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# AN INTEGRAL APPROACH FOR HANDLING AND MINIMIZING EFFLUENT GENERATION DURING PRODUCTION OF SINTERABLE GRADE $UO_2$ POWDER FOR PHWR FUELS

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**ABSTRACT –** Nuclear reactor grade natural uranium dioxide powder is being produced through Ex-AU route, which is further processed to manufacture $UO_2$ pellets by sintering process for making PHWR fuel assemblies. During $UO_2$ powder production, Ammonium Nitrate (AN) is a liquid effluent which is produced with different concentration at two process steps namely: a) Vapour ammonia neutralization of Uranyl Nitrate Raffinate (UNR), generated from slurry extractor b) Vapour ammonia precipitation of Uranyl Nitrate Pure Solution (UNPS). This effluent, after final treatment for removal of uranium, is checked for AN concentration and uranium activity before safe disposal. The AN concentration is on lower side in the effluent, generated after vapour ammonia precipitation of UNPS which makes it difficult for safe dispose.An integrated approach was developed to resolve the safe disposal problem because of different grade of AN effluent. In the proposed method, the low grade AN effluent is processed along with UNR, generated after slurry extraction. This process was standardized by optimizing parameters like ratio of UNR to AN, pH, Ammonia flow rate, temperature etc. This development has resulted in reduction of chemical consumption, effluent quantity and paved the way for optimization of process flow sheet for safe disposal.

## Introduction

In the PHWR manufacturing line, $UO_2$ powder is produced through series of chemical and metallurgical processes wherein, Uranium Ore Concentrate (UOC) is dissolved in commercial grade nitric acid to produce Crude Uranyl Nitrate Solution (CUNS) which is subsequently subjected to purification through solvent extraction route to produce Uranyl Nitrate Pure Solution (UNPS). The UNPS is precipitated by vapour ammonia to produce Ammonium Uranate (AU) slurry which is filtered using Vacuum rotary pan filter unit. The resulting cake is processed through series of heat treatment operations to get sinterable grade $UO_2$ powder for manufacturing of high density pellets.

During above chemical and metallurgical operations all three types of effluents (solid, liquid and gas) are generated and suitably treated before final disposal. The $UO_2$ powder production plant at NFC, Hyderabad always endeavor to reduce continuously its effluent generation and in compliance of ISO 14001 towards environmental protection. Aninnovative process was developed for optimization of effluents generation which is on par with international standards of operation.

Similarly, an innovative process is developed for treatment of liquid and solid effluent for marching towards zero discharge concept. The successful implementation of this developmental work has resulted many benefits beside reduction of effluents. The details of developments are given in subsequent sections.

## 1. Existing process flow sheet for effluent generation and its management

The UOC, in the form of $U_3O_8$ or $UO_2$ is dissolved in commercial grade nitric acid (60% $HNO_3$) to get CUNS. During this operation NOx gases are generated as effluent and required to be absorbed in series of water columns to convertit to Nitric acid solution and the residual NOx is treated with caustic lye solution before letting the off gases out of stack.

NOxgas absorption in watercan be explained as [1]

$$NO + NO_2 + H_2O \leftrightarrow 2HNO_2$$
$$2NO_2 + H_2O \leftrightarrow HNO_3 + HNO_2$$
$$3HNO_2 \leftrightarrow HNO_3 + H_2O + 2NO$$

NOx treatment with caustic lye solution is explained as [2]

$$NO + NO_2 + 2NaOH \leftrightarrow 2NaNO_2 + H_2O$$
$$2NO_2 + 2NaOH \leftrightarrow HNO_3 + HNO_2 + H_2O$$

The CUNS is mixed with dilute solution and nitric acid to prepare feed for solvent extraction. Tri-n-butyl phosphate along with kerosene is used for extraction of uranium from feed to produce UNPS. The raffinate, comes out of solvent extraction, consist of all impurities is called Uranyl Nitrate Raffinate (UNR). The UNR contains uranium less than 1gm/lit and is recovered by neutralizing with vapor ammonia to precipitate uranium along with some other impurities. The resulting slurry is filtered in pre-coat vacuum rotary drum filter unit. In this way two types of effluentsare generated after filtration of UNR slurry: Uranyl Nitrate RaffinateCake (UNRC) containing impurities along with traces of uranium as solid waste; the filtrate which contains mainly Ammonium Nitrate (AN) as liquid effluent. The UNRC is stored as solid waste and AN solution is treated using chemical coagulation method to scavenge traces of uranium before disposal [3]. This AN solution has high concentration of AN around 200g/lit because of which this liquid effluent is easily disposed by sale. This is called high grade AN liquid effluent.

The UNPS -the intermediate product- is precipitated by vapour ammonia to produce Ammonium Uranate (AU) slurry. The slurry is filtered using rotary vacuum pan filter and AU cake is taken for

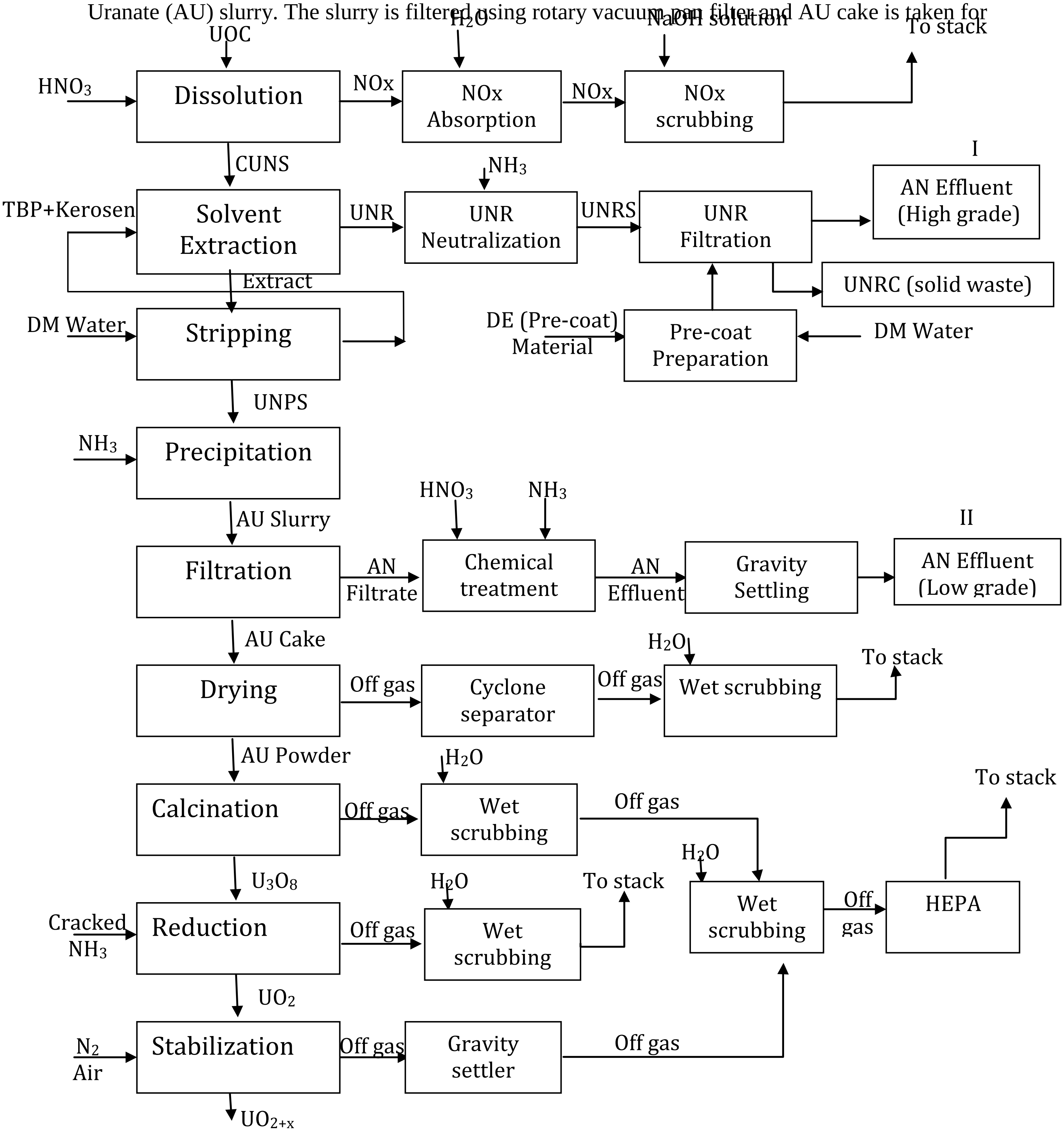



Figure 1 Process flow sheet of $UO_2$ powder production and effluent management

heat treatment operations. The resulting filtrate, liquid effluent, basically contains AN( 80 gm AN/lit) is low grade AN liquid effluent. It is neutralized by vapour ammonia after addition of nitric acid to increase AN concentration in solution to 120 gm/lit so that it can easily be disposed by sale.

