire plant to protect the operating personnel and the environment from getting contaminated due to air borne radioactivity. The processes and equipment used are modified to suit remote operation and maintenance.

Another important difference between traditional and nuclear chemical engineering is the need to provide a design that precludes the possibility of accidentally producing a self-sustaining nuclear chain reaction - the condition known as criticality- when large concentrations or quantities of fissile isotopes ($^{239}Pu$, $^{235}U$ or $^{233}U$) are handled. Safe operation of a reprocessing plant is generally achieved by criticality control techniques like mass, volume, and concentration control of fissile materials or geometry control of the equipment used.

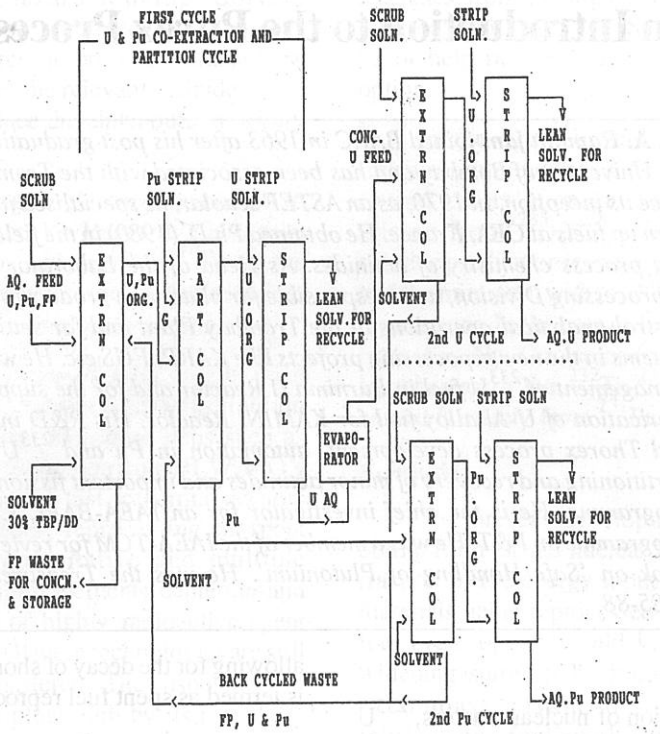


*Fig. 1 Flow scheme of Purex process*

**Purex Process**

World over, Purex process is followed for the separation and purification of uranium (U) and plutonium (Pu) from irradiated spent fuels after dissolving the fuels in nitric acid. Purex process is essentially a solvent extraction process which uses Tri-n-butylphosphate (TBP) diluted with dodecane as solvent to extract and further separate U and Pu from highly radioactive fission products. The U and Pu products are further purified and converted to oxides,while fission product waste solution is neutralized and stored for subsequent treatment and disposal. The general flow scheme used is given in Fig. 1.

The Purex process has the following major steps:

- Decladding or dejacketing
- Dissolution
- Feed preparation
- Co-decontamination and Partition cycle
- Final U purification cycle
- Final Pu purification cycle
- Pu and U reconversion to their oxides

The first three steps together are called head-end treatment steps meant to bring the fuel into dissolved aqueous form suitable for Purex process. The aim of the co-decontamination and partitioning step is to extract and separate U and Pu together from the rest of the fission product impurities and then further separate and purify U and Pu from each other. In the subsequent steps, U and Pu are purified further individually before conversion to their oxide forms.

The extent of purification or decontamination of U or Pu achieved in each step is generally expressed by a term called decontamination factor (DF) and is defined by the following expression:

$$DF = \frac{\beta, \gamma \text{ activity/g of U or Pu in feed}}{\beta, \gamma \text{ activity/g of U or Pu in product}}$$

The larger the DF one obtains in an extraction step, the greater is the purification and efficiency of the process. In general, the DF with respect to beta and gamma activities aimed in Purex process after 2 cycles of extraction is of the order of $10^6$ to $10^7$ for both uranium and plutonium.

### *Head End Process Steps in Purex Process*

*Decladding*

Fuels have different cladding materials such as aluminium, zircaloy and stainless steel depending on the reactor types. The removal of jacket material prior to processing is desirable, as otherwise it contributes greatly to the volume of highly radioactive process solution to be processed and the waste that must be stored. Based on the cladding material, the decladding method is selected, ie. chemical decladding or mechanical decladding. In the former method, the decladding material is preferentially dissolved in aqueous solution whereas the fuel core remains undissolved. In the latter method, the fuel assemblies are chopped and dissolved in nitric acid and the clad material remaining undissolved is disposed as solid waste. This technique is mostly adopted for spent fuel arisings from power reactors (PHWRs), as they are generally clad with zircaloy.

*Dissolution*

Concentrated nitric acid is used to dissolve uranium and uranium oxide fuels. Dissolution is carried out batch-wise. The dissolution is exothermic and the reaction is controlled by optimizing the concentration of acid as well as the temperature of reaction. Oxides of nitrogen liberated during the dissolution are reoxidised and put back in the dissolver using down draft condensers to reduce the consumption of nitric acid. Further, the gases are treated to remove the traces of nitric acid and volatile fission products, cooled and filtered before being exhausted through a tall stack.

Uranium dioxide dissolves in nitric acid by the net reaction:

$$UO_2 + 4H^+ + 4NO_3^- \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$$

It is possible to dissolve uranium without any net evolution of gaseous products except the gaseous fission products by sparging oxygen as reactant and this type of dissolution is called fumeless dissolution.

*Feed Preparation*

The solution resulting from the dissolution of spent fuels must be adjusted in most cases before it is ready for solvent extraction involving one or more of the following operations:

- Solids removal or feed clarification to avoid choking, plugging and emulsification during extraction
- Adjustment of feed acidity to obtain the extraction of the required component
- Adjustment of salting strength by dilution or evaporation of the feed to the desired uranium content level, to have maximum processing rate, wherever necessary.

In Purex process, at the end of the dissolution, uranium is present in sixth valence state and plutonium mostly in tetravalent state. For good extraction by TBP, tetravalent state of total plutonium is ensured by further addition of $NaNO_2$ followed by digestion at 50°C.

$$PuO_2^{2+} + NO_2^- + 2H^+ \rightarrow Pu^{4+} + NO_3^- + H_2O$$

$$Pu^{3+} + NO_2^- + 2H^+ \rightarrow Pu^{4+} + NO + H_2O$$

$$6Pu^{3+} + 2NO_2^- + 8\,H^+ \rightarrow 6Pu^{4+} + N_2 + 4\,H_2O$$

The dual function nitrite (i.e. it reduces Pu(VI) to Pu(IV) and oxidizes Pu(III) to Pu(IV)) makes it an ideal feed conditioning agent in Purex process. $NO_2$ gas can also be used for this adjustment, as it precludes the introduction of sodium ion as impurity and has other advantages as well.

### *Solvent Extraction with TBP*

As the major separation process steps are essentially solvent extraction cycles with TBP, the TBP extraction technique will be discussed briefly before a discussion on these process steps is taken up.

*TBP as an Extractant*

Several factors influence the choice of a solvent for the extraction process in the processing of irradiated fuel elements. A final choice involves a

compromise between various factors. TBP is generally favoured as it meets most of these conditions and is employed in most of the fuel reprocessing plants in the world. TBP is highly selective for U and Pu. As a commercial product, it is cheaply available and can be purified easily. It has a high boiling point (266°C) and is non-volatile. Its solubility in water is only 0.4 g/l. It has high chemical, thermal and radiation stability. It has very low extractability for fission products resulting in excellent purification of U and Pu. The only two unfavourable properties are its high density (0.973) and high viscosity which are compensated by diluting it with an inert diluent like kerosene. In the process, it can be purified by washing with $NaOH/Na_2CO_3$ and $HNO_3$ to remove the decomposition products. The difficulties in the ultimate disposal of used TBP (due to phosphates) have led to the evaluation of other solvents in some countries, but these have not had the full plant scale exploitation similar to that of TBP so far.

The diluent for TBP must be non-polar, unreactive towards $HNO_3$ and $HNO_2$ and stable to radiation. In addition, it should have a high flash point and low vapour pressure. These criteria limit the choice to aliphatic hydrocarbons containing 12 to 14 carbon atoms. Among hydrocarbons, straight chain hydrocarbons (paraffins) are more resistant than branched chain paraffins and both types are much more stable than aromatics. Generally n-paraffins, n-dodecane or n-tetra decane or the mixtures of the two (180 - 210°F) are the best diluents. Shell Sol T, Sol trol, etc., somewhat superior to kerosene, are also used widely.

A concentration of 30 volume per cent of TBP in suitable diluent has been prominent in all Purex process works. The choice of TBP concentration is a compromise between processing a minimum liquid volume and having a solvent phase with suitable physical characteristics to be processed. Generally, the Pu purification cycle uses lower percentage of TBP (20%).

*The mechanism of extraction by TBP*

TBP extraction process accomplishes separation of U and Pu together from fission products and from each other by taking advantage of the varying extent to which the three constituents present in the aqueous phase form nitrate complexes that are extracted by TBP. For $UO_2^{2+}$, $PuO_2^{2+}$, $Pu^{4+}$ and for few other ions in tetravalent state, complexing is considerable. But for a few exceptions like Ru(NO), $Zr^{4+}$, etc., the ability to form nitrate complexes is very poor for most of the elements that constitute the fission products.

Because of the similarity of U(VI) and Pu(IV) in the formation and extractability of nitrate complexes and the inextractability of fission products, an efficient separation of former from the latter is obtained by solvent extraction with TBP. Then taking advantage of the fact that Pu(III) is weakly extracted, a further separation of U and Pu is achieved by reducing Pu(IV) to Pu(III), in which state it gets stripped from the organic phase. TBP being a non-ionised solvent (dielectric constant 8), the mechanism of extraction is that U and Pu nitrates associate in the aqueous phase and are readily solvated by TBP and extracted into the organic solvent. If M is the metal atom, the species extracted are:

Trivalent state : $M(NO_3)_3$. 3 TBP

Tetravalent state : $M(NO_3)_4$.2 TBP

Hexavalent state : $MO_2(NO_3)_2$ .2 TBP

In all the cases, the co-ordination positions of the central metal atom are filled up. Nitric acid is extracted as TBP.$HNO_3$. The extraction of nitric acid is almost independent of temperature except at low concentrations of $HNO_3$. Nitric acid is back salted from TBP to the aqueous phase by uranyl nitrate, thorium nitrate and other extractable salts.

*Extraction of uranium and plutonium*

TBP is bound to metal ions by covalent bonds but to acids and water by hydrogen bonds. The extraction mechanism of U(VI) and Pu(IV) into TBP is well established and the reaction at equilibrium is:

$$UO_2^{2+} + 2NO_3^- + 2\ TBP \rightarrow UO_2(NO_3)_2.2\ TBP$$

$$Pu^{4+} + 4\ NO_3^- + 2\ TBP \rightarrow Pu(NO_3)_4.2\ TBP$$

The distribution ratio (D) of Pu and U is directly proportional to the square of free TBP concentration [TBP]. Generally, the extraction of Pu(IV) is directly proportional to the fourth power of nitrate ion

concentration [$NO_3^-$]. Similarly, the uranium extraction is proportional to square of the nitrate concentration in the aqueous phase. When the nitrates of U and Pu are extracted by TBP from varying concentrations of nitric acid solutions, D values initially increase sharply with aqueous nitric acid concentration, due to increase in the [$NO_3^-$] which enhances the formation of undissociated, neutral species that are readily extracted. But at high acidities, the $HNO_3$ itself competes with U and Pu and, therefore, there is a fall in the D values.

There is a difference in the extractability when 'trace' and 'macro' quantities of solute are present. When large amounts of solute are present there is a greater use of available TBP and so TBP gets saturated. This retards further extraction due to a reduction in the "free" TBP. The maximum concentration of uranium that can be achived in 30% (v/v) TBP (approx. 1 M) can be calculated to be 119 g/l (0.5 M) only, as per the formula $UO_2(NO_3)_2.2$ TBP.

***Chemistry of troublesome fission products and minor actinides and their extraction behaviour with TBP***

*Ruthenium and Rhodium ($^{106}Ru$-$^{106}Rh$):* The bulk of ruthenium is relatively easy to separate but a small part extracts in TBP and remains with the products in spite of drastic scrubbing of the organic phase. Nitrosyl ruthenium, $RuNO^{3+}$, is a very stable entity and has five co-ordination positions available to be filled in aqueous nitrate solutions by water, nitrate, the nitro group or the hydroxy ion. The nitro complexes are quite stable and are in the majority and are extracted only moderately by TBP. The nitrato nitrosyl ruthenium complexes are probably the specific trouble makers in Purex processes. After Ru(III) extraction has taken place as nitrato species, TBP can replace the water in the primary sphere. For example, $RuNO(TBP)_2(NO_3)_3$ formed from $RuNO(H_2O)_2(NO_3)_3$ has such large D values (of the order of $10^3$) that it cannot be be scrubbed from organic phase until it is converted to a less extractable species. The conversions back and forth between species are slow and occur in both phases and continue even in stripping contactors and releases Ru into the product streams. A fast extraction and scrubbing for long duration, at higher acidity and temperature is recommended for for better decontamination from Ru.

*Zirconium and Niobium ($^{95}Zr$-$^{95}Nb$):* In practice, a great part of the Zr exhibits the expected extraction behaviour in TBP but a small fraction is extracted and scrubbed out very slowly. It is this small fraction which so often limits the overall decontamination factor. The solutions from dissolved fuels contain some colloidal material which in combination with Zr extracts well and during scrubbing zirconium is released very slowly. Fission products like Technetium present as $TcO_4^-$ facilitate their own extraction and that of Zr by forming complexes that are extracted well in TBP. Zirconium has also a tendency to hydrolyse and polymerize at low acidity and high temperature. The degradation products of TBP (DBP and MBP) have strong affinity for Zr and affect the DF and form precipitates with Zr. Normally, Nb extracts very little but a small fraction follows the Zr pattern. DF for Zr and Nb are some times improved by using efficient filtration systems as silica is found to help in Nb sorption. In French plants, $F^-$ ion has been used to complex Zr and prevent its extraction.

*Americium and Neptunium ($^{241}Am$ and $^{237}Np$):* Am(III) present in the Purex feed (formed from beta decay of $^{241}Pu$), follows essentially the trivalent rare earths and gets concentrated in the high level raffinate waste. It is now considered prudent that Am(III) and other long-lived alpha emitting actinides present in the high level waste should be removed from the waste concentrates before their final disposal so that their long term radiological hazards are reduced significantly. $^{237}Np$ can exist in IV, V and VI oxidation states. The concentration of nitrous and nitric acids, uranium and temperature influence the conversion from one state to another. Therefore, the behaviour of Np in the Purex process very much depends on the redox conditions prevailing in various cycles. Usually a major amount of Np is present in the dissolver solution as Np(V), which is poorly extractable in TBP, in comparison to Np(IV) and Np(VI). Smaller fractions of Np tend to follow the U or Pu streams as a result of the conversion to extractable states due to redox processes. However, it is possible to devise schemes to avoid co-extraction of Np or to direct it to any particular stream by making use of its chemistry.

*Degradation of TBP*

TBP, though very stable, is subject to hydrolysis or de- alkylation giving rise to DBP $(R\text{-}O)_2$ P - OH), MBP and butyl alcohol. Nitric acid also reacts to give DBP and butyl nitrate. The formation of DBP is only the first step to complete dealkylation that leads ultimately to orthophosphoric acid. This hydrolysis can take place in both phases and is promoted by higher temperatures. At temperature in excess of about 120°C, TBP can be decomposed with explosive violence in presence of uranyl nitrate and nitric acid as oxidant.

The formation of DBP increases the extraction of U, Pu, and Zr. It interferes with the separation of U and Pu and makes their complete stripping difficult. Zr, Pu(III) and Pu(IV) form precipitates with MBP/DBP and phosphates, which are insoluble in both phases in usual Purex systems. However, DBP, being acidic, can be washed out with any basic solution and the TBP is usually washed with $Na_2CO_3$ and NaOH solutions before being recycled. However, the use of these wash reagents lead to a lot of salt bearing wastes in Purex process. Sorbants and vacuum distillation techniques have been tried with some success for organic treatment.

*Degradation of Diluent*

In the case of degradation of kerosene, Shell sol-T or n- paraffins, chemical attack by nitric and nitrous acids combined with radiolytic attack produces a spectrum of nitrogen compounds, ketones, esters and unsaturates. The general chemical effect is to produce new extractants more potent than TBP with great affinity for Zr, Pu and Ru. The degraded solvents after thorough clean-up often contain Ru as residual activity. These potent extractants cannot be easily washed away by acid or alkali.

***Co-decontamination and Partitioning Cycle:***

*Co-extraction*

The aim of this extraction step is to separate U and Pu together from fission products. After adjustment of the composition of the dissolver solution, it is fed to the centre of a contactor which might be a compound contactor consisting of extraction and scrub section. Nitrous acid is added to the feed stream to ensure that plutonium is present as Pu(IV). A solvent stream, 30% TBP in n- paraffin, is fed at the bottom of the contactor and a stream of 2 M or 3 M scrub $HNO_3$ enters the contactor from top. U and Pu are extracted together by solvent stream, the scrub stream scrubs out most of the small quantity of fission products that gets extracted. The fission products leave the contactor in the aqueous waste (raffinate) at the bottom and Pu and U leave the column in the solvent stream. This is the general pattern in which the extraction contactor of the co-decontamination step is operated. During the operation, a variety of variations are possible to optimise decontamination from the fission products Zr and Ru. For example, a high loading of uranium in solvent phase helps to reduce the extraction of fission products (as the available free TBP concentration becomes less after full uranium loading). Too much loading of uranium into organic, on the other hand, will prevent the extraction of plutonium also and, therefore, an optimum saturation of 60 to 85% is generally preferred. The extraction scheme generally used is given in Fig. 2.

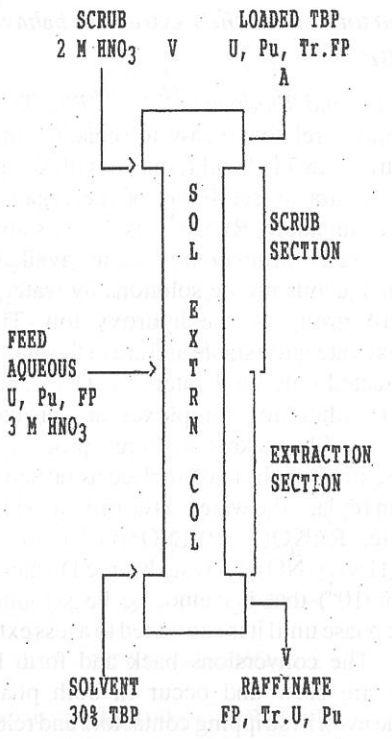


*Fig. 2 Scheme for extraction of U and Pu*

*Partitioning*

The loaded and scrubbed solvent containing U and Pu from the extraction column/ scrub column is taken to the partitioning contactor where uranium and plutonium are separated from each other. This is achieved by back extracting plutonium from TBP phase by reducing it to trivalent state with an aqueous solution containing a suitable reducing agent. Ferrous sulfamate or uranous nitrate stabilized with hydrazine have been the two most commonly used reducing agents. Although ferrous sulfamate was widely used as a reductant in Purex process in early days, it had the disadvantage of introducing Fe and sulfate (produced by the hydrolysis of sulfamate) into the solution giving rise to higher solid content in the waste due to iron and corrosion problems due to sulfate. Due to these reasons, uranous nitrate stabilized with hydrazine is preferred over ferrous sulfamate as reductant for the partitioning of U and Pu in many Plants. Various parameters governing the effective use of uranous are discussed below.

When uranous nitrate is used alone for the reduction of Pu(IV), the $HNO_2$ always present in extraction contactors oxidizes Pu(III) and U(IV). In the absence of a stabilizer, the oxidation of U(IV) by $NO_2^-$ is autocatalytic as can be seen from the following reactions:

$$U^{4+} + NO_3^- + H_2O \leftrightarrows UO_2^{2+} + NO_2^- + 2H^+ \text{ Slow}$$

$$U^{4+} + 2HNO_2 \leftrightarrows UO_2^{2+} + 2NO + 2H^+ \text{ Fast}$$

$$2\,NO + NO_3^- + H_2O \leftrightarrows 2H^+ + 3\,NO_2^-$$

Pu(III) reacts as follows:

$$Pu^{3+} + HNO_2 + H^+ \leftrightarrows Pu^{4+} + H_2O + NO$$

Due to these reasons, a stabilizer is always used along with uranous nitrate to remove or destroy $NO_2^-$ in the system. Hydrazine has been found to be very effective in this respect. It has been found that 0.1 M $N_2H_4$ removes $NO_2^-$ from 30% TBP phase as well.

$$N_2H_4 + NO_2^- + H^+ \leftrightarrows HN_3 + 2H_2O$$

$$HN_3 + H^+ + NO_2^- \leftrightarrows N_2O + N_2 + H_2O$$

Though $HN_3$ is a hazardous chemical, its concentration remains very little if 0.1 M hydrazine is used as stabilizer. The extractability of U(IV) in the organic phase means that a TBP scrub can remove the excess U(IV) being carried by aqueous product Pu(III) stream. This is one of the major advantages claimed for U(IV).

Because of the extractability of U(IV) in TBP, it has to be introduced at the centre of the contactor at or near the organic feed point. This brings it into immediate contact with plutonium bearing organic feed to reduce the bulk of Pu to Pu(III) and strip it from the organic phase. From here U(IV) is carried in both directions by the two streams giving reducing agent in both phases of all the stages of contactor. A similar aqueous scrub with U(IV) and hydrazine in dilute nitric acid is introduced from the top of the column to remove the residual Pu from the uranium bearing organic phase that leaves the column from the top. A general scheme for plutonium partitioning in Purex process is given in Fig. 3.

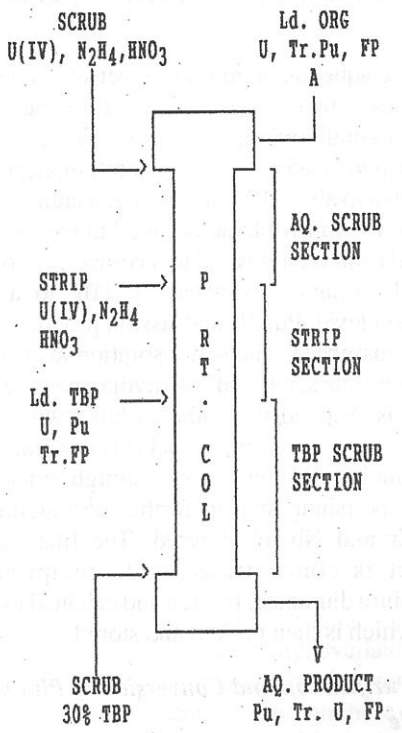


*Fig. 3 Scheme for Pu partitioning in Purex process*

$N_2H_4 + 2HNO_2 \rightarrow N_2 + N_2O + 3H_2O$

Considering various factors discussed above, the quantity of uranous used is always more than the stoichiometric amount required for the reduction of Pu(IV). After the partitioning, the aqueous plutonium product is sent for final purification.

*Stripping of Uranium*

The uranium bearing organic stream is stripped of uranium in the strip contactor. The uranium bearing solvent is fed from the bottom of the contactor. A dilute acid strip stream flows down from the top. Lowest acidity gives maximum stripping of uranium and plutonium as they have low Kd values at these acidities. But it should not be lower than 0.01 M to avoid plutonium hydrolysis. The organic feed contains some $HNO_3$ which gets stripped from the organic in the contactor thus increasing the acidity of the aqueous phase. The solvent after this cycle is generally sent for alkali washing to remove the degradation products of TBP, if any, before recycling.

***Final Purification and Conversion of Uranium to Oxide***

The aqueous uranium product with trace level impurities is taken to evaporators for concentration and after conditioning, before it undergoes a second cycle of purification. After evaporation, the solution is adjusted to about 1 M in $HNO_3$ and uranous nitrate stabilized with hydrazine is added to reduce Pu(IV) to Pu(III) and then it is fed to a compound contactor where U is again extracted by TBP to a higher saturation level. Pu(III) and fission products remain in aqueous phase. The scrub solution also contains uranous nitrate stabilized with hydrazine. The loaded solvent is stripped in another column with 0.01 M $HNO_3$ and the aqueous product U is concentrated by evaporation and then passed through silica gel as tail-end polishing step to further decontaminate it from Zr and Nb, if required. The final uranium product is concentrated and precipitated as ammonium diuranate, filtered and calcined to get the oxide which is then packed and stored.

***Final Purification and Conversion of Plutonium to Oxide***

The plutonium stream after the separation from bulk of the uranium in the first cycle is once again passed through a solvent extraction cycle to remove the traces of uranium and fission products present, as well as to get the desired product concentration required for precipitation. Here 20% TBP is preferred as extractant as the Pu feed to be processed has low Pu content (3-5 g/l). During the processing of research reactor fuels, anion exchange processes are also employed for plutonium purification. The anion exchange process for plutonium purification consists of three steps:

(i) An absorption or loading step in which Pu is absorbed from a 7.2 M nitric acid feed solution on anion exchange resin as the hexanitrato complex $Pu(NO_3)_6^{2-}$

(ii) A 7.2 M nitric acid washing step, in which impurities are removed from the plutonium-laden resin and

(iii) An elution step, in which plutonium is eluted from the resin with 0.5 M nitric acid to get a concentrated product solution. Plutonium is then precipitated as its oxalate, which is filtered and calcined to give $PuO_2$. The end product, oxide is packed in SS containers and stored in bird cages.

***Gaseous and Liquid Waste Management***

In fuel reprocessing, wastes are generated in solid, liquid and gaseous forms. The clad material, if left over at the end of the dissolution (in mechanical chop/leach process), is disposed off in suitable cement matrix in drums and buried in concrete trenches with engineered barriers. The raffinate concentrate wastes carry bulk of the fission product activity in highly concentrated form. These High Level Wastes (HLW) are stored in stainless steel underground waste storage tanks with provision for cooling to avoid boiling due to heat liberated from fission product activities. Finally the HLW is vitrified for long term storage. The medium or Intermediate Level Wastes (ILW) are neutralised and stored in carbon steel or stainless steel underground waste storage tanks, before further processing for disposal in suitable matrix. The Low Level Wastes (LLW) from the plant are treated and released to the sea at levels well below the maximum permissible limits.

