1. ABSTRACT

This paper describes about the Indian experience on the reprocessing of irradiated thoria both in Research as well as Pressurized Heavy Water Reactors. Based on the experience from pilot facilities in late seventies, engineering scale facilities have been designed, commissioned and operated successfully. Quantitative recovery of uranium and thorium with desired purity has been achieved using the solvent extraction based flow-sheets.

Keywords: Thorium, $^{233}$U, Reprocessing, THOREX process, Tri-n-butyl phosphate

2. INTRODUCTION

Exploitation of the abundant thorium resources to meet sustained energy demand forms the basis of the Indian nuclear energy programme. Reprocessing plays an important role to link our three stage programme wherein fissile and fertile nuclides are recovered and recycled back into appropriate nuclear reactors. India embarked on the field of reprocessing in the year 1964 with the commissioning of the first reprocessing Plant at Trombay for the processing of metallic spent fuel from CIRUS reactor using PUREX technology [1]. Prior to the Indian efforts, process like THOREX (THORium uranium EXtraction) and its variations viz. acid deficient and acid processes were already in vogue [2]. Since our programme had heavy reliance on the thorium fuel cycle in its third stage, it was decided to generate necessary expertise in the reprocessing domain along with other fuel cycle activities. Based on the extensive laboratory scale research and development studies, flow-sheets were developed for the recovery of $^{233}$U/Th. As the recovery of $^{233}$U alone was contemplated during the initial phase of the programme, more emphasis was given to process based on 5% TBP in hydrocarbon diluents. First pilot facility was designed, commissioned and operated successfully in 1970 for preferential extraction of $^{233}$U [3]. The successful recovery of $^{233}$U from irradiated thoria was followed by another pilot plant at IGCAR, Kalpakkam [4]. Based on the experience from these pilot facilities, later in 2002, an engineering facility, Uranium Thorium Separation Facility (UTSF), was designed and commissioned at Trombay for the processing and recovery of $^{233}$U from CIRUS irradiated thoria rods on a regular basis. All the modifications which were felt necessary from the pilot plants Trombay and IGCAR, Kalpakkam were incorporated in the facility. The facility was used to recover $^{233}$U and thorium from research reactor irradiated thoria employing 3% TBP and 38% TBP in n-dodecane respectively.

In some of the pressurized heavy water reactors (PHWRs), thoria was used for initial flux flattening. On discharge from reactor, it contained ~0.5-1.5% $^{233}$U. Based on the experience from UTSF, a new facility viz. Power Reactor Thoria Reprocessing Facility (PRTRF), Trombay was built. The facility is first of its kind designed, built and operated to handle $^{233}$U product containing high content of $^{232}$U (500ppm). The Indian experience on the reprocessing of thoria irradiated both in Research as well as PHWRs is presented in this paper.
3. THORIA REPROCESSING EXPERIENCE

3.1 Pilot Plant Facilities

Based on the extensive in-house data generation, the first pilot plant scale separation of $^{233}\text{U}$ from irradiated thoria in research reactor CIRUS was carried out in the year 1970 employing acid THOREX process [3]. As the recovery of $^{233}\text{U}$ alone was contemplated during the initial phase of the programme, more emphasis was given to the process based on 5% TBP in odourless kerosene as solvent. The pilot plant set up at Trombay was essentially comprised of two main sections, the dissolver cell for rod charging and decladding/dissolution operation and separation area where separation and purification was carried out in series of glove boxes, which housed the equipment systems for feed transfer, solvent extraction, aqueous product concentration, ion-exchange purification and precipitation. Since aluminium was the clad, chemical method using NaOH was adopted for decladding. The exposed thoria was dissolved in a thermosyphon dissolver (Fig. 1) in HNO$_3$ containing NaF and aluminium nitrate. The dissolution could be completed in $\sim$12h and the feed had thorium concentration of $\sim$200g/L at an acidity of $\sim$4M with $\sim$0.12% uranium. Since the irradiation was carried out at the thermalised low flux area, fission product activities were very low and $^{232}\text{U}$ content was $\sim$2-3ppm. In 5% TBP, $^{233}\text{U}$ alone was recovered wherein Th remained in the raffinate. Co-extracted thorium was scrubbed by 1-2 M HNO$_3$ and uranium product was stripped with demineralised water. Extraction, scrubbing and stripping were done in continuous air-pulsed mixer-settler comprising of 12 stages (Fig. 2). There were 5 stages for extraction, three for scrubbing and four for stripping.

Fig.1: Cell with Thermosiphon type Dissolver Fig.2: Mixer-Settlers Housed in Glove Box

The stripped uranium product was then concentrated in an evaporator. Further purification of uranium was carried out by anion exchange method. For carrying out separation by anion exchange, it was necessary to have uranium in chloride form, free from nitrate ions. Since concentrated uranium solution contained large amount of nitrate, uranium and thorium in the solution were first precipitated with ammonia, the precipitate washed free of nitrate and then dissolved in concentrated HCl. The solution was conditioned to $\sim$8M HCl and loaded on a preconditioned anion exchange column. The column was washed free of thorium with 8M HCl and $^{231}\text{U}$ was eluted with 0.5M HNO$_3$. The eluted product contained pure $^{233}\text{U}$ with few ppm of Th contamination. The product solution of $^{233}\text{U}$ was then precipitated with ammonia solution, filtered and washed to remove ammonium salts. Ammonium diuranate thus obtained was transferred to silica muffle and ignited at 850°C to get U$_3$O$_8$. This was followed by setting up of another pilot facility at Kalpakkam to test and standardise equipments and remote handling systems and also to validate the flow-sheet employed in the first facility. These facilities had provided enough impetus to develop acid THOREX process to a more robust process. $^{233}\text{U}$ recovered from the initial campaigns was used for fuelling the KAMINI reactor, which is the only reactor working today on $^{233}\text{U}$ fuel [5].

3.2 Further Developments

The successful recovery of $^{233}\text{U}$ from irradiated thoria was followed by process development studies to overcome some of the shortcomings encountered in the pilot plants [6-10]. The major areas addressed were: (a) Decontamination of thorium in $^{233}\text{U}$ product, (b) Tail end purification
of the separated $^{233}$U, (c) Testing of the equipments, (d) Thoria based fuel dissolution studies and (e) waste management issues. Summary on some of these areas is given below.

3.2 Engineering facilities

3.2.1 Uranium Thorium Separation Facility (UTSF), Trombay

In 2002, an engineering facility, UTSF (Fig. 3), was designed and commissioned at Trombay for the processing and recovery of $^{233}$U from CIRUS irradiated thoria rods on a regular basis. The modifications felt necessary from the pilot plant experiences of both Trombay and Kalpakkam facilities and from development studies were incorporated in the design of equipment and in the choice of process flow-sheets.

![Fig. 3: UTSF, Trombay](image)

Decaldding operation was similar to that adopted earlier using alkali. 13M HNO$_3$ containing 0.1M Al(NO$_3$)$_3$ and 0.03M NaF was used for dissolution. Unlike previous campaigns, the feed after dissolution was found to have acidity of ~5-6M HNO$_3$ with comparatively lower Th and $^{233}$U. Modified process flow-sheet using 3% TBP in n-dodecane was employed for preferential extraction of $^{233}$U with lesser co-extraction of thorium in the organic phase. Specially designed Combined Airlift Mixer-Settler Units (CALMSU) were used as contactors (Fig. 4). The mixer settler unit had 12 stages for extraction (2 modules), 18 stages for scrubbing (3 modules) and 12 stages for stripping (2 modules). The scrub section was extended sufficiently to provide adequate removal of thorium from the uranium loaded organic phase.

![Fig. 4: CALMIX Mixer-Settlers](image)

![Fig. 5: Process flow-sheet deployed for preferential extraction of $^{233}$U](image)

1AF – Aqueous Feed  
MS1A - Mixer Settler Extraction Module  
MS1S - Mixer Settler Scrub Module  
MS1C - Mixer Settler Strip Module  
1AW - Raffinate  
1AX - Organic Feed  
ICW - Lean Organic  
IX – Cation exchange Column, WT – Waste Tank  
IXW - Ion Exchange Elution Waste  
IXP - Ion Exchange Product  
IXPE - Ion Exchange Evaporated Product
Using this single cycle modified THOREX flow-sheet (Fig. 5), 56 thoria rods were processed in 8 batches. During reconversion operation, a pre-concentration step using ammonia as precipitant was used to concentrate Th and U product from the plant. This step gave a concentration factor of about 10. Subsequently, sequential precipitation technique developed in-house was adopted for purification [10,11] wherein Th from the concentrated solution was removed as oxalate in the first step using oxalic acid as precipitant. The supernatant containing $^{233}$U were subjected to carbonate precipitation under boiling conditions to remove iron if any in the second step. Uranyl carbonate was finally subjected to ammonia precipitation step for uranium. In this campaign, which lasted for ~2y, about 800g $^{233}$U of very good isotopic purity ($^{232}$U <3ppm) was recovered. The product was used for fuel development activities of the Department. This generated about 10m$^3$ of THOREX Raffinate.

