IRRADIATED THORIA-BASED FUEL

Experiences in Reprocessing

Sanjay Kumar and Smitha Manohar

ABSTRACT

With superior neutronic and material properties along with advantage of lower production of long-lived actinides, Th^{233}-U^{233} fuel has attracted the world towards its utilization for nuclear energy. The Indian three-stage nuclear power programme envisages a large-scale utilization of thorium due to its abundant availability, while uranium resources in India are limited. For a complete understanding of the Thorium cycle, laboratory studies were carried out to establish processing of irradiated thorium to recover U^{233} and Th^{232} and recycle these to the reactor. Thoria rods irradiated in a research reactor were successfully processed at the Uranium Thorium Separation Facility (UTSF). With know-how gained from the UTSF operating experience, processing of Thoria bundles irradiated in power reactors (PHWRs) was successfully demonstrated at Power Reactor Thoria Reprocessing Facility (PRTRF). The challenges like inertness of sintered Thoria for chemical dissolution, radiological hazards due to presence of ^{232}U contamination in ^{233}U, safe handling of highly dispersive gaseous decay product Radon-220 (^{220}Rn) during processing and increasing dose of ^{228}Th containing raffinate during its interim storage were successfully addressed at PRTRF.

Further, R&D activities were also carried out to process Advanced Heavy Water Reactor (AHWR) spent fuel. Three-component flow sheet for processing of AHWR (Th-U) fuel pins was successfully established after extensive studies on laboratory scale. The article gives a glimpse of the valuable experience gained while addressing the challenges encountered during the reprocessing of irradiated Thoria.

KEYWORDS: Reprocessing of thoria fuel, Radon-220, Uranium-232, Sintered thoria pellets, Three-component flowsheet, THOREX, UTSF, PRTRF.

IN INDIAN context, thorium is perceived as a long-term source of energy due to its abundant availability, which will ensure sustainable energy security. Thorium based fuels have better in-core performance as well as inherent proliferation resistance. Their superior neutronic and material properties, along with advantage of lower production of long-lived actinides in the ^{232}Th-^{233}U fuel, have attracted the world towards its utilization for nuclear energy. The feasibility of the thorium cycle has been demonstrated worldwide in a wide variety of reactors over the years. During irradiation in the reactor, ^{232}Th absorbs a neutron to transmute to ^{233}U, a naturally non-occurring fissile uranium isotope which has superior fission fuel properties in comparison to ^{239}Pu and ^{235}U. Reprocessing of irradiated Thoria fuel is necessary to recover ^{233}U for its utilization as fuel in a nuclear reactor.

R&D Activities for Irradiated Thoria Fuel Reprocessing

Initial R&D activities for developing a flow sheet for processing of irradiated Thoria fuel were limited to recovery of ^{233}U. With the well proven solvent, Tri Butyl Phosphate (TBP), used in PUREX process, ^{233}U recovery was successfully established. Pilot plant scale studies on the recovery of ^{233}U alone were taken up in India in the 1970s. Later the studies were extended to establish recovery of uranium as well as thorium. With single valence state of thorium, separation of U and Th could be achieved by varying TBP concentrations in two separate cycles. The reprocessing process flowsheet for irradiated Thoria fuel (THOREX) was successfully developed at FRD laboratory for U and Th recovery. ^{233}U is recovered in the first cycle using 3% TBP in n-dodecane and ^{232}Th is aimed to be recovered in second cycle with 38% TBP in n-dodecane.

Demonstration of Irradiated Thoria Fuel Reprocessing at UTSF

Thoria fuel rods cladded with aluminium were irradiated in research reactor CIRUS (J rods) up to a burn up of about 1000 MWD/Te. Processing of these rods was demonstrated successfully at UTSF. Processing consists of following steps:

A. Chemical decladding of the fuel to remove aluminium cladding using sodium hydroxide along with sodium nitrate solutions and subsequently dissolution of Thorium in concentrated nitric acid in presence of sodium fluoride catalyst along with aluminium nitrate as a complexing agent (to reduce corrosion effects of free fluoride in the system).

B. Separation of uranium using 3% TBP in n-dodecane in mixer settler, its final purification with cation exchange resin, concentration of uranium product by evaporation and final conversion of uranium product to oxide form using oxalate precipitation technique.

C. Processing of highly active raffinate stream (containing thorium as well as fission products) generated in the uranium recovery cycle, using 38% TBP in n-dodecanefor the recovery of thorium leaving behind the fission products in the raffinate. The Thorium-lean Raffinate (TLR) from the thorium recovery cycle was then transferred to a waste tank farm for interim storage. The management of TLR was successfully demonstrated following the vitrification of active components after necessary pre-treatment.

Thorium based fuels have better in-core performance as well as inherent proliferation resistance. Their superior neutronic and material properties, along with advantage of lower production of long-lived actinides in the Th^{232}-U^{233} fuel, have attracted the world towards its utilization for nuclear energy.

