PRODUCTION OF URANOUS NITRATE WITH HYDRAZINE NITRATE AS REDUCING AGENT IN PRESENCE OF ADAMS CATALYST FOR URANIUM RECONVERSION PURPOSES

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Abstract:

The reconversion of $^{233}\text{U}$ to its oxide was done through ADU route in Uranium Thorium Separation Facility (UTSF). As this process has some drawbacks an alternative route for uranium reconversion was envisaged. In this method uranium is first reduced to its tetra-valency and the tetra-valent uranium is precipitated as oxalate. Of the existing methods available for uranyl reduction, the reduction with uranium with hydrazine nitrate in presence of Adams catalyst was chosen and accordingly new equipment has been designed, fabricated and extensively tested for its performance. It was found that near 100 % conversion could be achieved even at the concentration normally encountered in PRTRF. As this method is simple and is amenable to remote operation, this method of reduction can be adopted in Power Reactor Thoria Reprocessing Facility.

Key Words: U IV conversion, Adams Catalyst, Thoria reprocessing, PRTRF, Uranium reconversion.

Introduction: India envisages a three stage nuclear power programme with $^{232}\text{Th} - ^{233}\text{U}$ as the driver fuel in its third stage. India opted for the $^{232}\text{Th} - ^{233}\text{U}$ driven nuclear power reactors because of the abundant availability of thorium resources. The thoria rods are irradiated to get $^{233}\text{U}$ and separation of the latter from thorium is quite a challenging task and involves various operations like dissolution of thoria rods, selective solvent extraction of uranium followed by its stripping, Ion exchange purification and ultimately the reconversion to its oxide. While processing the irradiated thoria rods of the research reactors, the reconversion of $^{233}\text{U}$ to its oxide was done through ADU route in Uranium Thorium Separation Facility (UTSF). But this process has some drawbacks like the supernatant after precipitation of uranium contains significant amount of uranium which cannot be sent for waste disposal. Also, ammonium nitrate generated is a potential hazard. Because of these reasons an alternative route for uranium reconversion was envisaged. In this method uranium is first reduced to its tetra-valency and the tetra-valent uranium is precipitated as oxalate. There are three routes for reduction of hexavalent uranium to its tetravalency viz. 1) Electrolytic reduction 2) Reduction with hydrogen gas using Adams catalyst [1] 3) Reduction with hydrazine nitrate using Adams catalyst [2].
While in Electrolytic reduction, the conversion rate from U(VI) to U(IV) is less (~ 60%), in the method where hydrogen gas is used as reductant elaborate safety measures are required which becomes quite cumbersome especially in a closed enclosure like glove boxes. The reduction with uranium with hydrazine nitrate in presence of Adams catalyst was earlier studied extensively and various parameters were optimised [2]. This method is simple and is amenable to remote operation. Hence, this method of reduction was opted for this purpose.

In the earlier method [2] the catalyst was taken in a column and a batch of the uranyl feed solution was taken in it. After reduction was over the solution was taken out through a filter. In this method the whole bulk of the solution was always along with adams catalyst and argon/ nitrogen gas was passed through the solution in order to keep the catalyst well suspended in the solution. So an alternative design was made to overcome these difficulties. The catalyst was trapped in SS cartridges and the uranyl solution was circulated through the cartridges. In this method the major portion of the solution is always free of the catalyst. A special uranous converter with this basic design feature was designed and fabricated and was tested in the reduction studies of uranyl ion of concentrations that would be encountered in Thorex process. Above 99 % conversion was observed in about three hours and thus revealing the utility of this method of uranyl ion reduction for Thorex process requirements. The process is simple but and as the converter is compact it can be handled in glove boxes remotely.

**Experimental :**

**Reagents & Chemicals**

**Uranyl nitrate Solution:** Stock uranyl nitrate solution of about 300 g/l was prepared by dissolving UO₂ supplied by UED, BARC, in HNO₃. This uranyl solution was taken to prepare uranium feed solution.

**Hydrazine nitrate solution:** Commercially available hydrazine nitrate ( 5 M ) was used in the preparation of feed solution.

