# REFINING PRACTICES IN INDIA TO PRODUCE CONSISTENT QUALITY URANIUM OXIDE POWDER FOR PHWR FUEL PELLETS

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## ABSTRACT

Uranium Oxide Powder for fuel fabrication for Indian Pressurized heavy water rector (PHWR) is produced through Ammonium Diuranate Route.

The yellow cake is dissolved in commercial grade nitric acid and resulting uranyl nitrate slurry is purified by solvent extraction. The equipment for extraction process is specially designed which eliminates energy and labour intensive steps. The pure uranyl nitrate solution is precipitated by batch precipitation process using aqueous ammonia as reactant. This is filtered, dried and calcined. The calcined oxide is reduced and stabilized to obtain reactor grade sinterable uranium oxide powder.

## 1.0 INTRODUCTION:

Nuclear Fuel Complex (NFC), Hyderabad is the sole manufacturer of natural and enriched uranium oxide for the water cooled nuclear power reactors in India. The pressurized heavy water reactors (PHWRs) are fueled with high density (≥ 96% T.D) natural uranium oxide pellets which are produced by the conventional "powder pellet" route involving cold pelletisation of $UO_2$ powder followed by high temperature (≥ 1700°C) sintering in hydrogen atmosphere. The sinterable grade $UO_2$ powder is produced by the ammonium diuranate (ADU) route, utilising solvent extraction as the purification step. The reproducibility of uranium oxide powder in terms of purity and sinterability has been excellent with the acceptability of powder being greater than 95%. This has been possible by close control of all process parameters at all the stages of production.

## 2.0 PROCESS DESCRIPTION:

The flow sheet for production of sinterable grade natural uranium oxide powder is shown in Figure-1. The important steps are:

- Dissolution
- Slurry extraction
- Precipitation
- Filtration and drying
- Calcination
- Reduction and Stabilization

## 2.1 Dissolution:

The as-received magnesium diuranate concentrate(MDU) is dissolved along with recycled /rejected oxide powder in commercial grade nitric acid. The basic aim of this step is to convert uranium into uranyl nitrate form so that the impurities are removed in the solvent extraction step. A typical analysis of as-received MDU is shown in Table-1. The process parameters namely temperature and digestion time are suitably adjusted to get crude uranyl nitrate slurry of 250 gm/lit uranium, 2N free acidity.

The chemical reactions in dissolution[5] are as follows:

$$MgU_2O_7 + 6HNO_3 \rightarrow 2\,UO_2(NO_3)_2 + Mg(NO_3)_2 + 3H_2O \qquad - (1)$$

$$U_3O_8 + 8\,HNO_3 \rightarrow 3\,UO_2(NO_3)_2 + 2\,NO_2 + 4H_2O \qquad . (2)$$

$$3U_3O_8 + 20\,HNO_3 \rightarrow 9\,UO_2(NO_3)_2 + 2\,NO + 10H_2O \qquad - (3)$$

$$UO_2 + 4\,HNO_3 \rightarrow UO_2(NO_3)_2 + 2\,NO_2 + 2H_2O \qquad - (4)$$

$$3UO_2 + 8\,HNO_3 \rightarrow 3\,UO_2(NO_3)_2 + 2\,NO + 4H_2O \qquad - (5)$$

As indicated by the reactions, $NO_x$ fumes are generated during dissolution. They are scrubbed with caustic soda and urea solution before safe venting to atmosphere.