Since the level of contamination of ^{232}U in ^{233}U product in thoria fuel irradiated in research reactor is only 2–3 ppm, it did not pose any significant radiological problems during

The authors are from Fuel Reprocessing Division, Bhabha Atomic Research Centre, Mumbai

processing. Valuable experience could be generated at UTSF demonstrating the reprocessing of irradiated thoria of research reactor origin.

Demonstration of Power Reactor Irradiated Thoria Fuel Processing at PRTRF

With the experience gained at UTSF a new facility named PRTRF was designed and set up for processing of power reactor irradiated thoria fuel. It was planned to process thoria bundles, used for initial flux flattening of PHWRs, with an aim to establish the reprocessing flow sheet for irradiated thoria fuel bundles in PHWR. The PRTRF with two concrete shielded hot cells was utilized for the same.

The major differences between the thoria bundles processed during the campaign of UTSF and PRTRF are with respect to the clad material, burn up and contamination levels of ^{232}U in the ^{233}U product. The fuel irradiated in PHWR was a 19-pin bundle with zircaloy cladding and having burn up of about 10000–12000 MWD/Te HM, contained about 0.5-1.5% ^{233}U with significant ^{232}U content in the range 100-500 ppm calling for special radiological attention. The process involved the following major steps:

A. Operation of Head-end system involving

- Dismantling of the fuel bundles to separate the fuel pins and cutting the individual pins into small pieces using a laser chopper
- Dissolution of the chopped pieces in concentrated nitric acid using sodium fluoride catalyst along with aluminium nitrate as a complexing agent to avoid corrosion due to free fluoride ions
- Filtration of zircaloy fines using air ejector assisted vacuum filtration system with polypropylene cloth as filter media
- Off-gas treatment using specially designed cleaning system for safe handling of the Rn-220 containing gases, generated during processing

B. Separation of uranium using 5% TBP in n-dodecane in mixer settler, its final purification with cation exchange resin, concentration of uranium product by evaporation and final conversion of uranium product to oxide form using oxalate precipitation technique

C. Interim storage of thorium-bearing highly active raffinate solution containing 99% of the fission products in waste tank farm before taking up its final management.

Challenges in Reprocessing of Thoria Based Irradiated Fuels

Radiation level in the recovered ^{233}U as well as thorium product increased due to the associated decay products of ^{232}U. Besides, dissolution of inert ThO_2 and management of highly dispersible gaseous ^{220}Rn pose major challenges during dissolution of Thoria fuel. Attempts were made to address these challenges during the processing campaigns at UTSF and PRTRF and same are summarized below:

- Extreme chemical inertness of ThO_2

Sintered thoria pellets are extremely inert towards chemical interactions making the dissolution a difficult task. Use of sodium fluoride catalyst along with aluminium nitrate as a complexing agent for free fluoride ions helped to overcome this challenge. With the addition of required concentration of aluminium nitrate, corrosion rate could be mitigated in the SS 304L dissolver.

- The radiological hazards due to presence of ^{232}U in ^{233}U

The ^{233}U produced in the reactor is always contaminated with ^{232}U ($T_{1/2}$ = 68.9 y) and its immediate decay product ^{228}Th ($T_{1/2}$=1.98 y) (Fig.1). The level of contamination depends upon the isotopic composition of uranium in the initial fuel, the burn up and neutron spectrum encountered in the reactor.

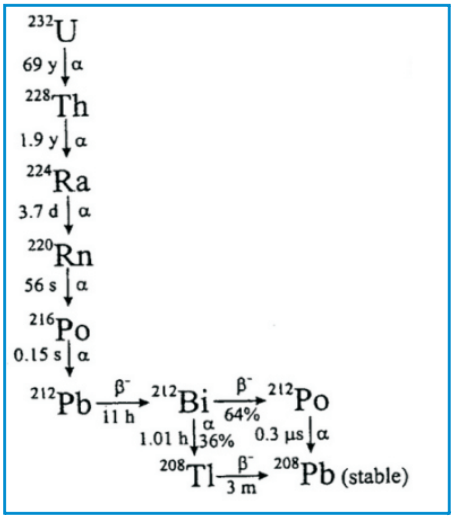

Fig.1: Decay chain of ^{232}U.

Daughter products of contaminants ^{232}U, ^{228}Th, viz: ^{212}Bi and ^{208}Tl, emit high energy gamma radiations during their decay. Hence, ^{233}U product pose very high radiation field due to presence of ^{212}Bi and ^{208}Tl. The high radiation field associated with handling ^{233}U, the , necessitates the provision of heavy shielding as well as remote handling systems for spent fuel transportation, reprocessing and fuel fabrication. Immediately after extraction from irradiated fuel, the radiation dose associated with ^{233}U is low for a few days driven by the lower concentrations of ^{228}Th and its daughter products (like ^{212}Bi and ^{208}Tl). It is well understood that a limited window period with lower radiation dose is available for easy handling of ^{233}U product (Fig.1). It is safe to handle ^{233}U product for fuel fabrication in shielded glove boxes within 28 days of extraction and purification of ^{233}U product stream.