**Nitric Acid :** Concentrated nitric acid was used to adjust the feed acidity.

**Feed:** Uranyl nitrate = 4 g/l, Acidity = 1.0 M, Hydrazine nitrate = 1.0 M

**Design Features of the Converter :**

The reductor system consists essentially of three SS cartridge filters each holding a PtO₂ amount of about 60 grams thus having a total PtO₂ inventory of approximately 180 grams. The sketch of the converter is shown in Fig 2.
Catalyst: The catalyst used was platinum oxide (PtO$_2$) also known as Adams Catalyst.

- Particle size of the catalyst: 30 microns
- Amount of catalyst per cartridge: 60 grams
- Total amount of the catalyst taken in the Reductor: 180 grams

Filter Cartridges:
- Material of fabrication: Sintered SS cartridge
- No. of Cartridges: 3
- ID: 76 mm
- Height: 250 mm
- Porosity: 10 µ

Filter Housing:
- Material of Construction: SS-316
- No. of Cartridges: 3
- ID: 230 mm
- Height: 510 mm
- Volume: 20 litres

Description of the Converter

The converter contains an SS filter housing of about 20 litres capacity with three SS filter cartridges each having dimensions of 250 mm Ht and 76 mm ID. U IV Convertor is having two compartments one over the other, communicating with each other through these three stainless steel sintered filter cartridges, which can filter up to sub micron particles. Each stainless steel sintered filter cartridge contains ~ 60 g of Adam’s catalyst (platinum powder). During the conversion process, uranyl nitrate solution from the bottom compartment enters into the cartridge fluidise the platinum powder, comes out of the cartridge in the upper compartment and thus the solution is re-circulated to get above 99 % uranous nitrate within 3 Hrs. This equipment is having cooling jacket, thermo well and necessary reagent lines. It is provided with various service lines for water cooling, temperature measurement, sampling etc.

Sequence of Operations:

1. Water circulation to cooling jacket is to be started
2. Fifteen litres of feed U VI solution to be taken in to the converter
3. Temperature monitoring system to be switched on
4. After feed charging in to the converter circulation pump to be started. The circulation of the solution is from top of the converter to the bottom so that the liquid enters in to the cartridge
(below the base plate) from bottom and oozes out from top portion of the cartridge (above the base plate)

5. Sampling at regular time intervals from the sampling line

6. After required conversion rate is achieved the circulation pump is to be stopped and reversed and solution to be transferred to the product tank by applying vacuum.

7. Next batch of feed solution to be taken and the above steps are to be repeated or else 0.5 M HNO₃ to be taken into the converter to keep the adams catalyst in wet condition.

8. Water circulation and temperature monitor to be stopped

**Results & Discussion:**

A batch of 15 litres of feed with composition U = 3.56 g/l, H⁺ = 0.75 M and N₂H₅⁺ = 1.2 M was taken into the converter and the sequence of operations as mentioned above were followed. The circulation rate was maintained at 90 ltrs/hr. Water circulation was done throughout the operation. 500 ml of hydrazine nitrate was added after the first and second hours. Sampling was done every hour and as can be seen from Fig 1 near 100% conversion was observed in about three hours.

![Fig 1: % Uranous vs Time](image)

Reduction of four batches of uranyl nitrate was carried out in this converter and the data is presented in Table 1. As can be seen from Table 1 about 98% to 99% conversion was observed in all these batches in about three hours.
Table 1

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Feed U(Total) (g/l)</th>
<th>Acidity (M)</th>
<th>Hydrazine (M)</th>
<th>Time (Hours)</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.48</td>
<td>0.75</td>
<td>0.95</td>
<td>3</td>
<td>99.69</td>
</tr>
<tr>
<td>2</td>
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<td>0.75</td>
<td>1.2</td>
<td>3</td>
<td>99.4</td>
</tr>
<tr>
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<td>0.65</td>
<td>1.25</td>
<td>3</td>
<td>99.2</td>
</tr>
<tr>
<td>4</td>
<td>3.39</td>
<td>0.65</td>
<td>1.25</td>
<td>3</td>
<td>98.13</td>
</tr>
</tbody>
</table>

Conclusion:

This method of production of uranous nitrate is simple, does not require pressurised hydrogen or high current requirement and highly suitable for even remote operation. Hence this process can be deployed for uranium reconversion purposes where uranium is handled in highly shielded alpha tight glove boxes.

References:
