6. Uranium Technology and Processes

Introduction

Uranium technology is vital to the nuclear energy programme. Given the lean sources of uranium in India, BARC has been concerned with the development of processes for recovery of uranium from secondary sources and dilute waste streams. The sea water has the lowest concentration uranium source, but holds enormous quantities of uranium. BARC has taken the first few significant steps in the long journey towards establishing an economically feasible process for recovery of uranium from sea water. The uranium metal production process is continually improved to enhance recovery and to handle different grades of feed material, such as, crude UF₄ from monazite. Abatement of pollution of nitrates has been taken up on a mission mode, while modifications to the process have ensured minimisation of waste. Progress in the novel indigenous process of plasma based hydrogen reduction of UF₆ to UF₄ is also described in this chapter.
6.1 URANIUM RECOVERY FROM LOW CONCENTRATE SOURCES

- Application of Liquid Membrane System for Recovery / Concentration of Uranium from Dilute Solution

- Development of D2EHPA - TBP Process for Uranium Recovery from Weak Phosphoric Acid
  
  An innovative dual cycle extraction process has been developed at laboratory and pilot plant scale for extraction of hexavalent uranium from 4-6 M phosphoric acid. The process incorporates selective scrubbing of co-extracted rare earths in second cycle, followed by two stage precipitation to yield high purity yellow cake. The process patent was filed in the US (Patent Application No. 09/947,349 dt 7/9/2001). The figure (on following page), gives the main steps of the process.

- Technology Demonstration, based on Alkaline Leaching Process, at UCIL Jaduguda for Recovery of Uranium from Tummalapalle Ore
  
  A joint developmental activity has been undertaken by the Chemical Engineering and Technology Group, Materials Group, BARC, Atomic Minerals Directorate and Uranium Corporation of India Limited, for recovery of uranium from Tummalapalle ore. The objective is to set up a pilot plant (Capacity-batch mode-250kg ore/batch; continuous mode-50 kg/hour) based on alkaline leach process. The pilot plant will incorporate complete process integration. The operation of the plant will confirm the laboratory results and generate experimental data to establish the techno-economic feasibility of the process for recovery of uranium from Tummalapalle ore. Further, engineering data, required for the design of production scale plant, will be collected. Detail engineering work has been completed and the pilot plant is being installed. When commissioned, it will establish an efficient process for recovery of uranium.

S.K.Ghosh <ghoshsk@barc.gov.in>
H.Rao <hrao@barc.gov.in>
D2EHPA-TBP Process to Recover Uranium from Phosphoric Acid

Acid Pretreatment

Oxidation

Extraction

Raffinate to post treatment and finally to host plant

Extract

Strip liquor

Dilution and Oxidation

Stripping

Solvent to washing and reuse in extraction

Strip liquor

Extraction

Raffinate

Extract

Scrubbing

Scrub liquor

Carbonate Solution

Stripping

Solvent washing, regeneration & reuse reextraction

Strip liquor

Yellow Cake Precipitation

Solvent D2EHPA-TBP

Reduced MGA (~55%P2O5)

Oxalic Acid/Sulphuric Acid

Carbonate Solution
Uranium Technology and Processes

Process Development for the Production of Nuclear Grade Uranium from Secondary Source (Crude UF₄)

Crude UF₄ is generated as a byproduct during thorium nitrate production from monazite. This crude UF₄ is treated with NaOH. The resultant UO₂ is dissolved in HCl. Crude uranium thus generated is purified using Alanin 336 and Tri-Butyl Phosphate. This has led to better management of resources with high recovery.

S. B. Roy < mrsued@barc.gov.in >
Flow sheet for production of nuclear grade uranium metal from crude UF₄.

6.2 RECOVERY OF URANIUM FROM SEA WATER

The effluent rejected from the desalination plant contains a number of materials and is a source for many chemicals. Some of the elements are very scarce and expensive. There is thus a strong motivation in recovering these elements from the reject brine of a desalination plant. This also adds value to a desalination plant apart from making it more environment friendly. Recovery of uranium (U), germanium (Ge) cesium (Cs), indium (In) and other high technology materials from the reject brine of desalination plant appears promising. The recovery of these materials is desirable not only for meeting the demand but also for reducing the cost of desalinated water.

R&D work on ‘Recovery of Uranium from Sea Water pilot programme (RUSWapp)’ has been taken up. Chemical synthesis
Uranium Technology and Processes

route and Ionising radiation route were pursued. Ionizing Radiation route using Electron Beam Irradiation was further pursued to provide irradiation grafting of ACN on a non-woven PP Fibre substrate availing the expertise of RTDS. About 130% grafting was achieved. Conversion of ACN to PAO up to 50-60% of the substrate weight was achieved.

Experimental data were collected for immersion depth, alkalination optimisation, bio and dirt fouling, tidal wave velocity and uranium pick up efficacy, at:

CIRUS Jetty head.
Kalapakkam, near seawater intake tunnel.
Tarapur 1&2 Seawater intake and outfall canals.
Andaman & Nicobar Islands.

