



# THOREX PROCESS

(Group number 7)

#### **Group Members**

Nivedita Jha – 2021UCH0023 P H Sai Siddharth – 2021UCH0024 Praval Kumar – 2021UCH0025





- The Thorex process was first introduced by A.T. Gresky in 1953. It is used for extraction of Thorium and Uranium from spent nuclear fuel using liquid-liquid extraction process by solvent extraction using Tributyl Phosphate (TBP).
- In 1962 Rainey and Moore proposed the Acid Thorex process. The only distinguisher of these two processes is that Thorex Process uses Aluminium Nitrate in the extraction zone whereas Acid Thorex Process uses Nitric acid in order to reduce the salt concentrations in the raffinate phase.

T. GRESKY, Solvent extraction separation of U-233 and thorium from fission products by means of tributyl phosphate, Proc. 1st Intern. Conf. Peaceful Uses Atomic Energy, Geneva 9, 505 (1955).

The steps involved in the process are as follows:-

• **Dissolution of the Nuclear Fuel:** The first step of the Thorex process involves the dissolution of the nuclear fuel in nitric acid to form an aqueous solution containing thorium, uranium, and other fission products. The reaction can be represented as:

$$UO_2(s) + 4HNO_3(aq) \rightarrow UO_2(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

• **Separation of Uranium:** The next step involves the selective extraction of uranium from the aqueous solution using an organic solvent, such as tributyl phosphate (TBP) in Dodecane. The reaction can be represented as:

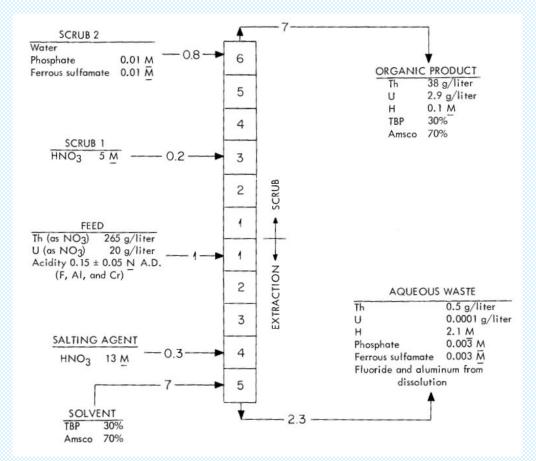
$$UO_2(NO_3)_2(aq) + 2TBP(org) \rightarrow UO_2(NO_3)_2(TBP)_2(org) + 2HNO_3(aq)$$

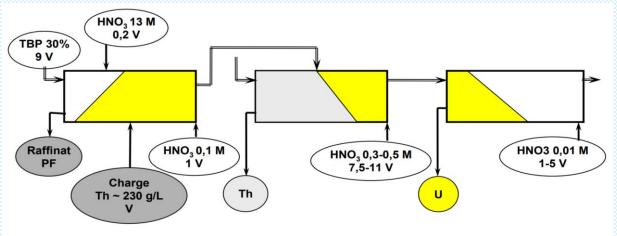
• **Separation of Thorium:** After the uranium is removed, the remaining aqueous solution contains thorium and other fission products. The thorium is then selectively extracted from the solution using TBP again. The reaction can be represented as:

$$Th(NO_3)_4(aq) + 2TBP(org) \rightarrow Th(NO_3)_4(TBP)_2(org) + 2HNO_3(aq)$$

• **Stripping of Thorium:** The final step involves the stripping of thorium from the organic phase back into the aqueous phase using a stripping agent, such as dilute nitric acid. The reaction can be represented as:

$$Th(NO_3)_4(TBP)_2(org) + 2HNO_3(aq) \rightarrow Th(NO_3)_4(aq) + 2TBP(org)$$







#### Fig. Acid Thorex process flowsheet

**Source:** <u>https://doi.org/10.13182/NSE61-A15380</u>

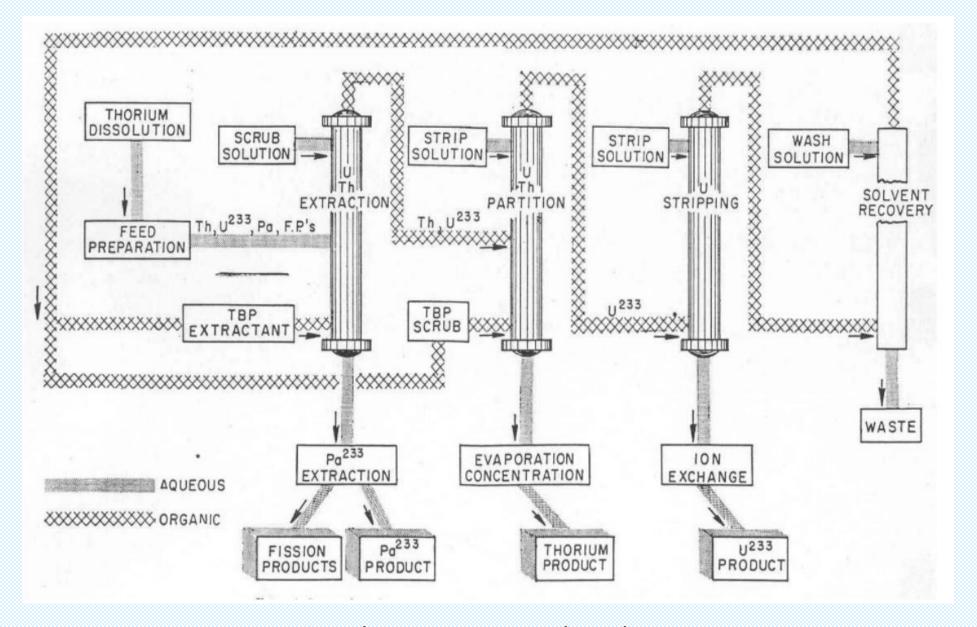




Fig. Thorex Process Flowsheet

**Source:** *IAEA* (2005)





- Thoria (ThO<sub>2</sub>), is practically inert with respect to nitric acid. The dissolution of thorium oxide (or thorium metal) fuel requires a mixture of nitric acid and hydrofluoric acid which causes equipment corrosion problems.
- There is a risk of formation of a third phase due to the low solubility of the Th(IV)-TBP complex in aliphatic solvents.
- There is formation of di-butyl phosphoric acid (HDBP), a product of TBP degradation by radiolysis and catalysed hydrolysis in the presence of macroscopic thorium concentrations with the formation of strong Th(IV)-DBP complexes. Formation of these complexes inhibit thorium from stripping off the organic phase during the stripping process.



## TYPES OF BATCH EXTRACTION

Single Batch Extractions

Multiple Batch Extractions

Countercurrent Batch Extraction





• In developing a flowsheet for the third uranium cycle, the following equilibriums must be considered:

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

• Increasing the concentrations of the above components will also enhance the extractability of the fission products that have persisted to the third cycle. Conditions must therefore be chosen to effect a suitable com promise between uranium loss and decontamination from fission products.





• Synthetic third cycle feed, containing aluminium nitrate, nitric acid, uranyl nitrate, and fission products, was extracted with Tributyl Phosphate in AMSCO in preliminary tests.

- Effect of Feed Aluminum Nitrate Concentration.
- Effect of Feed Acidity.
- Effect of Uranium Concentration.
- Effect of Aluminum Nitrate/Nitric Acid Ratio.





In a multiple extraction procedure, a quantity of solvent is used to extract one layer (often the aqueous layer) multiple times in succession. The extraction is repeated two to three times, or perhaps more times if the compound has a low partition coefficient in the organic solvent.





- The Counter Current Batch Extraction involves the use of two immiscible phases, typically a liquid and a solid, or two immiscible liquids, to selectively extract one or more components from the mixture. Depending on the component's solubility in each step, the two phases will distribute themselves differently between two phases, Raffinate and Extract which is the basis for the process.
- In the case of uranium extraction, the counter-current extraction process involves the use of two immiscible liquids: an organic solvent and an aqueous solution.
- The process consists of several stages, including extraction, scrubbing, stripping, and precipitation.

• Extraction stage: In this stage, the uranium-containing ore or concentrate is mixed with the organic solvent, typically a mixture of tributyl phosphate and kerosene. The solvent selectively dissolves the uranium while leaving behind other impurities. The organic layer is then separated from the aqueous layer and sent to the scrubbing stage.



- **Scrubbing stage:** In this stage, the uranium-rich organic layer is mixed with an aqueous solution, typically a mixture of sodium carbonate and sodium hydroxide. The scrubbing solution removes impurities, such as iron and aluminum, from the organic layer. The scrubbed organic layer is then sent to the stripping stage.
- Stripping stage: In this stage, the uranium is stripped from the organic layer using an aqueous solution of nitric acid.
- **Precipitation:** The uranium is then precipitated as ammonium diuranate or uranyl peroxide. The organic solvent is recovered and recycled back to the extraction stage.
- Compared to other extraction techniques, the counter-current batch extraction procedure has several benefits. A high-purity uranium product can be produced using it with little waste and harm to the environment. Due to its high efficiency, the maximum quantity of uranium can be recovered from the ore or concentrate.

#### SOLVENT RECOVERY



- Solvent recovery involves the removal of contaminants from used solvents to restore them to their original quality and purity.
- The process typically involves distillation or evaporation of the used solvent, which separates the solvent from the contaminants. The purified solvent can then be reused in the chemical process.
- In this process, the organic solvent, typically a mixture of tributyl phosphate and kerosene, is used to selectively dissolve the uranium and separate it from other impurities.