Some of the long-lived fission gases like $^{85}Kr$ and $^{129}I$ are liberated in the process during dissolution and other operations. The off-gases generated in the dissolver, evaporator and other process equipments are subjected to separate off gas treatment and filtration to remove the fission products and condensable vapours. After the treatment, the gases along with area ventilation air are released through a tall stack after filtration through High Efficiency Particulate Activity (HEPA) filters.

**Developments in Reprocessing**

Most of the Pu available today in the world has been recovered through Purex process. Simplification and improvement of the process for better U/Pu recovery and DF, reduction in the number of equipment and maintenance by proper choice have been the main thrust areas in reprocessing development field. Now, world over, only long cooled (>5 years) fuels are processed for which Purex process is well entrenched and most suitable. Purex process chemistry is reasonably well understood. In general, it can be argued that the process as such is viable in terms of its applicability for processing fuels currently encountered and for those anticipated in the near future. But developments are certainly needed in the application of new engineering techniques and modern technology to this process. Chemical engineering industry has progressed leaps and bounds in the recent years and all those development will have their application in Purex process too. One instance is the development of "Impurex" process which is a single cycle process that depends on automated computer control of solvent extraction column on the basis of on-line monitoring of process parameters by sophisticated and sensitive instrumentation systems. This helps the computer to monitor the column parameters like flow, density, temperature, interface control, pulsing efficiency, real time analysis of process stream compositions, etc., and to take corrective actions. Some of the new thrust areas where R&D can play a vital role in bringing about vast improvements in the Purex process performance are highlighted in the following discussion.

In the Head-End treatment step, development of dry storage techniques for spent fuel storage, laser cutting of spent fuels, design and development of continuous dissolver and utilization of zirconium/titanium as material of construction for fabrication of critical equipment such as dissolver, evaporator, etc., can lead to enhanced plant through-put and life.

In Solvent Extraction and Process Engineering, development of single cycle processes with good decontamination performance, development of maintenance-free short residence contactors, annular pulse columns that are safe with respect to criticality for extraction as well as partitioning and allow processing of larger amount of fissile material, use of in-situ photolytic and electrochemical techniques for reduction and partitioning of plutonium and neptunium, electrolytic techniques for an ultimate salt free process, recovery of useful isotopes like $^{237}Np$, $^{99}Tc$, Pd etc. in the process, minimization of plutonium losses to waste streams, improvements in solvent quality, direct denitration techniques for conversion of products to oxide and separation of long lived actinides and fission products from high level wastes to reduce their long term hazard potential and a general reduction in waste volumes generated in processing are some of the challenging tasks where R&D efforts are to be directed. New solvents such as mono amides which appear to be attractive from final disposal point of view are yet to be tested on commercial scale. Studies in the area of new techniques like membrane extraction and extraction chromatography for their applications in reprocessing and indigenous development of suitable ion exchange resins for separation and purification of plutonium would be worthwhile and rewarding. In Plant Process Control Instrumentation and Monitoring, the developments relating to computer applications in measurement techniques, data acquisition, process and radiation safety control, interlocks for safe process operations, in-line and on-line monitoring of process streams and near real time accountancy of fissile and fertile actinides will improve the safety and performance of the plant.

For a commercial plant to become viable, the major considerations are reliability, availability and long life with minimum personnel exposure in operation and maintenance. Based on these criteria, innovations in reprocessing field merit special attention, be it in the head-end process, extraction process, process control or in the maintenance.

Automation and robotics are the two technologies that can revolutionize reprocessing and meet the above objectives.

As a long-term goal, India's nuclear programme expects to use the large deposits of thorium in its third phase. Hence in the long term perspective, extensive R & D efforts should be devoted to reprocessing of irradiated thorium and allied areas as thorium based fuel cycle is the Nuclear Fuel Cycle of the future for India.

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# Experience on PHWR Spent Fuel Reprocessing in India

*Shri R.K. Singh joined Bhabha Atomic Research Centre in 1963 after completing his M.Sc. (Chemistry) degree from BHU. He received training in large scale safe handling of plutonium, Pu reconversion operations including Pu metal production. He has worked in Plutonium handling facility of CEN-FAR, Paris, France during 1969-70. He has actively participated in the preparation of Pu-Al alloy, Pu-Be neutron sources and production of plutonium metal. His field of work also includes development of various Electro-Chemical processes for its application in spent fuel reprocessing. He has 140 publications to his credit. Shri R.K. Singh is presently working as Head, Process Control & Plutonium Reconversion Section, PREFRE Plant at Tarapur.*

## Introduction

The need for fuel reprocessing, and an introduction to the Purex process have been provided in the previous articles in this issue. The Power Reactor Fuel reprocessing Plant (PREFRE) at Tarapur has been engaged in the task of reprocessing of irradiated fuel from the power reactors at Tarapur and Rajasthan. Several campaigns of reprocessing have been carried with domestic as well as with safeguarded PHWR fuel at PREFRE. Reprocessing of PHWR spent fuel under IAEA safeguards have been done as per the subsidiary arrangements. PREFRE has gained credibility of operating and meeting the regulatory requirements of International Safeguards, satisfactorily. This article describes the experience gained in fuel reprocessing and various innovative steps which have been introduced over the years to make improvements in the process.

## PHWR Spent Fuel Reprocessing at PREFRE

PHWRs use zircaloy clad natural uranium ($UO_2$) as fuel. Indian PHWRs generate about 15 tons of spent fuel per year per reactor. The spent fuel discharged from PHWRs has typical thermal burnup in the range of 6000-8000 MWD/Te of uranium. Fuel grade plutonium is formed in the spent fuel and is associated with about 6 kg of fission products in each ton of spent fuel processed.

## The Chop-leach and the Purex Process

The PREFRE plant uses a chop-leach head end step followed by the famous Purex process for recovery of U and Pu from the irradiated fuels. A detailed description of the Purex process has been given in another article in this issue. In the Head End step, the spent fuel is chopped into small pieces and dissolved in nitric acid. Fuel component gets dissolved completely and the fuel clad (zircaloy) remains undissolved as "hulls". After dissolution of chopped spent fuel, uranium and plutonium concentrations are maintained at about 350 g/l and 1 g/l respectively. Free acidity of dissolver solution is about 3M in nitric acid. For about one year cooled fuel, total fission product activity in dissolver solution is in the range of 80 to 100 Ci/l. The uranium separated from Pu and fission products is precipitated as ammonium diuranate (ADU) with $NH_3$ and calcined at 600°C to form $U_3O_8$. Pu is precipitated as Pu- oxalate with oxalic acid and calcined at 500°C to form $PuO_2$. About 1 Kg of $PuO_2$ is filled in each bird cage container. The design of the bird cage container ensures safety from criticality accident. Since nuclear material has strategic importance, toxicity, propensity to criticality and recycle value, it is essential to recover fissile and fertile material, meeting the product quality specifications as follows:

Total impurities including U in $PuO_2$ should be < 5000 ppm,

Pu in $U_3O_8$ should be < 0.4 ppm

FPs in $PuO_2$ should be < 20 μCi/g of Pu,

FPs in $U_3O_8$ should be < 0.4 μCi/g U

To meet these stringent specifications, it is essential to achieve a high degree of separation. The

magnitude of the problem of U, Pu separation from each other as well as from fission products can be expressed in terms of required decontamination factors which run into few millions for about one year cooled PHWR spent fuel.

**Features of Purex Process at PREFRE**

*Auxiliary Processes*

Uranous nitrate production: Electrochemical cells are used for generation of hydrazine stabilized uranous nitrate.

Solvent treatment: Repeated alkali-acid wash removes organic degradation products from TBP phase.

Off gas treatment: Off gases are treated for removal of NOx before releasing to atmosphere.

Waste evaporation: Acidity is lowered by boilng with HCHO and waste volume is reduced by evaporation.

*Special Features*

- Remote operation with 'hand on' maintenance
- Air pulsed columns for solvent extraction
- Vessels and equipments designed to meet stringent criticality control requirements
- Overall decontamination factor achieved is in the range of $1 - 2 \times 10^6$
- Adequate shielding to minimise exposure of plant personnel from radiation.
- Implementation of Measurement Control Programme.
- Nuclear material accounting at all key measurement points (KMP's).
- Gaseous and low level liquid waste discharge, as per stipulated safe limits.
- Sophisticated ventillation system for primary containment of radionuclides.

*Controls in the Process and Operations*

- Feed and strip solution acidity.
- Pu valency adjustment at various stages of decontamination cycles.
- Concentration of uranous and its extent of addition.
- Percentage of TBP in Solvent.
- Column operating parameters and liquid transfers.
- Acid killing by heating with formaldehyde.
- Adequate saturation of TBP phase with uranium.
- Solvent (TBP) treatment, inventory and accounting.
- Nuclear material accounting in calibrated KMP tanks.
- Monitoring of gaseous and liquid effluent discharges.

*Some Problems in Reprocessing:*

- Long time of dissolution of fuel in chop leach process.
- Pyrophoricity of Zircaloy fines during chopping.
- Efficient filtration of dissolver solution below 20 micron particle size.
- Heterogeneous contamination during solvent extraction.
- Poor decontamination of U & Pu product with respect to fission product ruthenium.
- Presence of tritium from low level liquid waste.
- Contact maintenance of highly radioactive parts needing excessive Man-Rem.

**Process and Engineering Developements**

PREFRE flow sheet was initially designed for processing of BWR (TAPS) spent fuel and accordingly the process equipment were fabricated [Fig.1] . On the basis of experience gained during low burn up spent fuel reprocessing at Plutonium Plant, BARC, Trombay and at PREFRE plant, Tarapur, necessary changes in the process flow sheet were incorporated [Fig. 2].

*Feed Clarification*

During PHWR fuel chopping and dissolution it was noticed that zircaloy fines are generated. Due to this, feed pump strainer was getting choked frequently resulting in failure of pump and exposure of maintenance staff during replacement of strainer. To overcome this problem, remotely replaceable filtration system was introduced in the head end process. This had improved the quality of feed solution and significantly reduced the zirconium fines during solvent extraction.

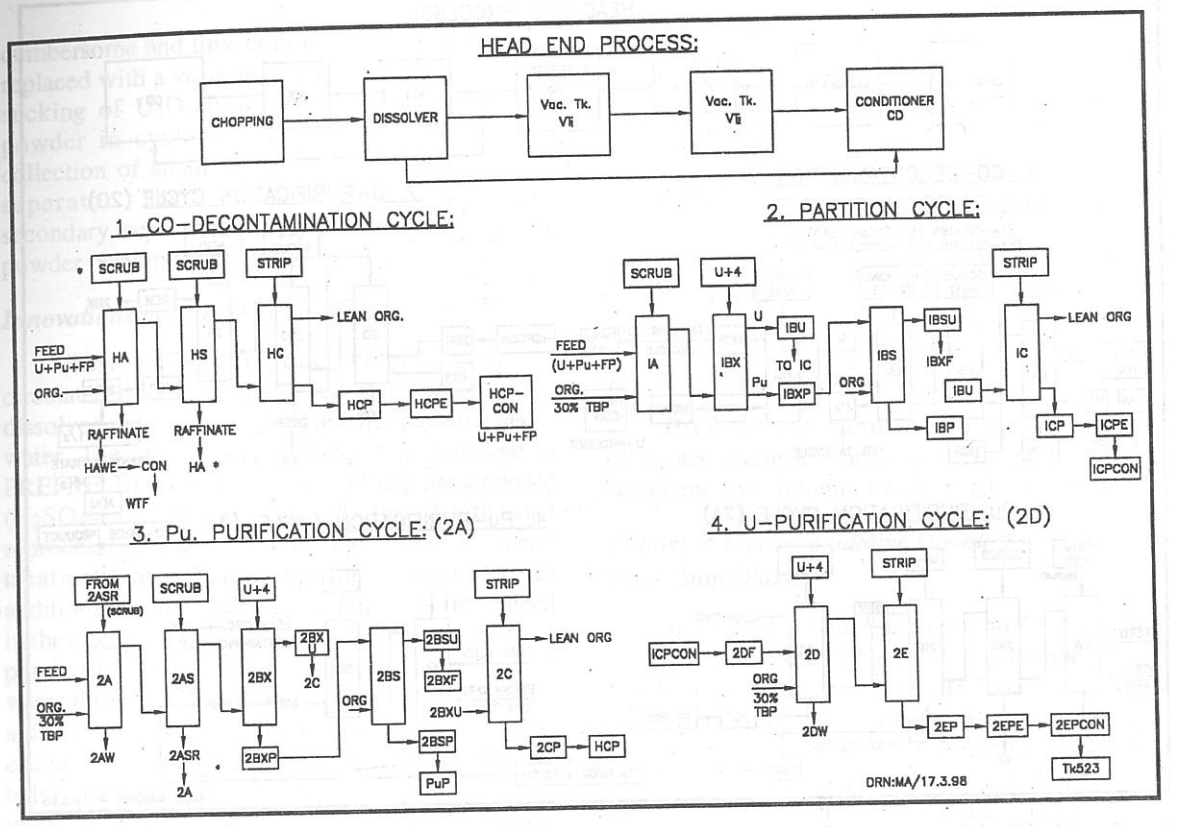



*Fig. 1 Designed flow sheet for reprocessing of BWR spent fuel*

### *Introduction of Co-decontamination cum Partition Cycle*

With the original co-decontamination cycle before U-Pu partitioning, the operating experience showed that dilute Pu containing solutions were getting generated requiring further concentration by evaporation before subjecting to next cycle. To avoid boiling of Pu containing solutions, co-decontamination cycle was modified to co-decontamination cum partitioning cycle to partition U and Pu. Now, after partitioning of U and Pu, plutonium solution goes directly to Pu-purification cycle. This improvement has reduced Pu-purification efforts to obtain better quality Pu-product.