A total of about 800 μg of U was collected in 5 campaigns from CIRUS Jettyhead, about 1.8 mg from TAPS seawater intake and outfall canals and around 200 μg from Andaman & Nicobar Islands. The specific collection was found to be from 60 to 160 μg/g of PAO in 12 to 24 days. This can be compared to adsorption-equilibrium of 1000 μg/g of PAO in 52 days at 25°C in laboratory condition results as reported by Japanese researchers. It was observed that vanadium is also getting collected on the adsorbent.

A 100 grams per year U pilot plant facility RUSWapp100 is under installation as shown in the Figure.

P.K.Tewari < pktewari@barc.gov.in>
6.3 URANIUM METAL PRODUCTION

- Production of 450 Kg Uranium Metal Ingots in India

In India, for fabrication of research reactor fuel, production of uranium metal ingot was started in Uranium Metal Plant, BARC with the production of a 44 kg uranium ingot by calciothermic reduction of uranium tetra fluoride. Thereafter, in the intervening years, there has been a substantial scale up of production and extensive investigation of the metal and its compound. Recently in Uranium Extraction Division, an augmented uranium metal production facility (AUMP) for safe and secure production of 450 kg U ingot has been successfully commissioned by magnesiothermic reduction of uranium tetra fluoride.

- Pelletized Charge Magnesiothermic Reduction (MTR) for Production of U metal

Charge pellet was prepared under controlled atmosphere using hydraulic press. In a MgF₂ lined reactor of 5 Kg capacity, pelletized charge was randomly stacked and fired for completion of reaction. Pellets for handling could be prepared without compromising purity of product and recovery. This facility is to be scaled up to the required plant size.
Recovery of Uranium from Scrap U-Cu Cluster Generated during Fuel Fabrication

With the objective of maximising overall recovery in the fuel production cycle, a process has been developed to selectively remove copper from U-Cu clusters, and thereby making available the uranium for fuel fabrication without reprocessing. It involves preferential leaching of Cu with HNO₃ under controlled conditions. Uranium in the leach liquor (0.6 %) is recovered as ammonium diuranate by ammonia precipitation. High recovery of 99.4 % is achieved during solid-liquid separation. Typical batch size is ~100 Kg.

Production of Uranium Powder

A process has been developed for production of a specified grade uranium powder. It involves metallothermic reduction of UO₂. The product uranium powder is recovered by selective leaching of the slag mass at controlled condition. This has led to production of high purity metal powder of reproducible quality.

Study of Uranium Peroxide Precipitation for Reduction in Nitrate Waste

Studies were carried out with the objective of developing a process for UO₃ without generating nitrogenous liquid waste and obtaining UO₃ of required chemical purity and physical characteristics, suitable for uranium metal ingot production. Uranium compound (oxide or diuranate) is dissolved in sulphuric acid. Uranium is precipitated as UO₄ by maintaining stringent parameters and filtered to get UO₄ cake. The product UO₄ is chemically nuclear grade. The effluent generated in this process is disposable as per MPCB guidelines. Physical characteristics of the UO₄ and the UO₃ obtained after calcination are to be of suitable grade for further conversion to metal ingot.

S. B. Roy <mrsued@barc.gov.in>

---

Process flow sheet for production of nuclear grade uranium metal from crude ADU
6.4 NEW PLASMA BASED PROCESS FOR CONVERSION FROM UF₆ TO UF₄

UF₆ is the only known compound of Uranium which is highly volatile at ordinary temperature. UF₆ is used as a feed material in enrichment processes like gas diffusion, gas centrifuge etc. The enriched UF₆ as well as tails of the enrichment plant cannot be stored in cylinders for a longer duration of time because of their toxic and corrosive nature. Hence they should be converted to more stable compounds like UF₄/U₃O₈ for storage. Conventionally UF₆ is reduced to UF₄ by hydrogen at about 600ºC. Thermal plasma process offers a clear, faster and advanced technology for processing waste UF₆ without needing any additional chemical and hence significantly reducing the waste generated.

\[
\begin{align*}
\text{UF}_6 + \text{H}_2(\text{g}) &= \text{UF}_4(\text{g}) + 2 \text{HF}(\text{g}) \quad \Delta G_{\text{prod}}^{\circ} = -315.6 \text{kJ} \quad (1) \\
\text{UF}_6 + 2 \text{H}(\text{g}) &= \text{UF}_4(\text{g}) + 2 \text{HF}(\text{g}) \quad \Delta G_{\text{prod}}^{\circ} = -923 \text{kJ} \quad (2) \\
\text{UF}_6 + 2 \text{H}_2(\text{g}) &= \text{UF}_4(\text{g}) + 2 \text{HF}(\text{g}) \quad \Delta G_{\text{prod}}^{\circ} = -1900 \text{kJ} \quad (3)
\end{align*}
\]

A plasma chemical process is currently being developed for efficient conversion of UF₆ to UF₄. A special constricted arc plasma generator has been designed and fabricated at Laser and Plasma Technology Division to produce argon-hydrogen plasma that exits through a nozzle into a plasma reactor. Additional hydrogen and UF₆ gas will be input in the reactor that has been designed in three sections namely the inlet and mixing zone, reaction zone and collection zone.