- In the evaporation and distillation processes, the uranium-rich organic solvent is heated, and the solvent is evaporated and condensed in a separate container. It removes impurities and contaminants from the solvent, making it suitable for reuse in the extraction stage.
- The recovered solvent is typically recycled back to the extraction stage, where it is used to extract additional uranium from the ore or concentrate.
- The solvent recovery process is crucial to the overall efficiency of the Thorex process, as it allows for the maximum amount of uranium to be extracted from the ore or concentrate while minimizing the amount of waste generated.

#### **CURRENT INFORMATION**



- The Thorex uranium extraction process is not commonly used nowadays as it has been largely replaced by other methods that are more efficient, safer and environmentally friendly.
- One of the main drawbacks of the Thorex process is that it produces large amounts of radioactive waste that requires careful handling and disposal.
- Modern uranium extraction methods include in-situ leaching, heap leaching, and conventional mining with milling. These methods involve a range of technologies, including chemical extraction, ion exchange, and solvent extraction, among others.
- Countries that are major producers of uranium, such as Canada, Australia, Kazakhstan, and Russia, use various uranium extraction methods depending on the specific geological and environmental conditions of their mines.
- However, the Thorex process played an important role in the development of the uranium mining industry, particularly in Canada, and helped to establish the country as a major producer of uranium



#### **CONCLUDING REMARKS**

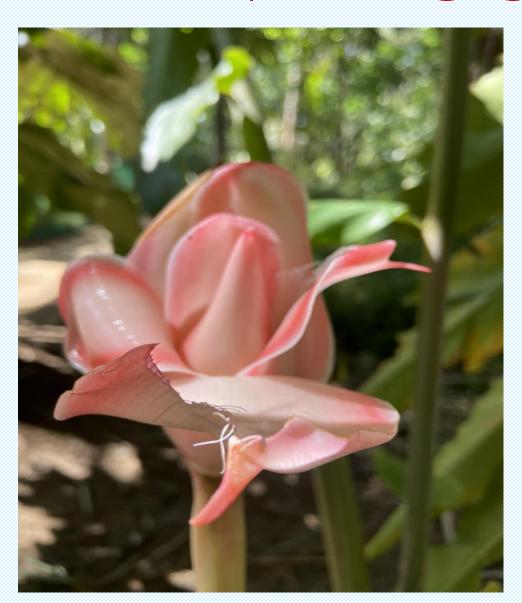
We have seen what is a Thorex Process, challenges in using it, Various types of Extraction Processes (Single Batch Extraction, Multiple Batch Extraction, Counter-Current Extraction) and Solvent Recovery.



#### REFERENCES FOR FURTHER READING ST

- "Uranium Extraction Technology" by B. Gupta and A. K. Suri.
- "Solvent Extraction Principles and Practice" by Jan.
- "Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle" by T. W. Todd and J. F. Leach.
- "The Future of Nuclear Power" by John Gittus.
- "Uranium Processing and Properties" by John E. Mattox.
- Research Papers Link
- Acid Thorex Process <u>Link</u>

# THANK YOU



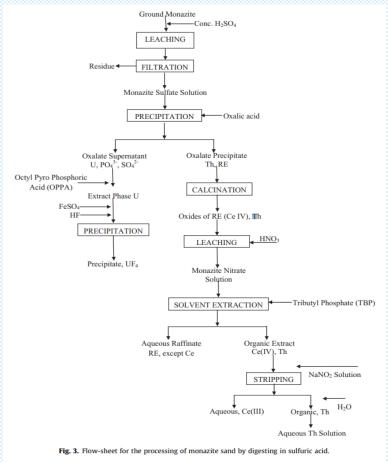
#### **QUERIES ASKED DURING PRESENTATION**



Q - Can the same process of solvent extraction be used in Monazite processing?

Ans – There is a solvent extraction step involved in the Monazite processing wherein the same process is used with the same solvents, Nitric acid in aqueous phase and Tri butyl phosphate in organic phase.

\*The reference is attached besides.



Archana Kumari, Rekha Panda, Manis Kumar Jha, J. Rajesh Kumar, Jin Young Lee, Process development to recover rare earth metals from monazite mineral: A review, Minerals Engineering, Volume 79, 2015, Pages 102-115, ISSN 0892-6875,

https://doi.org/10.1016/j.mineng.2015.05.003

### **QUERIES ASKED DURING PRESENTATION**



#### **Q** – What is Partition coefficient?

**Ans** – A partition coefficient is the ratio of the concentration of a substance in one medium or phase  $(C_1)$  to the concentration in a second phase  $(C_2)$  when the two concentrations are at equilibrium; that is, partition coefficient =  $(C_1/C_2)_{\text{equillibrium}}$