### *Pu-purification Cycle*

To achieve saturation of solvent with U and Pu decontamination factor, 20% TBP in n-DD was introduced in this cycle.

### *Short-cooled Fuel Reprocessing*

While reprocessing short cooled PHWR spent fuel, it was observed that off grade uranium product solutions were getting generated necessitating frequent recycle and affecting the overall throughput of the plant. To overcome this problem, a decision was taken to temporarily store the off grade uranyl nitrate product solution in interim storage tanks and concentrate on separation and production of quality plutonium product. At the end of campaign, an additional scrubbing column was introduced in uranium purification cycle. Uranous nitrate was used as scrub for separation of Pu traces. In the endeavour

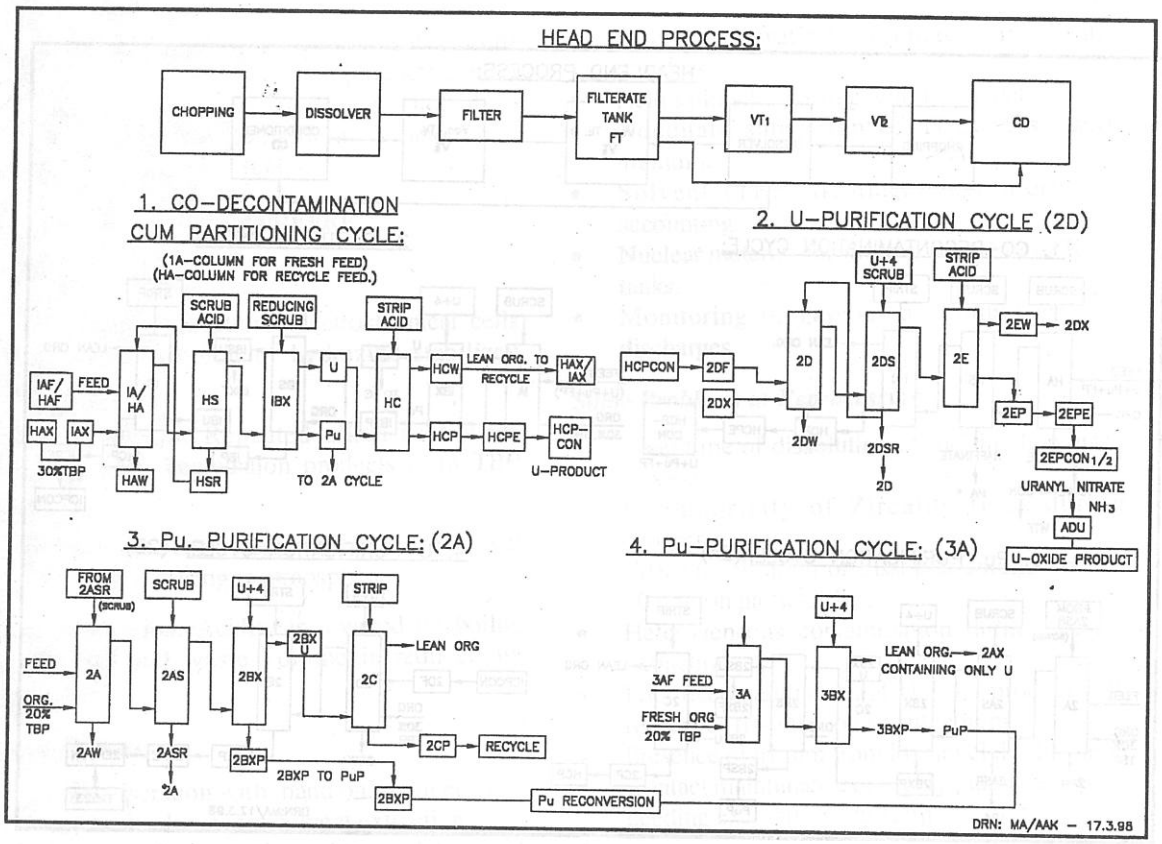



*Fig. 2 Modified flow sheet of PREFRE*

to achieve high quality uranium product, extraction column was operated at maximum uranium saturation which resulted in slightly higher uranium losses in raffinate. This increased the recycle processing load.

### *Ion Exchange Cycle*

Ion Exchange cycle was introduced to provide additional DF for Pu stream during short cooled reprocessing campaign. But half way through the campaign serious degradation of ion exchange resin was noticed. The degradation of resin led to choking of column several times. Due to this experience, ion exchange cycle was replaced in subsequent campaign with an additional solvent extraction cycle for plutonium purification.

### *Salt Free Process*

In the early period it was common practice to add $NaNO_2$ solution to dissolver solution for adjusting the oxidation state of plutonium to Pu(IV). Possibility of localized hydrolysis of plutonium leading to polymerization of Pu and high salt content in acidic waste streams were the two serious problems encountered in this conditioning step. To overcome these problems, $NO_2$ gas generating reactor was installed in make-up area and $NaNO_2$ solution addition was replaced by $NO_2$ gas sparging for Pu-valence adjustment in dissolver solution.

### *Filling of $U_3O_8$ Powder in Drums*

Earlier a manual method was used for filling $U_3O_8$ powder in 200 litre capacity drums and scoop proportionate sampling was adopted to get representative samples. This manual method was

cumbersome and time consuming. Now it has been replaced with a vacuum transfer system. It involves sucking of $U_3O_8$ powder from trays, mixing of powder in cyclone separator and simultaneous collection of small fraction (~1-2%) in secondary separator. The powder fraction collected in secondary separator offers a better representative powder portion for proportionate sampling.

***Innovations in Fuel Handling Area***

Normally, fuel pond water (DMW) is circulated through a mixed bed unit to remove the dissolved radioactive cations and maintain the pH of water. The same practice was initially followed in PREFRE. But the large volume of regenerant waste ($H_2SO_4$ and Caustic) could not be mixed with usual reprocessing waste streams and required special treatment at separate facility. Therefore, an additional cation exchange column was introduced in the circuit for removal of radioactive cations from pond water. It was followed by circulation of pond water through MBU for maintaining the pH. Nitric acid was used for regeneration of the cation exchanger. The regenerant waste ($HNO_3$ medium), being compatible to acidic waste streams generated in reprocessing operation, could be directly taken to process tank. This change has drastically reduced regeneration of MBU.

To cope up with the insoluble residue getting formed in the fuel pond, a candle filter assembly was introduced. Water is continuously recirculated through the filter assembly to remove the radioactive insoluble particles. This helps in maintaining the water clarity and keeping the pond water activity below the stipulated limits of 1000 pCi/ml.

**Research and Development Activities**

To find a solution to the problems faced during PHWR reprocessing, several development works were undertaken. Some of those projects were highly successful and were amenable for direct introduction in the main process.

***Electrolytic Generation of Uranous Nitrate Using Cation Exchange Membrane***

Cation exchange membrane cell was designed, fabricated and tested for near cent percent conversion of uranyl to uranous nitrate. Titanium as cathode & TSIA as anode were used as electrodes. Operating conditions were optimised for achieving the near cent percent conversion of uranyl to uranous nitrate at reasonably good production rate.

***In-situ Electrolysis***

Electropulse column and electrolytic mixer settler were designed, fabricated and tested for in-situ reduction cum stripping of plutonium from loaded organic phase.

***Electrolytic Conditioning***

Electrolytic conditioner was designed, fabricated and tested for oxidative decomposition of hydrazine and plutonium valency adjustment.

***Catalyzed Electro-oxidative Dissolution of Plutonium Dioxide***

Dissolution of $PuO_2$ is an essential prerequisite for the regeneration of long stored $PuO_2$ and for the purification of impure $PuO_2$. For this purpose, a quick, room temperature operation, silver catalyzed electrolytic $PuO_2$ dissolution method has been developed. A three litre capacity critically safe cylindrical dissolver, with platinum and titanium electrodes, has been fabricated and it is in use for dissolution of $PuO_2$ at PREFRE.

***Electrochemical Process for the Recovery of Plutonium from Laboratory Solid Wastes***

The silver catalyzed electro-oxidative process has been further extended for the complete decomposition of cellulose and ion exchange resin alpha waste into gaseous products for total recovery of plutonium.

***A Compact Electrochemical Concentrator***

A three compartment electrochemical membrane cell has been developed. Feed containing metal ions is passed through middle chamber filled with cation exchange resin. Under the influence of electric field, the ions loaded on resin are transferred to catholyte chamber. Loading and regeneration of ion exchange resin takes place simultaneously. A concentration factor of 40 for cesium and 10 for uranium have been achieved.

*Development of a Process for the Treatment of ILLW*

A process has been developed for the partitioning of ILLW into small volume HLLW and large volume of LLLW. Incidentally, the process recovers actinides from ILLW in small volume. The process involves neutralization of carbonate, precipitation of uranium and plutonium and removal of cesium on sapcolite resin bed. Plant scale application of this process has been taken up by WIP, Tarapur.

**Nuclear Material Accounting**

For the purpose of nuclear material accounting the one MBA process has been divided into three accounting sub areas (ASA) namely, Fuel receipt area, process cells including reconversion laboratory and uranium, plutonium store. Nuclear material accounting in the process ASA-II is carried out at key measurement points like, conditioner tank, high active raffinate waste tank, organic waste stream tank, $U_3O_8$, $PuO_2$ product lot etc. It is necessary to achieve measurement performance as good as or better than specified LEMUF target values to determine true magnitude of MUF (Material Unaccounted For). Hence a measurement control and evaluation programme to determine systematic and random error components associated with sampling, analysis and bulk measurement of each stratum in material balance equation have been carried out. The stringent SNM accounting practice has been continued during the reprocessing of unsafeguarded MAPS fuel as well.

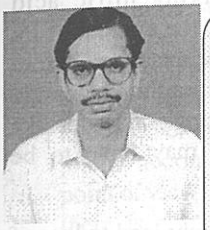
**Future Challenges in Nuclear Reactor Spent Fuel Reprocessing**

- Processing of BWR fuel: Nuclear poison required to be added to dissolver.
- Stringent international safeguards requirement to be met.
- Adopting proliferation resistant measures e.g. resorting to coprocessing.
- Near total recovery of actinides from high level liquid waste.

**Conclusion**

The modified flow sheet has given highly encouraging results as regards to required decontamination factors, reduced waste volumes, avoidance of plutonium solution boiling, tighter control over MUF and improved recovery of actinides. It has been felt that there is a need to review the theme of actinide recovery in the broader concept of nuclear fuel cycle (inclusive of reprocessing and fuel fabrication) and improve the total SNM recovery to more than 99.5 %. This is very important for achieving shorter fissile material doubling time in future and exploit the breeding gains to India's advantage. This will ultimately meet the goal of attaining self sustained equilibrium thorium cycle.

# Challenges in Fast Reactor Fuel Reprocessing



***Shri R. Natarajan*** *is presently the Head, Fuel Reprocessing Process Division, Reprocessing Group, IGCAR. He joined the 19th batch of training school in 1975 after obtaining his Bachelor's degree in Chemical Engineering from Annamalai University. He is responsible for the design of Fast Reactor Fuel Reprocessing Plant (FRFRP). He has evolved the Process flowsheet and the overll plant design. He is in charge of the erection and commissioning of the hot cell facility at the Reprocessing Development Laboratory (RDL) in which the irradiated FBTR fuel processing will be demonstrated. his other field of specialisation is the design and operation of Thorium-Uranium cycles. He has participated in the J-Rod process compaigns at RDL and the Uranium-233 recovered has been useful for the KAMINI reactor. He has interests in equipment and system design of radioactive offgas circuits, ventilation design of radiochemical plants, design of clarification system of dissolver solution and in acid recovery systems. he has over fifty technical presentations and publications to his credit.*

## Introduction

Fast Reactor Fuel Reprocessing (FRFR) involves handling of much higher concentrations of Pu, with Pu/(U+Pu) in the range of 0.15 to 0.7 as compared to 0.002 to 0.004 in Thermal Reactor Fuel Reprocessing (TRFR). The specific activity handled is also much higher in the case of FRFR (of the order of 1000 Ci/l) as compared to TRFR (of the order of 200 Ci/l). The reprocessing of the fuel from the Fast Breeder Test Reactor at Kalpakkam has an added dimension because the fuel used is a carbide. Further, presence of liquid metals in the spent fuel leads to the problem of handling.

The PUREX process, in which vast operating experience has been logged for TRFR, promises to be an attractive one also for FRFR, even though efforts have been put in USA, Belgium and Russia on alternative methods of reprocessing, such as fused salt or metal extraction or volatility processes. But the PUREX process has to be adapted to meet the demands of spent FBR fuel reprocessing. This article highlights the challenges encountered in the different stages of FRFR for a typical PUREX type plant.