Provision for measurement of gas temperature at various sections has been done. A 2D axisymmetric simulation for temperature and velocity mapping has been carried out.

L.M. Gantayet <headlptd@barc.gov.in>
A. K. Das <akdas@barc.gov.in>

6.5 POLLUTION ABATEMENT THROUGH DENITRATION

- Recovery of Nitrate Values from Raffinate Stream, as Concentrated Metal Nitrate and Nitric Acid by Evaporation and Distillation

Based on the studies conducted on lab scale earlier in Chemical Engineering Division, a facility has been set up capable of processing 40-60 litre/hr of dilute nitrate waste stream. The process consists of filtration, organic removal (TBP) by diluent wash / ion-exchange, and vapor feed rectification for recovery of 6-8 M nitric acid. This facility, when operated with raffinate stream of uranium refining plant, will generate engineering data and establish the process on pilot scale. This will also provide a concentrated nitrate solution suitable for thermal denitration plant.

S. K. Ghosh <ghoshsk@barc.gov.in>
H. Rao <hrao@barc.gov.in>
- **Development of Fluidized Bed Thermal Denitration Technology.**

The thermal denitration programme is targeted for processing both product and waste nitrate streams of nuclear fuel cycle. Using fluidized bed thermal denitration, streams with high concentration of nitrate values (> 200 gm/lit) will be denitrated. The nitrate values will be recovered as nitric acid (for reuse) while the metal values as oxide for storage or further usage. A bench scale plant of 5 litres per hour capacity has been commissioned. The process flow sheet is represented below.

The various sub-systems in the plant are solid handling system, feed spray system, heat input system, off-gas treatment system. The plant is under operation for comprehensive development of the fluidized bed thermal denitration technology.

- **Chemical Denitration**

A uranium recovery from Uranyl nitrate raffinate cake (UNRC) and silica cake cum denitration process of aqueous waste containing nitrates, has been developed. Bench scale trial on 1 kg batch of UNRC and silica cake has been carried out. UNRC and silica cake generally contains 2-5% uranium and 2-10% nitrate. The process involves leaching of UNRC and silica cake with dilute sulfuric acid and reduction of nitrate to nitrogen gas with metallic reductant.
Uranium values are recovered as carbonate. This process has been tailored to process UNRC and silica cake from the Uranium refining plant and will help in the disposal of these wastes.

S. K. Ghosh <ghoshsk@barc.gov.in>
H. Rao <hrao@barc.gov.in>

Nitrogenous effluent management at Uranium Metal Plants

Purification of Crude Diuranate Cake Without Generating Nitrate Waste

A process has been developed for purification of crude diuranate cake without generating nitrate waste. This should obtain ammonium diuranate (ADU) of required chemical purity and physical characteristics, suitable for uranium metal production. The crude diuranate cake is dissolved in sulphuric acid and ADU is precipitated in presence of selective complexing agents namely CDTA to obtain nuclear grade ADU. This results in almost total recovery of uranium and it does not generate any nitrate waste.

Lab Scale Studies on Biodegradation of Nitrogenous Waste

Removal of nitrogen from nitrogenous effluent generated during uranium metal production process by biodegradation is an attractive option for treatment of nitrogenous waste. Bench scale set up consisting of nitrification and denitrification reactors has been designed and rigged up for feasibility and efficiency studies. The process schematic is shown in the figure.
In nitrification reactor more than 90% reduction efficiency has been consistently achieved with ammoniacal nitrogen feed concentration up to 450 mg/L. In the denitrification reactor more than 99% reduction efficiency has been consistently achieved with nitrate nitrogen feed concentration up to 1450 mg/L. Cascading of two reactors and scale up of the reactors will be tried.

Acclimatization of bacteria for higher concentration nitrogenous effluents more specifically for ammoniacal effluent is a challenge to be met.

Development of Process for Decontamination of Byproduct Hydrofluoric Acid

A process was developed in Uranium Extraction Division with the objective of obtaining zero fluoride effluent discharge and thereby by reusing/recycling the treated effluent. Concentrated aqueous HF was treated to remove radioactivity. After clarification it was suitable for industrial utilization. Dilute aqueous HF solution was treated to fix the fluoride as insoluble salt and recycle the filtrate for process requirement. These processes reduce the load on effluent management to a considerable extent.

Raffinate Recycle

Recycle of raffinate will utilise the nitric acid for plant recycle. This will also result in reduction of nitrogen bearing effluent. Laboratory scale trials have been conducted under a controlled temperature with conditioned feed. Nitric acid concentration was increased from about 1.5 N to 6 N which is suitable for plant recycle. The process is being scaled up.