## 2.2 Slurry Extraction:

This is the most important step as it leads to a product with high chemical purity confirming to nuclear requirement. The two sub-steps are as follows:

2.2.1 <u>Extraction:</u> The crude uranyl nitrate slurry is extracted with tributyl phosphate (TBP) solvent in a counter current extractor. The solvent is diluted with kerosene to improve its physical characteristics for ease of phase separation. The uranium is transferred to the organic phase leaving the impurities in the aqueous phase. Since the distribution coefficient is very high for uranium in comparison to impurities, this process ensures a very high separation. In addition, the distribution coefficient of impurities decreases as the concentration of uranium increases in the organic phase. This leads to a very high separation at high loading of the solvent. Hence, in the extraction process, the parameters are suitably adjusted to get saturation of more than 85% in the extract. The extraction of uranium by TBP is expressed by means of following reversible reaction[5]..

$$UO_{2aq}^{+2} + 2NO_3^{-}{}_{aq} + 2TBP_{org} \rightleftharpoons [UO_2(NO_3)_2\, 2TBP]_{org}$$

The slurry extraction process is carried out in an indigenously developed slurry extractor, which accepts the feed in the form of slurry thereby eliminating a number of steps prior to extraction as shown in the Figure-2, which are labour and energy intensive[1]. The slurry extraction battery consists of seven stages, each stage having a mixer, a dis-engager and a settler. The design is different from conventional counter current stage contactor in the sense that aqueous phase is not allowed to form a separate layer at the bottom of settling tank except in the last stage. The organic to aqueous ratio decreases with the depth in the settler but the ratio never becomes zero. This arrangement helps in keeping solids in suspension, thus avoiding settling of solids. This equipment is in continuous use for more than a decade without any operational problems. In this design, loading of the solvent is always more than 85% which in turn ensures consistency and high purity of the product. Loss of solvent is less than that in pulsed perforated plate column and there are no recycles due to chemical impurity. It is so well balanced that scrubbing section which is normally used in solvent extraction system for obtaining final purity is altogether eliminated and the extract is pure enough to go to stripping section directly. Slurry extration being a stage-wise contactor does not produce dilute solution during start up period and the extract concentration is consistently high.

2.2.2 Stripping: The loaded extract is stripped with de-mineralised water to recover uranium from the organic solution. The lean solvent is recycled after processing. The organic to aqueous ratio in stripping is adjusted to get uranyl nitrate pure solution of 100 ± 10 gm/liter of uranium which is suitable for direct precipitation. Because of the use of slurry extraction unit, strip solution concentration is always about 100 gms. This is suitable for precipitation without any need of evaporation to increase the concentration unlike the uranyl nitrate solution normally obtained in pulsed perforated columns. A typical analysis of purity level is shown in the Table-2. The stripping operation is carried out in a box type mixer settler.

### 2.3 Precipitation :

The physical properties of uranium oxide powder are greatly influenced by precipitation conditions[2]. The precipitate quality determines the design of the process equipment down the line. The physical condition of ADU precipitated from uranyl nitrate solution depends on concentration of uranyl nitrate solution, rate of addition of aqueous ammonia, pH of precipitation, temperature and rate of mixing. The chemical reaction in the precipitation process is:

$$UO_2(NO_3)_2 + (x+2)\, NH_4OH \rightarrow UO_3\,(NH_3)_x\,(H_2O)_{2-x} + 2NH_4NO_3 + (2-x)H_2O$$

At NFC, ammonium di-uranate having ammonia/uranium ratio of 0.35 - 0.42 is precipitated from uranyl nitrate solution with aqueous ammonia. It may be noted that the di-uranate $(NH_4)_2U_2O_7$ probably never exists in aqueous solution[2]. The parameters of precipitation are selected to get a precipitate of desired particle size distribution.

The precipitation process has been changed from continuous precipitation to semi-continuous precipitation which is an equilibrium precipitation. This has been adopted in the plant to obtain greater reproducibility and consistency in the process and to obtain ADU with good filterability.

## 2.4 Filtration & Drying:

The precipitate produced by equilibrium precipitation process is fast settling in nature. Hence, rotary vacuum pan filter is used to filter the slurry. The wet cake contains 20 - 25% moisture which is dried in a turbo dryer at a temperature of 250°C to yield a product in which moisture is less than 1% by weight. The dried product is collected in a closed container to minimize air borne radio activity.

## 2.5 Calcination:

ADU is calcined to $U_3O_8$ in rotary calcination furnaces. It is well known that calcination plays a significant role in sinterability of ceramic powder. The temperature of calcination is the most important parameter which decides the specific surface area of the powder[3]. At NFC, an optimum specific surface area of calcined $U_3O_8$ powder in the range of 3.5 - 4 $m^2/g$ is maintained.

## 2.6 Reduction & Stabilization:

$U_3O_8$ powder of specific surface area in the range of 3.5 - 4 $m^2/g$ is reduced in cracked ammonia atmosphere to yield uranium oxide powder. The reduction temperature is optimised on the basis of complete conversion of $U_3O_8$ to $UO_2$ without local sintering to desired surface area. The freshly reduced powder is highly active and gets readily oxidised if handled in air. Hence, it is stabilized in the presence of nitrogen and air to reduce its activity towards oxidation[4]. The oxygen to uranium ratio is maintained below 2.1, which results in an uranium oxide powder suitable for obtaining high density $UO_2$ pellets for PHWRs.

Rotary furnaces are used for calcination, reduction and stabilization operation. These furnaces are designed for efficient solid-gas contact as well as effective heat transfer to ensure uniformity of temperature and thus consistency in quality. The internals of the furnaces have been changed to ensure higher hold up volume as shown in Fig.3 which has resulted in higher productivity.

The process has evolved from laboratory scale trials to the present scale of 600 ton per year of production by complete in-house design, development and continuous improvements in process and equipment design. Some of the improvements/ modifications are as follows:

- Process of direct dissolution of rejected sintered pellets which has eliminated laborious milling, blending and material handling operations.

- Slurry extraction in place of pulsed columns for purification step
- Use of turbo dryer in place of static bed dryer
- Use of rotary furnace for thermal treatment steps instead of tunnel furnace.
- Change of internals of rotary furnaces which has resulted higher productivity.

## 3.0 CONCLUSION:

NFC has developed the know how and equipment to obtain sinterable grade ceramic uranium oxide powder of consistent quality in terms of sinterability. The effective process control and parameter selection has resulted in the production of uranium oxide powder which sinters to high density pellets without micro and macro structure defects.

## 4.0 ACKNOWLEDGEMENT:

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## TABLE-1, ANALYSIS OF REPRESENTATIVE BATCH OF MAGNESIUM DIURANATE CONCENTRATE

(percentage on dry basis when dried to 110±2$^0$C)

| | |
|---|---|
| $U_3O_8$ | 75.49 |
| Halides (as Chlorides) | 0.39 |
| $SO_4$ | 1.13 |
| Fe (Total) | 0.40 |
| $SiO_2$ | 4.69 |
| Acid Insoluble | 2.28 |
| Ca+Mg (as Mg O) | 5.54 |
| $P_2O_5$ | 0.098 |

## TABLE 2 - PURITY LEVELS OF URANYL NITRATE SOLUTION

| Element | In ppm |
|---|---|
| Al | <25 |
| Ca | 20-25 |
| Cd | <0.2 |
| Cu | <10 |
| Cr | <15 |
| Fe | 50-75 |
| Mg | 150-200 |
| Mn | <10 |
| Mo | <5 |
| Ni | <20 |
| Si | <50 |
| B | 0.40-0.50 |
| Dy | 0.15-0.25 |
| Er | 0.10-0.20 |
| Eu | 0.10-0.20 |
| Gd | 0.10-0.30 |

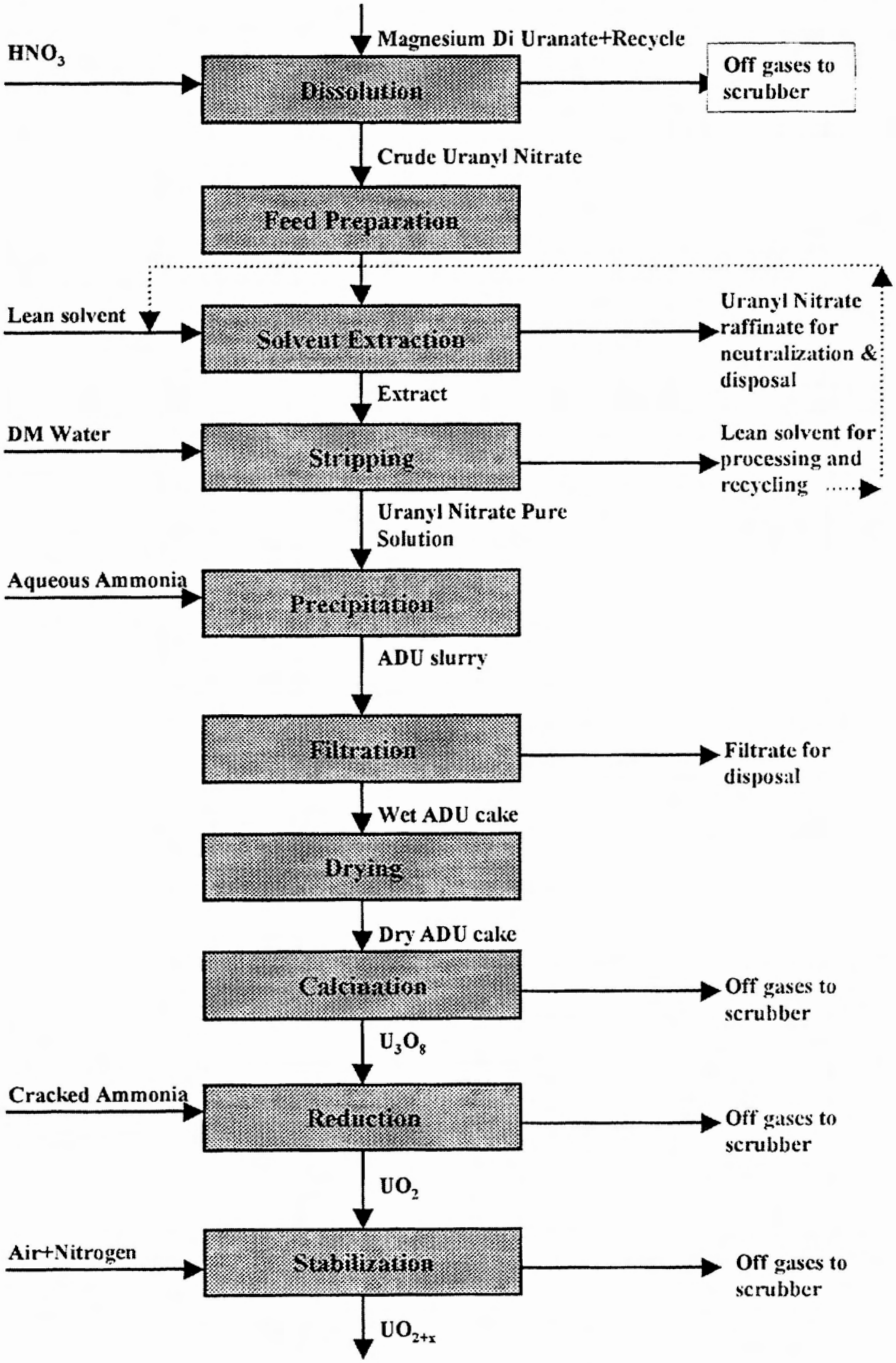


FIGURE-1 URANIUM OXIDE PLANT FLOW SHEET

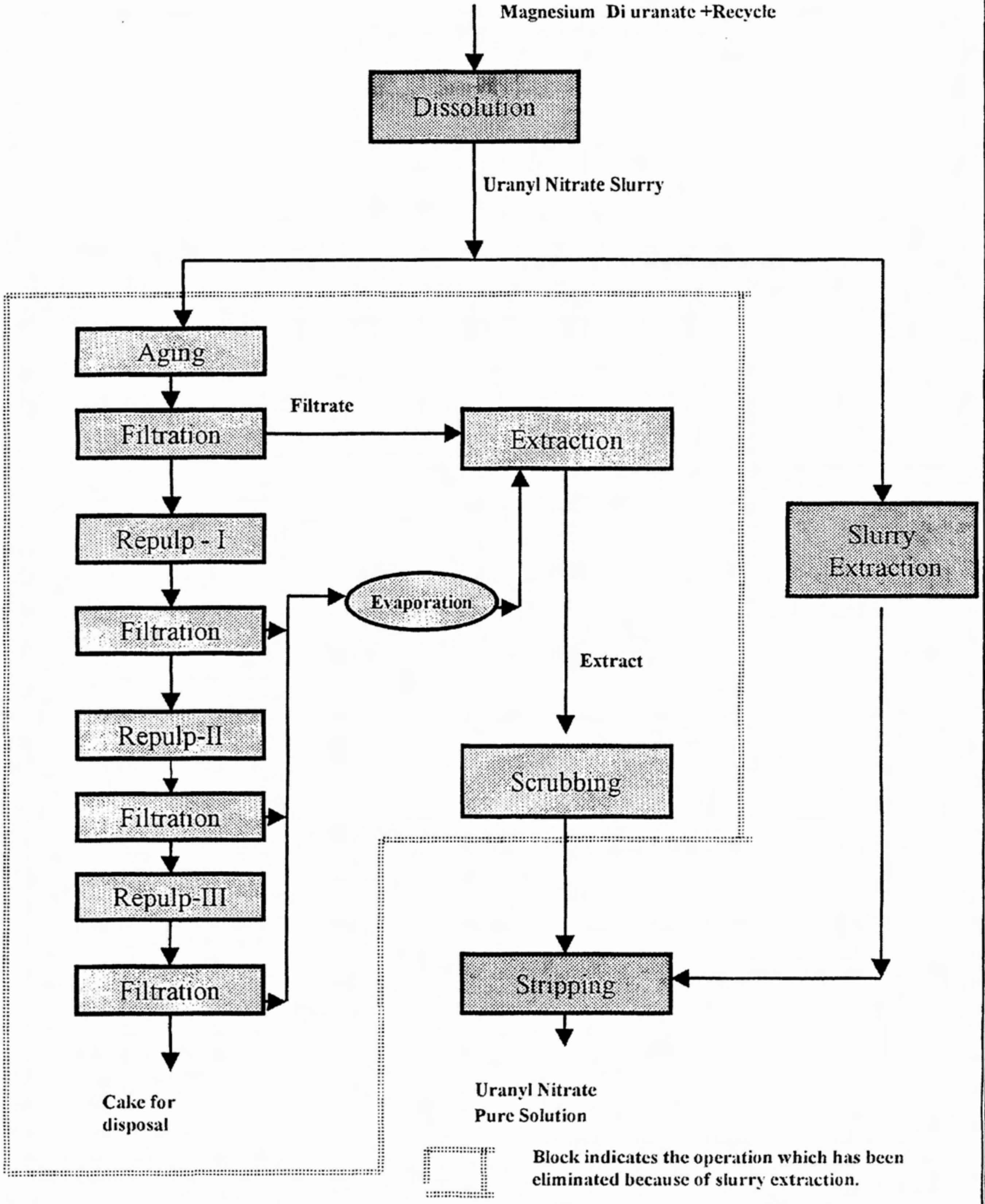
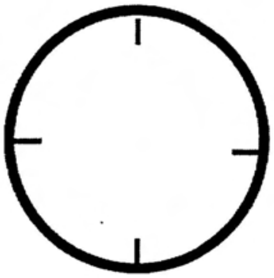
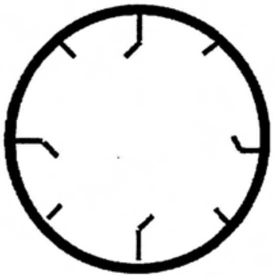


FIGURE-2 COMPARISONOF URANIUM EXTRACTION CYCLE



BEFORE MODIFICATION



AFTER MODIFICATION

FIGURE-3 CROSS SECTIONAL VIEW OF
ROTARY FURNACE CAGE