- Increasing dose of Thorium product

Due to presence ^{228}Th along with their hard gamma emitter daughter products, ^{212}Bi and ^{208}Tl, in the purified stream of recovered Thorium from irradiated fuel, its handling

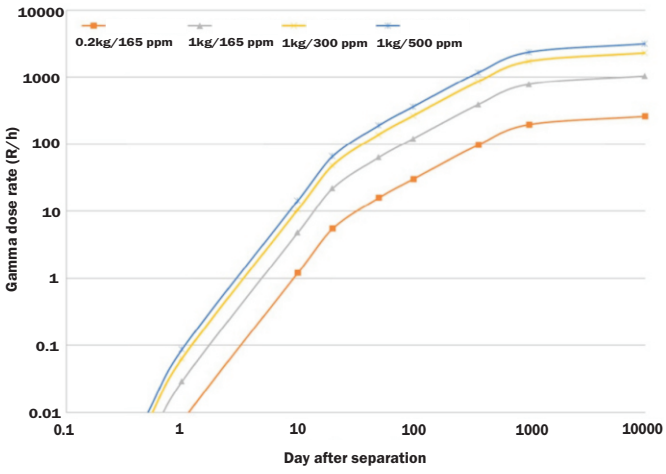

Fig.2: Radiation dose rate build up trend for ^{233}U with ^{232}U contamination.

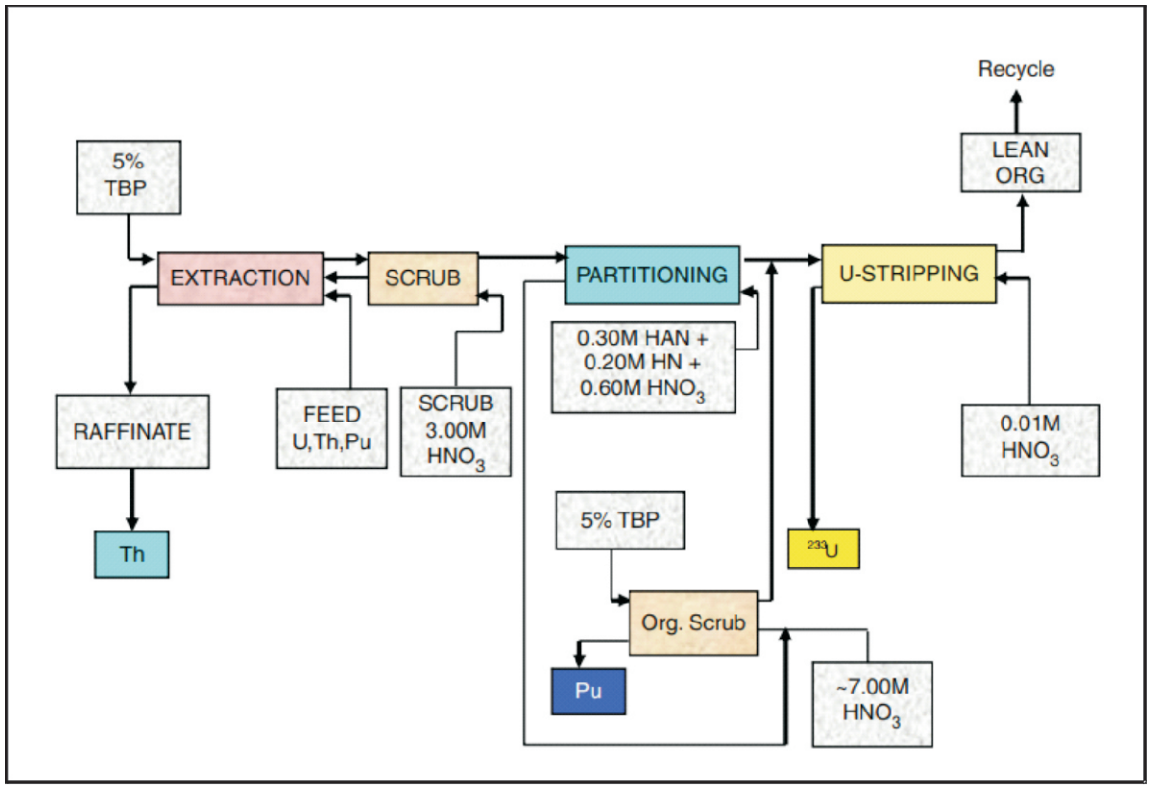

Fig.3: Three-component process flow sheet for AHWR spent fuel reprocessing.

is highly challenging after a short cooling period. A cooling period of approximately 20 years is required to bring down the gamma dose associated with the thorium product, which necessitated adequate storage facility for same.

- Special feature for off gas filtration system:

^{220}Rn (220-Radon), the noble gas & one of the decay products in the ^{232}U decay chain, can pass through the High Efficiency Particulate Air (HEPA) filters and then further decay into solid particles of ^{212}Bi and ^{208}Tl, which are hard gamma emitters. Following considerations were given while designing the head-end as well as off-gas systems to handle highly diffusive ^{220}Rn, released during chopping and dissolution of the fuel:

- Minimum carrier gases were used in the system
- Hold up time of 10 minutes was provided in the off-gas system
- Charcoal bed filter was used for delay and decay of ^{220}Rn
- Areas were provided with higher air changes to avoid back diffusion of ^{220}Rn into working areas.

An efficient off gas system was provided with important features like double HEPA filters and a hold up volume (to give a delay of about 10 min to the off gas) in between to hold the Radon gas till it decays to solid material. The first HEPA filter collects the solids generated prior to ^{220}Rn decay, while the second HEPA filter removes the solid decay products of ^{220}Rn from the off gases. The high radiation level not only calls for gamma shielding for these off gas system components but also its remote maintenance.

Processing of AHWR Fuel

As no fissile isotope is present in thorium, the initial production of ^{233}U requires a source of neutrons in reactors using other fissile elements like ^{235}U or ^{239}Pu as fuel. As the fuel for AHWR is expected to be a combination of Pu-Th, the discharged fuel after irradiation is expected to have three components U, Pu and Th, calling for specially designed reprocessing flow sheet for recovery of all the three components[2].

The extensive R&D work on various aspects of ^{232}Th-^{233}U based fuel along with our expertise on the PUREX process over five decades resulted in formulating a conceptual process flow sheet for three-component reprocessing of long cooled AHWR fuel on laboratory scale (Fig.2).

Considering the high radioactive field while handling the off-gas system filters as well as the ^{228}Th and ^{233}U product, remote handling mechanism is inevitable in the reprocessing and fuel fabrication facility.

TBP in n-dodecane as a solvent with different concentrations along with Hydroxyl Amine Nitrate (HAN) plays important roles in separation and purification of U, Pu and Th products. The number of purification cycles for U, Pu and Th would depend on the desired extent of products purity.

For taking care of radiological hazard, chemical separation of ^{233}U containing 1000-2000 ppm of ^{232}U from ^{228}Th can be carried out just before delivery of ^{233}U to the fuel fabrication facility. Provision can be made at the reprocessing plant to store ^{233}U solution in shielded cells. Final purification of ^{233}U can be taken up as per the schedule of ^{233}U requirement from fuel fabrication plant.

Considering the high radioactive field while handling the off-gas system filters as well as the ^{228}Th and ^{233}U product, remote handling mechanism is inevitable in the reprocessing and fuel fabrication facility.

Conclusions

Exploration of Thorium fuel cycle is inevitable for India for its self-sustained nuclear energy program. Thorium utilization calls for addressing significant technological challenges right from fuel chopping to product storage in the ^{233}Th-^{232}U fuel cycle, essentially arising out of the associated radiological hazards and also due to extreme chemical inertness of ThO_2. Extensive laboratory studies were carried out to address the challenges and the processing was demonstrated successfully. Three-component process flow sheet for AHWR spent fuel reprocessing was formulated on the basis of the experience gained during UTSF and PRTRF processing campaigns. Higher levels of contamination of ^{232}U in the product pose major challenges in handling the Thoria-based fuel during reprocessing as well as fuel fabrication calling for co-locating fuel fabrication and reprocessing facility as well as meticulous planning of the reprocessing activities as per the fuel fabrication activities.

Acknowledgements

Authors acknowledge the efforts made by scientific and technical teams of Fuel Reprocessing Division, Nuclear Recycle Group. Authors also express their gratitude towards past and present mentors to guide the team and also to provide valuable know how for successful demonstration of Thoria fuel reprocessing. Authors extend their sincere thanks to C. P. Kaushik, Director, Nuclear Recycle Group for providing immense support towards research reactor fuel reprocessing activities.

References

[1] J. K. and Frank N von Hippelb, "U-232 and the Proliferation Resistance of U-233 in Spent Fuel", Science & Global Security, 2001, **9**, 1-32.

[2] B. Bhattacharjee, "An overview of R&D in fuel cycle activities of AHWR", 2003, INSAC, Kalpakkam.

[3] P. S. Dhami, *et al,* "Validation of the flow-sheet proposed for reprocessing of AHWR spent fuel: counter-current studies using TBP", Desalination and Water Treatment, 2012, **38**, 193-198.