The difficulties encountered in FRFR can be broadly classified under the following heads:

- Process
- Equipment
- Instrument and control
- Cell design
- Material of construction

## Process

The different steps involved in the process are:

- Transportation and storage
- Chopping, dissolution and feed clarification
- Solvent extraction
- Partitioning
- Off-gas treatment

### *Transportation and storage*

Since FRFR fuels have to be processed after short cooling times, the decay heat associated is generally high. Thus, it is considered advisable to locate the reprocessing plant near the reactor itself. If the reprocessing site is far away from the reactor, then transportation of the fuel bundles with axial blankets may demand bulky shipping casks, because of the need for decay heat removal. During transportation as well as storage of irradiated fuels with a decay heat of 70 watts/kg, cooling is generally required. Cooling may be done using either forced air or water. While forced air cooling involves large secondary systems, like compressors and power units, use of water as coolant requires deactivation of liquid metals adhering to the pins as a prerequisite. Large storage of spent fuel requires water cooling but for storing of failed fuel pins, special precautions

have to be taken to avoid Pu contamination. Encasing these failed fuel pins in another container is one of the options.

*Chopping, Dissolution and Feed Clarification*

The dissolution of FR fuels containing mixed oxides of U and Pu in concentrated nitric acid is a function of Pu concentration and the physical state of the fuel like the extent of sintering, porosity, irradiation levels and the dispersion of Pu in the matrix of U+Pu. Some of the above parameters are interdependant. It has been reported that it may be extremely difficult (almost impossible) to dissolve solid solutions of U+Pu containing Pu > 40 wt % using boiling 10 M nitric acid. The insoluble residues reportedly contain high % of Pu [1]. 60 MWD/kg burn-up fuel from Dounreay containing 15% Pu mixed oxide prepared by coprecipitation process was dissolved in 8 M $HNO_3$ within 4 hrs. An insoluble residue of 0.4 to 0.8 weight % was present containing 0.02 to 0.04 weight % Pu [3]. 25-30% Pu containing mixed oxide fuels, irradiated to 75 MWD/kg have been dissolved in 11 M $HNO_3$. It has been observed that though the initial dissolution rates are fast, satisfactory dissolution was completed in 10 hrs [4].

Very limited work has been done on direct dissolution of mixed carbide fuels. In contrast to the dissolution of mixed oxide fuel, where U dissolution is faster than Pu leading Pu rich phases in the solid fuel phase, the dissolution of carbides is quasi-congruent. It has been reported that dissolution of mixed carbides containing 20% Pu is complete with 8M $HNO_3$. Electron microprobe analysis of the residues of dissolution of 5.3 at % burn-up mixed carbide fuel, proved the absence of carbide phases. The fraction of undissolved Pu is low (0.11 to 0.68%). The total weight of the residues is between 0.3 and 0.6%. The actinide-noble metal phases which are formed during irradiation in stoichiometric carbides, are hardly soluble in $HNO_3$ [5]. Interestingly, increased solubility of aged residues have been reported.

There have been very few studies on the dissolution of mixed carbide fuels with high Pu content such as the FBTR fuel with 70% Pu. At IGCAR, mixed carbides of U and Pu containing 70% Pu has been successfully dissolved in 13M nitric acid under refluxing conditions in 20 hrs even though 3% of the initial carbide is present in the dissolver solution [2]. Direct dissolution process of mixed carbide fuels is found to be unpredictable. Though complete dissolution in refluxing nitric acid conditions is a strong possibility, the amount of Pu in undissolved residues have to be evaluated before finalising the process option. In case the Pu content is very high, then, stronger oxidizing conditions like in Electrolytic Oxidation etc., may have to be resorted to.

The insoluble residues not only lead to loss of Pu, but also create problems in solvent extraction by accumulating in the interfaces. To remove these fines which are of the order of 0.5 μ, high speed centrifuges that can be remotely operated and maintained, are successfully used. However, ingenious techniques have to be evolved to retain these fine particles so that they do not accumulate in the pipe lines or in the equipment before the centrifuge feed clarification process.

*Solvent Extraction*

Since TBP has preferential affinity for U and Pu over the fission products, the PUREX process can be redesigned to cater to the needs of FRFR. But the challenges are encountered from the following directions:

- High Pu content
- High burn-up and short cooling times
- Possibility of presence of organics in dissolver solution
- Solvent and diluent damage
- Presence of Technetium

*High Pu content*

(a) The extraction kinetics of Pu is slow, typically half that of U, while the stripping kinetics is faster around four times that of U. This implies that use of fast contactors like centrifugal extractor may pose some problem during extraction.

(b) Since Pu is known to polymerise under low acid conditions, stripping of Pu should be done under highly controlled condition. Normally dual strip is used: one with very low acid and another with moderate acid condition. Momentary loss of flow of this second strip

under plant upset condition can lead to polymerisation.

(c) It has also been seen that TBP-Pu (IV) complex has limited solubility in the alkane diluent. When the organic Pu loading is increased beyond a certain value, the organic separates into two phases, one with low Pu concentration and another with high Pu concentration. This phenomenon presents difficulties from the point of view of operation of the extractor. Also there is risk of Pu accumulation leading to criticality incidents. Though earlier works [6] indicated that the presence of U(VI) decreases the limiting concentration of Pu uniformly, recent works [7] have shown that this phenomenon depends on acidity: it is more pronounced at higher acidities (3.8 to 5 M $HNO_3$) than at lower acidities (2.2 to 3.6 M $HNO_3$). Prediction of this condition is a very difficult task as the phenomenon is not totally understood. The detection of this condition is also a challenging task. Thus, any small upsets in the aqueous to organic flow ratios into contractor, may lead to Pu loss or poor DF which points to lesser flexibility during operation.

(d) Since it is advisable to avoid inter cycle evaporation to ensure low Pu losses, dilute solutions have to be processed, which leads to larger sized equipment.

*High Burn-up and Short Cooling Times:*

The burn-up of fast reactor fuels are of the order of 75 to 100 MWd/kg compared to 10 to 30 MWd/kg for thermal reactor fuels. Also the fast reactor fuels are generally taken for reprocessing as early as possible, say in 100 days, while even 10 years cooling for thermal reactor fuels are not unusual. This means a quantum jump in the specific activity of the fuel. The feed solution will contain upto even 1000 Ci/l compared to around 100 to 200 Ci/l for TRFR.

It was reported that while using mixer settlers for the I cycle of extraction during the processing of mixed oxide fuel (25 MWd/kg) solutions with radioactivity level of 1000 Ci/l, in Marcoule:

(a) There was a significant drop, in about 10 days operation of the plant, in the Zr decontamination factor from a few thousand to few hundred

(b) After an interval varying between a few days to about ten days, an increase in the residual activity of the recycled solvent, of the order of 1 mCi/l, which was not eliminated during alkaline treatment of the solvent has been observed. This was found to be mainly due to Ru.

(c) Even if the mixer settlers were rinsed and restarted, the decrease in the Ru and Zr decontamination factors was found to be more pronounced from one run to the next.

The above phenomenon is explained as follows:

(a) The radiolytically degraded phosphates DBP-MBP-$H_3PO_4$ react with Zr to form extractable Zr complexes leading to the formation of insoluble compounds. This leads to decrease in the Zr decontamination factor. Also these precipitates collect at the interphases in the mixer settler leading to acceleration of the above phenomena.

(b) DBP-MBP form compounds with nitrato-nitrosyl Ru and then polymerise on Zr phosphate precipitates which act as support. The polymerised species are soluble in the solvent.
It is suggested that a, reduction of contact time by a factor of about 100, without affecting the mass transfer, reduces the above problem. To achieve this the contactors shall be isolated from the other radiation sources in the cell.

(c) To extract Pu quantitatively, the nitric acid concentration during extraction and scrub is kept high (4M and 3M $HNO_3$ respectively). Though the ruthenium distribution coefficient is known to decrease with acidity, the advantage is compensated due to the higher yield of $^{106}Ru$ ($^{106}Ru$ yield during the fission of Pu by fast neutrons is around 10 times greater than that achieved during the fission of $^{235}U$ by thermal neutrons). Thus there will not be any significant gain in the decontamir ation of Ru.

It is mainly for Zr that a strong acidity is detrimental. However, at the radioactivity levels encountered in the reprocessing of fast reactor fuel, it is not the Zr extraction with tributyl phosphate that determines the decontamination factor, but its reactions with the tributyl phosphate radiolysis products, namely, di and monobutyl phosphoric acids. Though flouride complexing of Zr has been suggested [4] as a measure for improving Zr decontamination factors, it is not a favoured step because of the risk of increased corrosion rate of stainless steel, which is the material of construction.

*Possibility of Presence of Organic in Dissolver Solution*

Even after treatment with permanganate, the solution, obtained from the dissolution of the mixed carbide (20% Pu irradiated to 20 MWD/kg) dissolved in 13.2 M $HNO_3$, has been reported to contain 25 to 32 % of the initial carbon and retain 0.4% of Pu during stripping [8]. Dissolution experiments [2] with unirradiated mixed carbide fuel (70% Pu), indicate that with refluxing of the dissolver solution for 20 hrs, upto 95% of the initial Pu can be stripped without any difficulty.

It has been reported that the phase separation behavior of the mixed phase containing dissolved organic is very poor. This implies that the dissolver solution must be checked for this condition before feeding into the extractor. This can be done by conducting phase separation run with the dissolver sample.

*Solvent/Diluent Cleaning*

Both TBP and the diluent undergo radiation and acid degradation. The conventional process to clean these degradation products of TBP (HDBP, $H_2MBP$) before recycling, is by treating the solvent with sodium carbonate. The carbonate solutions form sodium nitrate after neutralization with nitric acid and constitute the main portion of medium active waste (MAW) which for FRFR comes under the purview of waste. This waste volume can be reduced by the use of hydrazine carbonate instead of sodium carbonate since the spent hydrazine solution can be degraded in an electro-oxidation cell [8]. This type of solvent cleanup will be useful in FRFR to reduce the MAW volume.

*Presence of Technetium:*

$^{99}Tc$ is present in significant quantities in fast reactor fuels, primarily due to high burn-ups. During processing it follows the U-Pu route in coextraction cycle. During partitioning it follows Pu route. The presence of Tc also interferes with partition, since hydrazine is destroyed by it. Thus, if not controlled, Pu product will be contaminated with this $\beta^-$ emitter.

One possible flowsheet [10] for improving the decontamination from Tc is based on additional scrubbing of the first cycle coextraction loaded organic (which contains Tc), at high nitric acid, in order to strip most of Tc. The aqueous phase produced by this scrubbing, which cannot be recycled to the main extraction due to the presence of Zr, is treated by a supplementary extraction. The solvent resulting from this secondary extraction is sent to the main extraction bank, to avoid the losses of U and Pu.

***Partitioning***

In thermal reactor fuel reprocessing plants, U(IV) is employed for the reduction of Pu(IV) to Pu (III). For this chemical reduction, usually, 3 to 10 fold excess over the stoichiometric U(IV) are required. In the case of fast reactors fuel reprocessing, unduly large quantities of U(IV) will be required to be handled, because of the high 'Pu' content. Electrolytic in-situ partitioning is an attractive option under these circumstances. Both mixer settlers and pulse columns for electrolytic partitioning have been demonstrated for TRFR conditions [9]. Because of low U/Pu ratios in FRFR conditions, the advantage of in-situ reduction of U for reducing Pu may be limited. The current densities are likely to be limited by Pu. Since the degradation products of TBP are likely to holdback Pu in the organic phase, Pu losses may also be unacceptable.

Pulse columns seem to be attractive from the point of view of avoiding criticality. The design of the pulse column should take into consideration the requirement of low current, which implies very high electrode areas. Since hydrogen is evolved at the cathode invariably, design has to ensure that the risk of $H_2$ explosion is avoided.

Another option for partitioning is to utilize the solubility of uranium oxalate in nitric acid, as

compared to that of Pu. By a suitable choice of precipitating conditions, it is possible to design a flow sheet for partial partitioning. The mother liquor will primarily contain U while the precipitate will contain U and Pu. This option is useful when the product can be mixed oxide. The U stream has to be concentrated and passed through an ion exchange column to remove the residual Pu.

*Off Gas Treatment*

For small sized FRFR plants the off gas control is not different from TRFR. But for large FRFR plants, because of the high inventories of radioactive rare gases like Xe, Kr and I, special methods have to be evolved for a safe discharge to the environment, especially in an era of increased environmental concern.

Problems of radioactive iodine, especially $^{129}I$, which is a long lived radioactive isotope, assume greater importance with respect to fast reactor fuel reprocessing because of the short cooling time. During dissolution of carbide fuels, iodine gets converted into various chemical forms such as methyl iodide, iodate, etc. which makes the process of treatment complicated. It has been proposed to use caustic scrubber followed by a mercuric nitrate or concentrated nitric acid scrubbing process for large sized FRFR plants. These are being supplemented by absorbers using a variety of solid absorbents such as molecular sieves of silver zeolites, silicic acid impregnated with silver nitrate etc.

For removal of radioactive rare gases, selective absorption of noble gases in refrigerant $CCl_2F_2$ cold traps, have been demonstrated [12].

**Equipment**

Special equipment have to be designed and developed for use in FRFR. Equipment like dissolver and extractor are a few of them. Since exotic conditions are required for dissolving the mixed oxides or carbides, the conventional thermosyphon dissolver is not adequate for FRFR. Electrolytic dissolver is one possible candidate. Short residence time contactors, like centrifugal extractors, have to be used to reduce the consequences of solvent damage. A detailed description of the extraction equipment developed for FRFR are described in another paper [13] of this issue.

**Instrumentation and Control**

The detection of Pu in hulls and in undissolved solids from the dissolver solution filter is a challenging task. Active neutron interrogation is required to achieve the required sensitivity levels.

On-line anlaysis of Pu in raffinate streams is a necessity to reduce the rework of raffinate streams. The required level of detection is <10 mg/l for Pu in a stream with $\beta$, $\gamma$ activity over 500 Ci/l.

Though flow control of aqueous and organic is important from the point of raffinate losses in TRFR, it is even more significant because of the possibility of third phase formation due to the high Pu content. It has been found from mathematical modelling [14], that the safe allowable variation in the flow rates in aqueous feed and solvent is $\pm 10\%$. This means that there should be a suitable flow control mechanism to ensure that the limit is not exceeded.

Mathematical modeling of extractors is vital to ensure criticality safety of the plant during plant upsets. This analysis will enable the parameters that are sensitive and also the setting their limits.

**Cell Design**

Since high Pu concentrations are encountered right from the dissolution step, direct maintenance of the plant shall be limited. Therefore, remote operation and maintenance must be the basis of the cell design. The cells must be designed for $\alpha$ tightness. This calls for special openings for material transfer.

To reduce the radiation dose to the solvent, the cell layout shall be such that the process vessels handling the solvent, are located in such a way to ensure this.

The vent headers of tanks shall be segregated not only activitywise but also based on Pu concentrations.

**Material of Construction**

As already mentioned, FBR fuel dissolver needs materials like Titanium or Zirconium. Since the balance material of construction of the plant is SS 304L, the joints of Ti/SS or Zr/SS, shall be designed and fabricated with care so as to withstand the plant

operating conditions. It is now a common practice in the construction of reprocessing plants, to use Zr as the material of construction for evaporators.

To avoid criticality, even though single parameter control may be feasible for small FRFR plants, for other plants, ingenious methods have to be evolved like poisoning the solution or by using poisons in the material of construction.

**Conclusion**

Though this article has highlighted the FRFR from PUREX processing point of view, with TBP as the solvent which is a tested workhorse, one has to keep the options open on solvents such as Tri-isoamyl phosphate, trihexyl phosphate, tri ethyhexyl phosphate and carboxylic acids which also seem to have a potential for use as the extractant in Purex process, especially for fast reactor fuel reprocessing.

The FRFR plants have so far been designed for the delivery of pure Pu and U, either mixed or separate, with very low activity to enable glove box operation for fuel refabrication. If FRFR plants are integrated with fast reactors, with remote refabrication, then new flow sheets / processes can be evolved. The Russian BOR-60 & BN-600 reactors are using dry process for reprocessing successfully with reduced plant size as well as wastes.

This article has enumerated some of the challanges of the Fast Reactor Fuel Reprocessing. Very valuable experience in this field is going to be achieved when reprocessing the first core of FBTR fuel is undertaken in the Lead Mini Cells, currently under erection at IGCAR.

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# Equipment for Spent Fuel Aqueous Reprocessing : The Scope and the Challenges

***Dr. Sudhir B. Koganti*** *joined 18th Batch of BARC Training School in 1974 after graduating from the Banaras Hindu University and is presently heading R&D Section, Reprocessing Group, IGCAR. He obtained his MS (Nucl. Engg.) from Ohio State University, Columbus and Ph.D (Chem. Engg.) from I.I.T. Madras. He has made substantial contribution to the development of Liquid-Liquid Extraction equipment and was invited to a SX forum of select invitees, styled after the informal Gordan Research Conferences. He played a vital role in trouble shooting the irradiated thorium fuel processing facility and was mainly responsible for making the plant operational. Dr. Koganti is associated with research work on fluidic devices, non ideal effects and property correlations of interest to reprocessing. Single pin shear, rotary continuous dissolver, ejector mixer settlers and centrifugal extractors are his significant contributions. His other areas of interest include two phase fluid flow & heat transfer, heat pumps, modelling, numerical methods and solution thermodynamics. Dr. Koganti has to his credit over 50 research papers in various national/international journals and in the proceedings of international conferences.*

## Introduction

The field of nuclear fuel reprocessing offers great excitement both in the areas of equipment design and equipment development suiting the requirements of the plant. While designing of equipment using known principles requires assimilating the available knowledge and information, new developments often need fresh innovation in addition to the understanding of the principles. At the outset, let us recall that almost all the unit operations and the related equipment employed in spent fuel reprocessing are based on established principles like momentum, mass and heat transport, solution thermodynamics and reaction kinetics. In contrast to the conventional chemical industries, the reprocessing plants employ equipment which are designed for maintenance-free operation or remote maintenance.

The basic process steps in aqueous fuel reprocessing have been described in other articles in this issue. It is obvious from the reprocessing flow sheet that the most important equipment that should be considered are:

- Pin shearing unit
- Spent fuel dissolver
- Feed clarification unit
- Feed conditioning unit
- Liquid-liquid extraction equipment
- Fluid transport and metering
- Solvent wash and recovery unit
- Adsorption and diluent wash

This article discusses the salient features and the principles of operation of these units and presents some of the important designs reported by various groups working in this area.

## Shearing Unit

Shearing operation is carried out for exposing the fuel material to the acidic environment for dissolution and subsequent solvent extraction step; shear is generally preferred over cutting for avoiding the generation of particulates. Shear units are designed for shearing the fuel bundle as such or shearing a single fuel pin, depending on the throughput of the processing plant. We have chosen to develop an indigenous single pin shear unit (2kg/day) for processing FBTR fuel. The three important systems of the shear unit are; a) fuel magazine, b) push rod mechanism and c) the gripper and shearing mechanism. The schematic of the single pin shear unit is shown in Fig.1. The removable fuel magazine is placed and locked inside a fixed, rotatable magazine holder supported between two ball bearings on either ends. The magazine holder, along with the magazine, is rotated in fixed steps around the axis employing a ratchet mechanism

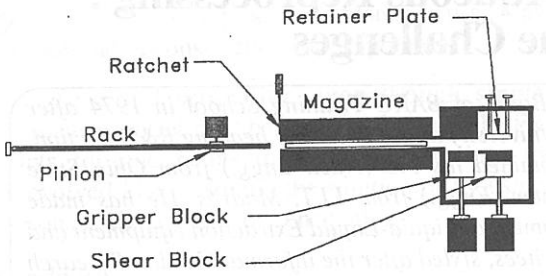


*Fig. 1 Schematic of a single pin shear unit.*

actuated by a small pneumatic cylinder. Ten individual pins are placed inside thin tubes welded symmetrically around the axis with two tube sheets on either ends. A rack and pinion push rod mechanism driven by a stepper motor gives a programmable push to the pin into the gripper and shearing mechanism actuated by another set of two pneumatic cylinders. The unique feature of this unit is that the sheared bit is prevented from flying away with high speed and thereby avoids undesirable spillage of fuel powder within the unit. The design also takes into account the replacement of components like stepper motor for push rod, gripper and shear block edges, the shear tool the pneumatic cylinders etc., with the aid of manipulators during maintenance. This is an example where simple and innovative methods can lead to excellent designs.

**Spent Fuel Dissolver**

The dissolution rate of spent fuel generally depends on the type and exposed surface area of the fuel, temperature and concentration of the nitric acid, burn-up and the amount of agitation. Temperature and acid concentration can be altered easily within some limits set by corrosion and other considerations whereas the variation in surface area, by breaking the fuel integrity, is not generally resorted to. Providing agitation can be achieved by many ways leading to variety of designs of the dissolver. The design of the ORNL rotary continuous dissolver, shown in Fig.2, incorporates a rotary cylindrical drum divided into a number of compartments interconnected by eccentric cones with opening all along the length of the cone. This dissolver operates in two modes; a) mixing mode and b) transfer mode. In mixing mode, the sheared fuel bits are continuously lifted up to the top of the drum and released within the same compartment once every rotation. The tumbling action of the sheared fuel pins enhances the dissolution rate. During the transfer mode, the drum is rotated by one complete rotation in the counter direction and the leached pins from a given compartment move to the next compartment within the drum. The fuel pin and the nitric acid move counter current to each other within the rotary drum. The primary advantages of this unit are high dissolution rate, high throughput, and semi-continuous nature of the operation. Sheared bits are charged at one end of the dissolver and the leached hulls are discharged at the other end eliminating many remote operations to be carried out while using a conventional thermo-syphon batch dissolver.

Though the ORNL design has been tested on the scaled up version, industrial experience on this unit is not available as no commercial plants have been subsequently built. Another version of the semi-continuous dissolver was developed by the French nuclear group and is routinely employed in their reprocessing plants. At IGCAR, a model of continuous dissolver similar to the ORNL type has been tested for the transfer and mixing modes. It is

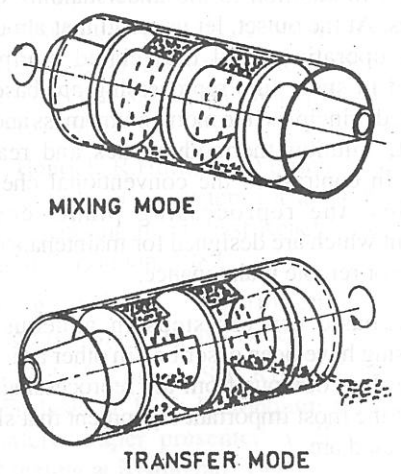


*Fig. 2 Continuous rotary dissolver (a) mixing mode and (b) transfer mode operations*

possible to couple these units with electrolytic cells and realise the additional benefits of electrochemical effects.

**Feed Clarification Unit**

During the dissolution of the irradiated fuel, platinum group fission products remain as insoluble residues. The amount of residue is more in case of FBRs fuelled with Pu, as the fission yield of these metals from plutonium fission is far higher than that from uranium fission and the insoluble residues increase with increase in burn-up of the fuel. The fission products such as Mo, Tc, Ru, Rh and Pd are the main components of the residue with Mo and Ru constituting the majority. The particle size of the residue varies from sub micron level to a few microns. The fine particles of these fission products physically distribute themselves between the aqueous and organic phases, leading to poor decontamination of the final product U and Pu. As long as these fine particles are physically carried by the liquid phase, increasing the number of cycles and altering the flow sheet conditions will not help much in getting the clean product. These insoluble residues are also the major cause for the interfacial crud formation in extraction equipment, upsetting the hydraulic behaviour of these units. The importance of the feed clarification prior to solvent extraction step has been realised in eighties and large sized high speed centrifuges to separate residue from the dissolver solution are being developed. For the fuel processing capacity of FBTR, a centrifuge with a smaller disposable bowl (~40 mm i.d) operating at 15-20,000 rpm will suffice, while for plants like PREFRE and KARP, a bigger diameter (~350-500 mm) washable fixed bowl, with floating design, operating around 5000 rpm is essential. These designs call for a thorough understanding of rotor dynamics and vibration analysis.

**Feed Conditioning**

Pu may exist in various oxidation states in the clarified feed solution. Pu has to be converted to Pu(IV) state prior to solvent extraction step. This "conditioning" of Pu can be achieved by the addition of nitrite salts or by dispersing $NO_2$ gas in the solution. Better mass transfer can be achieved by increasing the gas hold-up fraction ($\varepsilon$), which can only be realised by adding energy to the system. Special equipment such as bubble columns have to be used rather than simply bubbling $NO_2$ gas in liquid tanks. More recently, pulsed perforated plate columns are increasingly studied for gas-liquid operations, the main advantage being high $\varepsilon$, leading to high interfacial area and enhanced mass transfer coefficients. The use of such units should reduce the consumption of $NO_2$ and additionally electrochemical steps should also be considered for effecting the change in Pu valancy.

**Liquid-liquid Extractors**

The important unit operation, liquid-liquid extraction, popularly known as solvent extraction is the heart of spent fuel reprocessing. The basic principles underlying this unit operation is that, two immiscible liquids are brought into intimate contact so that the solute of interest is transferred from one phase to the other; the rate of solute transfer depends on the concentration difference, the interfacial area through which transfer occurs and the resistance to mass transfer. Interfacial area can be increased by dispersing one of the phases into small droplets of a desired size in the other continuous phase by putting in the necessary energy to over come the interfacial tension of the liquid pair; smaller the drop size, more is the dispersed phase hold-up ($\varepsilon$) and the interfacial area. The transfer resistance depends on the turbulence in the interface which is governed by the relative velocities between the phases induced by the field (gravitational, centrifugal or electrical) existing at that place. The relative velocities depend on the drop diameter. The turbulence is also governed by the condition of the drop, whether rigid or oscillating, which again depends on the diameter of the drop.

Industrial extractors can be broadly classified into various categories: agitated or unagitated, gravitational or centrifugal and differential (equilibrium is never achieved between the phases in any part of the unit) or stage wise (both the phases attain equilibrium within each stage) etc. There are as many as 30 types of extractors which are popular in chemical industry depending on the liquid system and the application. For better overall solute transfer, extractors are always operated in counter-current mode. Considering the special requirements of nuclear fuel reprocessing, many seemingly more efficient units employed in conventional chemical

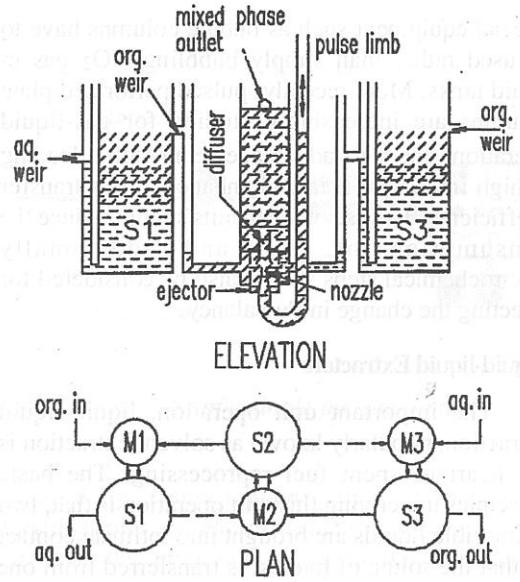


*Fig. 3 High efficiency ejector mixer settler*

industry are not useful for nuclear applications. The following three extractors are usually employed in fuel reprocessing plants.

- Mixer settlers
- Liquid pulsed columns
- Centrifugal extractors

***Mixer-Settlers***

Mixer settlers are mostly individual stage units and are simple to construct and operate and also are cost effective up to certain throughput. For very large throughputs in the range of thousands of $m^3$/hr, design basis for column type extractors is not available and only mixer-settlers are employed. A typical example is the extraction of copper with LIX solvent where the demand for the throughput of the plant is increasing year after year but no column unit of this size has ever been built. The typical settler size for these plants often exceeds the size of a giant swimming pool. As for the design aspects, established correlations are available for designing mixer but surprisingly the drop coalescence models are not available until recently for the proper design of settlers. Therefore most often they are designed using thumb rules and a few limited correlations. Phase dispersion can be achieved either by properly designed impellers or by air pulsing through perforated probes as is the case with the mixer-settler developed by BARC [1].

A novel air pulsed ejector mixer settler [2] shown in Fig.3 has been developed by our group, wherein both dispersion of one of the phase and liquid transfer between the stages are achieved by the ejector. The diffuser section of the ejector is known to be a good mixing device and the mass transfer efficiency of this unit is near 100% even with as low as 40 cpm pulse frequency. Another important feature is the hydraulic independence of the stages. A scaled down version of this unit incorporating 20 theoretical stages into a single SS block of 400 x 130 x 60 mm has been built with settler volume of 14 ml and mixer volume of 4 ml. These units are most ideal for process development and flowsheet testing with active liquids. Adjustable weirs can be built into the unit so that the unit can handle liquids of different densities. There are important alternative designs reported by other workers in the category of mixer settlers [3,4 ].

***Liquid Pulsed Columns(LPC)***

Extensive work in liquid pulsed columns has been carried out, primarily due to their large scale use in nuclear processing applications. They are differential in nature and simple to construct and operate. The basic operating principle is that both the phases are fed at opposite ends of the column and move counter current to each other through a stationary perforated plate stack. A designated amplitude of liquid pulse is given at the bottom of the column which move the contents axially upwards. These contactors have only one interphase either at the top or at the bottom depending on which phase is dispersed unlike that of mixer settlers, with as many interphases as the number of stages. The over all contact time for LPC is about 1/3 to 1/2 of that of mixer-settler resulting in lower damage to the solvent. Axial mixing which is the departure from plug flow behaviour tends to reduce the mass transfer and should be properly taken into account during the design stage. In fact axial mixing data for the liquid systems of interest to reprocessing is very scarce.

***Centrifugal Extractors***

The high burnup of fuel and the resulting high radiation dose to the solvent in fast reactor fuel

reprocessing has necessitated the development of fast solvent contactors such as centrifugal extractors with phase contact time of 5-10 seconds as opposed to 2-6 minutes in conventional liquid pulsed columns and mixer settlers. Contact times are lower due to enhanced centrifugal field (200-1000 g) depending on the bowl diameter and the operating speed. Many designs of centrifugal extractors are available commercially both of differential and individual stage type for applications in chemical industries. Though centrifugal contactors are highly efficient and have many advantages in reprocessing, the applications have so far been limited mainly due to the rotary components involved. Initial development work for nuclear applications was carried out at Savannah River Laboratory (SRL) and later Argonne National Laboratory (ANL) group has extended the work [5] to a simpler and cost effective design devoid of any seals and the only maintenance is that of bearings in the drive motor.

Robatel, a French company has developed multistage extractor for nuclear applications which, however, may not be the right choice due to the interstage seals. Russians have done extensive work [6] on these units and have a dedicated laboratory for the development of centrifugal extractors. More recently, Britain and Japan are concentrating in the development of these units in collaboration with US. Recently these units are increasingly being used even in other areas like nuclear waste management and in hydrometallurgy etc. Based on our experience gained in using centrifugal contactors in a thorium reprocessing facility for the recovery of U-233, we intend to use these units in all the cycles of FBTR fuel reprocessing demonstration facility, except in the partitioning and final U purification steps. The Reprocessing Group at IGCAR has developed remotely maintainable centrifugal contactors (Fig.4) of capacities varying from 5 to 1000 l/hr [7] employing a unique liquid seal.

**Fluid Transport And Metering**

Another important area of fuel reprocessing is the fluid transport and metering of highly radioactive fluids between the individual process steps. Conventional mechanical pumps cannot be used for obvious reasons and zero maintenance devices like air lift pumps, ejectors, fluidic pumps have to be resorted to. Air lift pumps are based on the

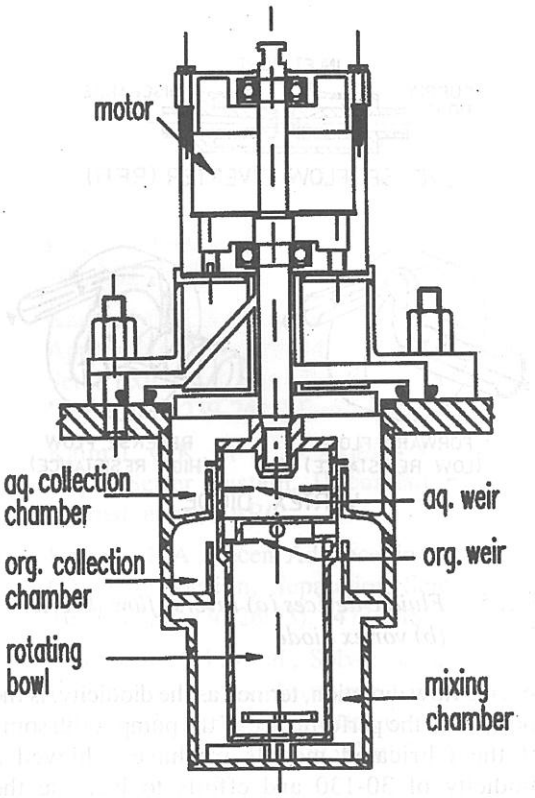


*Fig. 4 Schematic of centrifugal contactor*

momentum balance between the single phase and two-phase limbs. These pumps contribute to the entrainment of the active liquids to the ventilation system and also have the tendency to choke due to crystallisation at the air inlet point. These considerations have led to the development of passive fluidic devices [8], the reverse flow diverter (RFD) and the vortex diode shown in Fig.5, which are gaining importance for fluid transport in radioactive environment.

***Vortex Diodes and Reverse Flow Diverter***

The opposed flow nozzle arrangement in RFD is more energy efficient than the steam ejectors. For modelling purpose, the individual streams are treated as quasi dynamic in nature. The vortex diode (leaky non-return valve) operates analogous to its electrical counter part, wherein fluid resistance in the vortex flow mode is many times more than the reverse flow direction. The pressure drop ratio of the forward to

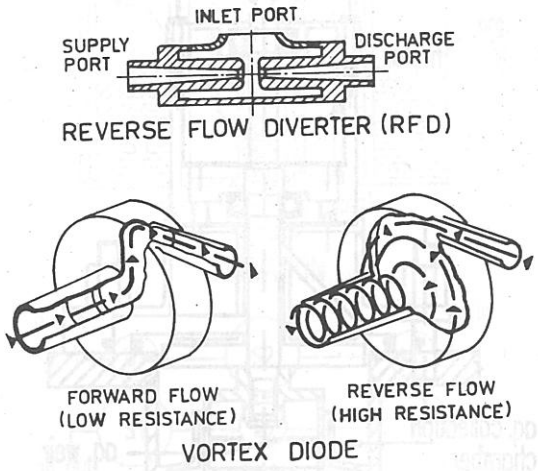


*Fig. 5 Fluidic devices (a) reverse flow diverter (b) vortex diode*

reverse flow direction, termed as the diodicity, is the measure of the performance of the pump. With some of the fabricated models we have achieved a diodicity of 30-130 and efforts to increase the diodicity employing computational fluid codes are planned. Both vortex diode pumps and RFD pumps have been extensively used in fuel reprocessing and effluent treatment plants at THORP site at Sellafield in U.K.

***Constant Volume Feeders (CVF)***

An analysis of the reprocessing flowsheet for FBTR fuel shows that ±10% variations in flow rates to the solvent contactors will result in Pu loss or inadequate stripping from the organic streams depending on the particular step. This kind of precision in flow rate is difficult with air lift pumps without controllers backed up by good measuring techniques and instruments. Constant volume feeders consists of a vessel in which rotating bucket wheel driven by stepper motor is submerged. As the wheel rotates, each bucket on the wheel scoops up a definite volume of liquid and delivers to the outlet. The flow rate depends on the rotational speed, the number of buckets on the wheel, and the bucket capacity and is independent of density of the liquid. The buckets can be made of simple bent pipes and machined cups of the desired size for a particular flow rate. Some standard designs can cater to different flow rates. With a stepper motor as drive unit, exact metering can be obtained which will not vary due to any other process loads or variations in densities. The reprocessing group at IGCAR has developed both bent tube and machined cup versions for low flow rate applications.

**Solvent Wash and Recovery Unit**

The solvent, a mixture of 30% TBP and n-dodecane, comes in contact with 4N $HNO_3$ and receives an intense dose of $\alpha$, $\beta$ and $\gamma$ radiation, which can be as high as 30000 Ci/kg of fuel. The radiation and chemical degradation of TBP have been described in other articles in this issue. Washing the solvent with alkali can only remove the TBP degraded products and is not effective for the diluent degradation products. A French process exists, wherein the degraded organic stream is first dehydrated and subsequently evaporated at very low pressure to minimise thermal degradation. The distillation process yields almost pure dodecane as the distillate and 60-70% TBP as the bottom product leaving all the degraded products along with the retained activity in the 3-5% of the sludge generated in the evaporator. This process step is used on-line with the reprocessing plant and a small percentage of the solvent forms the feed stock for this process. The engineering challenges lie in distributing the liquid film on the walls of the evaporator and carrying the distillation with least pressure drop across the rectifying unit. Basic studies such as generation of vapour liquid equilibrium data under low pressures are essential for a proper design of this process.

**Adsorption and Diluent Wash**

Other essential areas of equipment development and characterisation are the understanding of the adsorption of dissolved TBP in aqueous streams on non-ionic macro-porous resins such as Amberlite XAD-4 [9] and the use of diluent for extractive removal of dissolved TBP. Both the processes require the solubility data of TBP in aqueous streams; the estimation of mass transfer zone (MTZ) length is an important parameter for adsorption process and correlation of this parameter with the mass flux of TBP in aqueous feed is essential for the design of adsorption columns. For the second

process, liquid pulse columns are often used. For the purpose of design the equilibrium data of TBP between aqueous and diluent are essential.

## Summary and Conclusions

Some of the equipment design and development aspects needed for fuel reprocessing have been highlighted in this article, with specific reference to the developments carried out at IGCAR. Applications of rotary continuous dissolver, washable high speed centrifuge, fluidic devices and the solvent recovery unit should be pursued seriously also in thermal reprocessing plants. In addition many other electrochemical equipment find applications in fuel dissolution, acid killing, decontamination, destruction of organic laboratory wastes etc., and these units should be perfected and used in future reprocessing plants. Further development should aim at design and application in the generation of $NO_2$ for feed conditioning, electrolytic mixer-settlers and elctropulse columns for partitioning step to achieve salt free flowsheet to minimise the waste generated. Scope exists in developing continuous precipitators and better units for other reconversion steps. In addition robotics find applications in many areas like sampling and remote analytical facility for quick analysis. Scope for developing special tools, gadgets, cranes and viewing systems which find application in remote maintenance is limitless. With so many systems yet to be implemented in reprocessing plants on a routine basis in our nuclear programme, spent fuel reprocessing area offers real challenges and tremendous scope for innovation.

## Acknowledgements

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# Pyrochemical Methods for Fuel Reprocessing

*Dr. K. Nagarajan after graduating in Chemistry from Madurai University in 1974, joined 18th batch of the BARC training school. In 1975, he joined IGCAR (earlier known as RRC). He obtained his doctorate from Madras University in 1991. He was a receipient of the post-doctoral research fellowship of Japan Society for the Promotion of Science in 1994-95. He has been working in pyrochemical reprocessing for the last twelve years and is leading a group working on the molten salt electrorefining process. This group has set up and is operating a laboratory scale facility for these studies. He has also been working in high temperature calorimetry for the last 18 years. He has carried out calorimetric studis on many alloys and ceramic compounds of relevance to nuclear technology. He has more than fifty journal and conference publications to his credit.*

## Introduction

Reprocessing methods, in general, can be classified into two categories namely, aqueous and non-aqueous methods. The well known example of aqueous methods is the Purex process which has extensively been used worldwide for reprocessing irradiated fuels. Non-aqueous methods can be broadly classified into two groups, namely, (i) Methods based on volatilities and (ii) Pyrochemical methods. Nitrofluor process [1] and the fluoride volatility process [2] belong to the first group. In these methods, the higher volatilities of the hexa fluorides of U and Pu compared to those of the fission products are utilised for achieving the separation among them. They have the disadvantage that they use highly corrosive gases at high temperatures, besides having low decontamination factors. Pyrochemical processes, as their name implies, employ chemical reactions at high temperatures. The pyrochemical methods comprise (i) Melt refining (ii) Salt transport process (iii) Salt cycle process and (iv) Molten salt electrorefining. A brief description of these methods will be given here.

## Advantages and Disadvantages of Non-aqueous Methods

Molten salts and molten alloys used in the non-aqueous reprocessing methods can withstand higher levels of radiation compared to their aqueous counter parts and hence they can be used with short cooled fuels leading to reduction in the doubling time. Since higher concentrations of U and Pu can be handled by a given volume of these solvents compared to the aqueous solvents, the process volumes are low and the process equipment and the plant are compact. This has even led to the concept of locating the reprocessing and the refabrication plants at the same site as the reactor which helps in avoiding the problems associated with the transportation of irradiated and refabricated fuel between the reactor and the plants. The waste generated in these processes is in solid form and less compared to aqueous processes which makes waste disposal easier. The absence of aqueous reagents enables reduction in the problems related to criticality. Of all these processes, the molten salt electrorefining process offers an additional advantage, namely, the Actinide Recycle which will be dealt with later. In spite of these advantages, most of these non-aqueous methods have mainly been confined to laboratories and have not been used at plant scale. The main reason for this is the requirement of high temperature operation and the need for sophisticated remote handling equipment for reprocessing as well as refabrication of the fuel. Besides, the decontamination factors achievable by using these methods are of the order of $10^3$ which is about $10^3$ to $10^4$ times less than those attainable by Purex process. However, these decontamination factors are sufficient for fast reactor fuels and as will be described later, the molten salt electrorefining process is emerging as a promising process for advanced fuels.

**Melt Refining process**

This method [3] was used for reprocessing EBR-II fuel which was an alloy of U (enriched in $^{235}U$ upto 52.18%) and fissium. Fissium is an alloy of noble metals having the following composition : 2.5 wt.% Mo, 2 wt.% Ru, 0.26 wt.% Rh, 0.19 wt. % Pd, 0.1 wt.% Zr, 0.04 wt.% Si and 0.01 wt.% Nb. This process, also known as oxide slagging process, takes advantage of the differences in the thermodynamic stabilities of the oxides of fuel materials and fission products for achieving the separation. In this process, the irradiated fuel is melted in a calcia stabilised zirconia crucible at 1400°C under inert atmosphere wherein the highly reactive barium, strontium, rare earth metals, and a part of U and Pu react with the crucible to form their respective oxides which adheres to the crucible in the form of a "skull". Noble metals follow molten U which is poured out. The rare gases and the alkali metals are released as vapours during the process. Mo and Ru show no preference to the poured out melt or the skull. Their removal depends on the pouring yield. Recoveries of U and Pu are of the order of 90-95% only. U and Pu in the skull are recovered by another process known as the skull reclamation process. This process consists of oxidising the skull under Ar-$O_2$ atmosphere at 700°C to make it mainly a mixture of $UO_2$ and $U_3O_8$ and then reducing these oxides by using molten Zn and Zn-Mg alloys in presence of molten halide salts. However, Pu follows the Zn-Mg alloy to the waste stream. Hence this method is not suitable for fuels containing higher amounts of Pu.

**Salt Cycle Process**

This is an electrochemical process [4] for the reprocessing of $UO_2$ based fuels for thermal breeder reactors. It is based on the fact that $UO_2$ can be produced by electrolytic reduction of molten uranyl chloride, $UO_2Cl_2$. In this process, the mixed oxide fuel is first oxidised to convert $UO_2$ to $U_3O_8$ and then, dissolved in a molten chloride salt mixture (NaCl-KCl) by reaction with $Cl_2$ and or/ HCl. Crystalline $UO_2$ can be deposited by the electrolysis of the salt using graphite electrodes and a cell potential as low as 0.5 V. Decontamination factors of the order of $10^3$ are obtained for rare earths. For elements such as Zr which also gets deposited with $UO_2$, no separation is possible. Co-deposition of $UO_2$ and $PuO_2$ is achieved by sparging the salt with $O_2/Cl_2$ gas mixture. The mechanism is believed to involve the oxidation of Pu(IV) to V or VI by the sparging gas followed by the electroreduction to IV at the cathode. By controlling the temperature, the salt composition and the ratio of oxygen to chlorine, the ratio of U to Pu in the deposit can be varied. In RIAR, Russia the method has been used for the production of granulated fuel for BOR-60 and test asssemblies for BN-600 and BN-350 reactors and these production processes are considered as the prototypes for future reprocessing by this method [5].

**Salt Transport Method**

This method [6] was developed for the reprocessing of mixed oxide fuels for fast reactors. It is based on the differences among the thermodynamic stabilities of the chlorides of fuel materials and fission products. In this process, the oxide fuels are at first reduced by Ca in a Ca-Cu-Mg alloy in presence of a molten salt mixture containing $CaCl_2$. U and Pu metals along with the rare earth and noble metals are brought to the Cu-Mg alloy phase. Alkali and alkaline earth metals which form more stable chlorides distribute to the salt phase. Selective transportation of Pu from this donor alloy to an acceptor alloy which is generally a Zn-Mg alloy is achieved by equilibrating a salt mixture containing $MgCl_2$, known as the transport salt. At the donor alloy salt inter phase, $MgCl_2$ oxidises Pu to $PuCl_3$ and the acceptor alloy-salt interface $PuCl_3$ is reduced to Pu by the Zn-Mg alloy. During the alloy-salt equilibrations, metals such as rare earths whose chlorides are more stable than $MgCl_2$ prefer the salt phase and those whose chlorides are less stable than $MgCl_2$ prefer the metal phase. The distribution behaviour of actinides whose chlorides have stabilities closer to $MgCl_2$ will be dictated by the activities of the metal in the alloy. Hence if Pu has to be transported from a donor alloy to an acceptor alloy, then, the activity of U alloy has to be high in the donor and low in the acceptor alloy. Thus the donor and acceptor alloys are suitably chosen to achieve the selective transport and the desired separation between the U and Pu and the fission products.

Table 1. Gibbs free energies of formation of chlorides in kcal/g.eq. of chlorine

| Relatively stable (salt phase) | | Electrotransportable to cathode | | Relatively unstable (anode) | |
|---|---|---|---|---|---|
| Compound | $-\Delta G_f^0$ | Compound | $-\Delta G_f^0$ | Compound | $-\Delta G_f^0$ |
| CsCl | 87.8 | $CmCl_3$ | 64.0 | $CdCl_2$ | 32.3 |
| KCl | 86.7 | $PuCl_3$ | 62.4 | $FeCl_2$ | 29.2 |
| $SrCl_2$ | 84.7 | $NpCl_3$ | 58.1 | $NbCl_5$ | 26.7 |
| LiCl | 82.5 | $UCl_3$ | 55.2 | $MoCl_4$ | 16.8 |
| NaCl | 81.2 | $ZrCl_2$ | 46.6 | $TcCl_4$ | 11.0 |
| $LaCl_3$ | 70.2 | | | $RhCl_3$ | 10.0 |
| $PrCl_3$ | 69.0 | | | $PdCl_2$ | 9.0 |
| $CeCl_3$ | 68.6 | | | $RuCl_4$ | 6.0 |
| $NdCl_3$ | 67.9 | | | | |
| $YCl_3$ | 65.1 | | | | |

**Molten salt electrorefining**

This method [7] was proposed for the reprocessing of irradiated U-Pu-Zr alloy fuels of the conceptual Integral Fast Reactor (IFR) proposed by ANL, USA. The core fuel of IFR is of the composition 70 wt % U-20 wt% Pu-10 wt% Zr and the blanket is U-10wt%Zr. The same molten electrorefining process can be used for processing both the irradiated fuel and the blanket.

A schematic diagram of the molten salt electrorefining process is shown in Fig.1. This process is based on the differences among the thermodynamic stabilities of the chlorides of fuel materials and fission products. The Gibbs free energies of formation of some of these chlorides are shown in Table 1. In the molten salt electrorefining process, carried out at 500°C, cut pieces of the irradiated fuel along with the clad immersed in the molten salt used as the anode, molten LiCl-KCl containing about 2 mol% of $UCl_3$ and $PuCl_3$ to enable the elctrotransport of U and Pu is used as the electrolyte and either a solid low carbon steel rod or molten cadmium is used as the cathode. Any deposit falling out of the solid cathode into molten cadmium at the bottom of the vessel can be again transported to the cathode by making the cadmium as the anode.

During the electrorefining process, the alkali, alkaline earth and rare earth fission products whose chlorides are highly stable are easily oxidised to the salt phase and remain there. U and Pu whose chlorides are of intermediate stability are selectively electrotransported to the cathode and deposited there. Noble metals whose chlorides are the least stable are not oxidised at all and stay in the anode itself. The choice of the cathode enables one to achieve either the selective deposition of U or the co-deposition of both U and Pu on the cathode. The different deposition behaviours on different cathodes arise due to the fact that $PuCl_3$ is more stable than $UCl_3$. When a solid rod is used as the cathode, any Pu deposited on the cathode will undergo the following reaction

$$Pu(cathode)+UCl_3(salt) \rightarrow U(cathode)+PuCl_3(salt)$$

which has a large negative Gibbs free energy change. But, when molten cadmium is used as the cathode, the difference between the activity coefficients of U (88.4) and Pu ($10^{-4}$) compensate for the difference in the thermodynamic stabilities of the respective chlorides and codeposition of U and Pu becomes

possible. Thus in the reprocessing plant, molten salt electrorefining will be done with molten cadmium as the cathode for processing irradiated core fuel. But, for processing the irradiated U-Zr blanket, which will contain about 2 wt.% of Pu, a solid cathode rod will be used for depositing only U, thus enriching the blanket in Pu upto 25 wt.% after which the enriched blanket will be processed along with the core using molten cadmium cathode. In the consolidation step, cadmium solvent and the salt occluding the deposit will be distilled off before heating the remaining actinides to 1300°C, when molten actinide particles coalesce together forming an ingot on cooling. The refabrication of the recovered fuel materials is done by the injection casting method.

As was mentioned earlier, this process has the potential for actinide recycling. The minor actinides, namely, Np, Am and Cm also get electrotransported to the cadmium cathode like U and Pu and hence are a part of the refabricated fuel. The minor actinides are thus burnt in the reactor and thus are removed from the waste stream which has less risk potential. Their presence in the fuel does not affect the neutron economy because their absorption cross sections are low in the fast neutron spectrum. On the other hand, their favourable fission cross sections help to generate more energy by burning them. Separating the minor actinides from LWR spent fuel after converting them to metals and processing them by molten salt electrorefining along with U and Pu for making fuel alloys for fast reactors has been thought of as a strategy for easier disposal of LWR waste stream which stems from the actinide recycle potential of this process. Eventhough this reprocessing method is ideally suited for metallic fuels, as the fuel materials are maintained in the metallic state throughout the process, it can be used for processing advanced fuels like the mixed carbides and especially nitrides. The possibility of recovering the $^{15}N$ released during the dissolution of the nitride fuel in the anode cadmium makes it economical compared to other processes.

Until 1994, laboratory scale processing of U-Pu alloys have been carried out for several years and engineering scale demonstrations on fuels containing U and inactive surrogate elements for Pu have been done by ANL, USA. They were discontinued for political reasons. In a typical engineering scale experiment, upto 15 kg of U is deposited on a solid cathode and 4 kg of Pu can be deposited on a cadmium cathode together with about 1 kg of U and several hundred ppm of rare earths. Actinide recoveries have been reported to be >99.5%. The decontamination factors for the alkaline earth metals, zirconium and rare earth metals are between 1000-2000.

In the Radiochemistry Laboratory, IGCAR, studies on molten salt electrorefining process were carried out with U-Zr and U-Ce-Pd alloys by using a cell attached to an argon atmosphere glove box [8]. A laboratory scale facility comprising four argon atmosphere glove boxes and an air glove box was later set up, and commissioned for carrying out molten salt electrorefining studies on Pu containing alloys and other fuel materials. Studies on the effect of $UCl_3$ concentration on the current in the electrorefining cell were carried out in this facility to arrive at a value of 2.4 mol% to be the optimum value to achieve maximum current [9]. Besides the electrorefining cell, this facility comprise the consolidation set up, an injection casting facility and a cadmium distillation set up. Studies on electrorefining of U alloys with a view to optimise the process parameters for maximising the transport rates as well as the recovery of U are in progress.

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