To recover thorium from such raffinate stream, detailed laboratory studies [12] were undertaken to understand the physicochemical parameters such as solubility of thorium as a function of nitric acid concentration, limiting organic concentration of thorium at ~5.5M HNO$_3$ in the solvent concentration range of 30-42% TBP in n-dodecane etc. Extraction and stripping of thorium by TBP in n-dodecane were carried out using simulated raffinate initially and based on those results counter-current extraction and stripping studies were carried out for thorium recovery. The study established the scheme of extracting thorium from the THOREX raffinate using 38% TBP in n-dodecane. The limiting organic concentration of thorium under the experimental conditions was found to be well above 30 g/L. Thus an organic to aqueous phase ratio of 3:1 was employed for extraction. Counter-current extraction, scrubbing and stripping under various experimental conditions provide useful data for designing the flow-sheet on an engineering scale operation. Based on the above studies a scheme was proposed (Fig. 6) and deployed for the recovery of thorium from THOREX raffinate generated during the recovery of $^{233}$U from research reactor irradiated thoria rods at UTSF, Trombay using 38% TBP in n-dodecane.

**Fig. 6: Flow-sheet used for Thorium Recovery**

The product with an acidity of ~2M HNO$_3$ was subsequently stored as thorium nitrate in one of the process tanks. About 18m$^3$ thorium lean raffinate (TLR) (Table 1) was tankered to Waste Management Plant, Trombay for further treatment.
Table 1: Thorium Lean Raffinate from Reprocessing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Volume</td>
<td>18,700 L</td>
<td>$^{137}$Cs</td>
<td>6.34 mCi/L</td>
</tr>
<tr>
<td>Acidity</td>
<td>2.1 M HNO₃</td>
<td>$^{90}$Sr</td>
<td>7.5 mCi/L</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$9 \times 10^{-3}$ mCi/L</td>
<td>$^{125}$Sb</td>
<td>$9.13 \times 10^{-3}$ mCi/L</td>
</tr>
<tr>
<td>$\beta$</td>
<td>23.25 mCi/L</td>
<td>$^{106}$Ru</td>
<td>$2.92 \times 10^{-3}$ mCi/L</td>
</tr>
<tr>
<td>Th</td>
<td>0.245 g/L</td>
<td>F</td>
<td>106 mg/L</td>
</tr>
<tr>
<td>Al</td>
<td>1.97 g/L</td>
<td>Fe</td>
<td>126.65 mg/L</td>
</tr>
</tbody>
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The facility was once again made operational in 2013 for processing of 12 thorium rods leftover from research reactor origin using 3% TBP process. Operation was completed successfully in two batches and recovery and product specifications being similar to that achieved in earlier campaigns. The Raffinate generated from this campaign was processed using 30% TBP based solvent extraction process.

### 3.2.1 Power Reactor Thoria Reprocessing Facility (PRTRF), Trombay

Based on the operating experience from pilot as well as UTSF, an engineering facility was built for reprocessing of thorium irradiated in PHWRs. Hot commissioning of Power Reactor Thoria Reprocessing Facility (PRTRF) was carried out on 15th Jan. 2015. Irradiated thorium bundle end-plate cutting was carried out by laser and fuel pins were dismantled. Subsequently, chopping of the fuel pins was carried out by single pin mechanical chopper. The fuel was dissolved in nitric acid containing Al(NO₃)₃ and NaF. It took about 100 h to complete the dissolution. First batch, ~48 kg of thorium from four bundles irradiated in RAPS 3 & 4, was processed using 5% TBP based THOREX process employing CALMIX mixer-settler unit. The Uranium product from solvent extraction process was passed through cation exchange resin column to remove traces of thorium present in uranium product. This stream was concentrated and subjected to catalytic reduction using Adams catalyst in batches. The U(NO₃)₄ solution was finally precipitated as U(C₂O₄)₂. Supernatant from each precipitation batch was treated with KMnO₄ solution to destroy oxalate ions prior to sending it back to process for recycling. Calcination of the oxalate product was carried out using a predetermined temperature profile. The uranium product was found to have isotopic impurity of $^{232}$U in the range of 150-500 ppm. Solidified product in the laboratory is being monitored for increase in dose rate as a function of time.

![Fig. 7: Dismantled Fuel Pins after Laser cutting of end plate](image1)

![Fig. 8: $^{233}$Uranium Oxide](image2)
4. CONCLUSIONS

Reprocessing experience gained over the years has given sufficient technical knowhow to reprocess the irradiated thoria fuel which will be useful in processing futuristic thorium based fuel.

5. NOMENCLATURE

THOREX: THORium uranium EXtraction
UTSF: Uranium Thorium Separation Facility
CALMSU: Combined Airlift Mixer Settler Unit
TLR: Thorium lean raffinate
PHWR: pressurized heavy water reactors
RAPS: Rajasthan Atomic Power Station
PRTRF: Power Reactor Thorium Reprocessing Facility
TBP: Tri-n-butyl phosphate
ppm: parts per million
Th: Thorium

6. REFERENCES