The AN solution, subsequently [3] subjected to treatment by chemical coagulation method using ferric chloride and Tri sodium phosphate. Ammonia is added when pH of the effluent is less than 7. TheAN effluent is checked for AN concentration & uranium activity before safe disposal.

## 2. Experimentation

Diatomaceous Earth (DE) material is used for preparation of pre-coat for filtration of UNR slurry in vacuum drum filter. Generally pre-coat material is used for slurry which contains large quantity of fines which was the case for UNR neutralization by sodium hydroxide. In case of neutralization by vapour ammonia, settling characteristics has improved and resulted in relatively coarser particle in slurry. The settling characteristics of UNR slurry is given in **Figure *2*** .

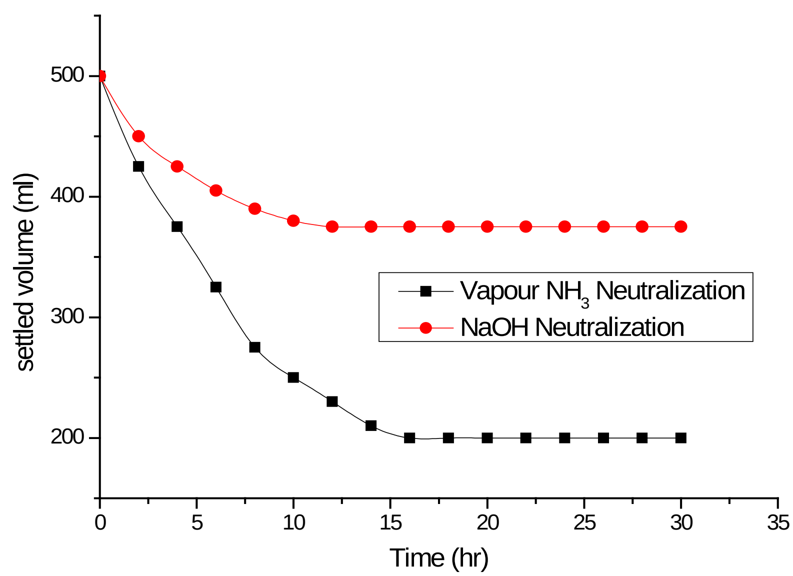



**Figure 2**Settling characteristics of UNR slurry produced byvapour ammonia and NaOH routes

It is clear from the above graphs that characteristics of slurry is improved after neutralization byvapour ammonia hence pre-coat is not required for filtration of UNR slurry. Since, UOC, the raw material is relatively pure material and UNRC mostly contains pre-coat material and increases the volume of solid waste. Thus filtration without pre-coat material was carried out and results are provided in **Table 1** .

**Table 1 volume of solid waste (UNRC) generation**

| Sr. № | Condition | Volume of UNR | Volume of UNRC |
|---|---|---|---|
| 1 | With pre-coat | 3000 lit | 400 lit |
| 2 | without pre-coat | 3000 lit | 50 lit |

Hence it is decided to mix UNR generated after solvent extraction with AN filtrate generated after UNPS precipitation to generate single grade of AN liquid effluent instead two grades for easy disposal. Experiments were carried out with varying volume ratio of UNR to low grade AN effluent, ammonia flow rate, pH and temperature of initial temperature of heating. Experiments are carried out in batch mode where a fixed ratio of UNR to low grade AN effluent is taken as batch in the tank of 6KL capacity. The tank is provided with 3 stage paddle type agitator. The solution is heated (if required) to a particular temperature and then vapour ammonia is added in continuous mode at fixed flow rate. During heating and ammonia addition agitator will be ON to avoid un-reacted ammonia coming out of tank and its spread to surroundings. Ammonia flow rate is measured by highly accurate mass flow meter. During the reaction acidity of solution, due to presence of UNR, is neutralized with ammonia and pH of solution is slowly raised up to 8 and then ammonia addition is stopped. The neutralized solution is immediately transferred to gravity settlers where they are allowed to settle for 18 to 24 hr. Subsequently the supernatant liquid is sent for effluent treatment and disposal. The settled slurry is sent for filtration to obtain UNRC (solid waste) and residual filtrate, too, sent for effluent treatment and disposal.

## 3. Result and Discussion

### 3.1 Effect of mix ratio on AN concentration in effluent

The reaction for neutralization of acidity is as follows [4]

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

The total generation of AN effluent for 1 ton production of $UO_2$ production is around 11 KL which is total of approximately 3000 lit(high grade AN) generated from UNR and 8000 lit (low grade AN) generated after UNPS precipitation and filtration. Different mix are experimented on plant scaleat constant ammonia flow rate, no initial heating and final pH at 8. The resultsare given in **Table 2** .

**Table 2 Effect of mix ratio on AN concentration**

| Sr.№ | Mix ratio | UNR (lit) | AN low grade (lit) | Estimated AN conc. (gm/lit) | Observed AN conc. (gm/lit) |
|---|---|---|---|---|---|
| 1 | 3/8 | 3000 | 8000 | 112.7 | 110 |
| 2 | 3/7 | 3000 | 7000 | 116 | 117 |

| Sr.№ | Mix ratio | UNR (lit) | AN low grade (lit) | Estimated AN conc. (gm/lit) | Observed AN conc. (gm/lit) |
|---|---|---|---|---|---|
| 3 | 3/6 | 3000 | 6000 | 120 | 122 |
| 4 | 3/5 | 3000 | 5000 | 125 | 123 |
| 5 | 3/4 | 3000 | 4000 | 131.4 | 134 |

Form the **Table 2**, it is observed that with increase in the mix ratio,the resulting AN concentration is decreasing in liquid effluent. Mixed ratio of 3/8 is acceptable for safe disposal.

### 3.2 Effect of pH

After optimizing the mixed ratio it is imperative to analyze the trace amount radioactive element i.e, uranium in AN effluent. The process parameters are optimized such that the trace of uranium is minimized to as less as possible. To study the effect of end pH (of the solution) on uranium concentration in effluent, trials were carried out on plant scale with ammonia flow rate of 30kg/hr and mix ratio of 3/8. No initial heating was given for all the trials. At various end pH from 4 to 9 of the batch trials, uranium concentration was analyzed in AN effluent and results are plotted in**Figure 3**.

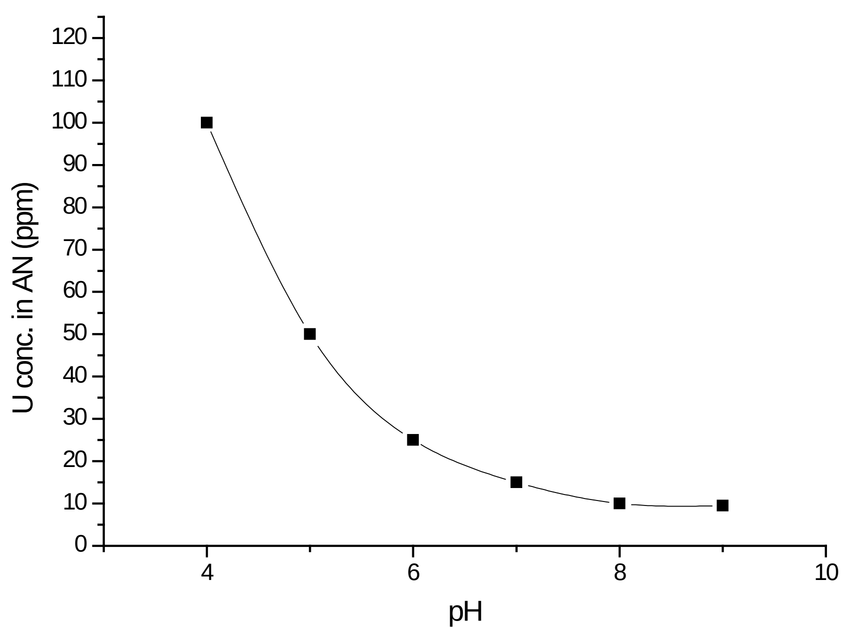



**Figure 3 Effect of end pH on Uranium concentration on final AN Effluent**

As end pH increases uranium concentration in AN effluent decreases. At 6 pH Uranium concentration in AN effluent is 100 ppm and it reduces to 10 ppm at 8 pH in AN solution. It is due the solubility of uranium which decreases with increase of pH.After 8 pH decrease in Uranium is not much significant but there is increase of ammonia consumption after 8 pH. Hence 8 end pH is taken for further trails.

### 3.3 Effect of Ammonia flow rate

Accordingly, flow rate of ammonia was varied to fixed mix ratio of 3/8 and no heating with end pH 8.The effect of ammonia flow rate is shown in **Figure 4**.

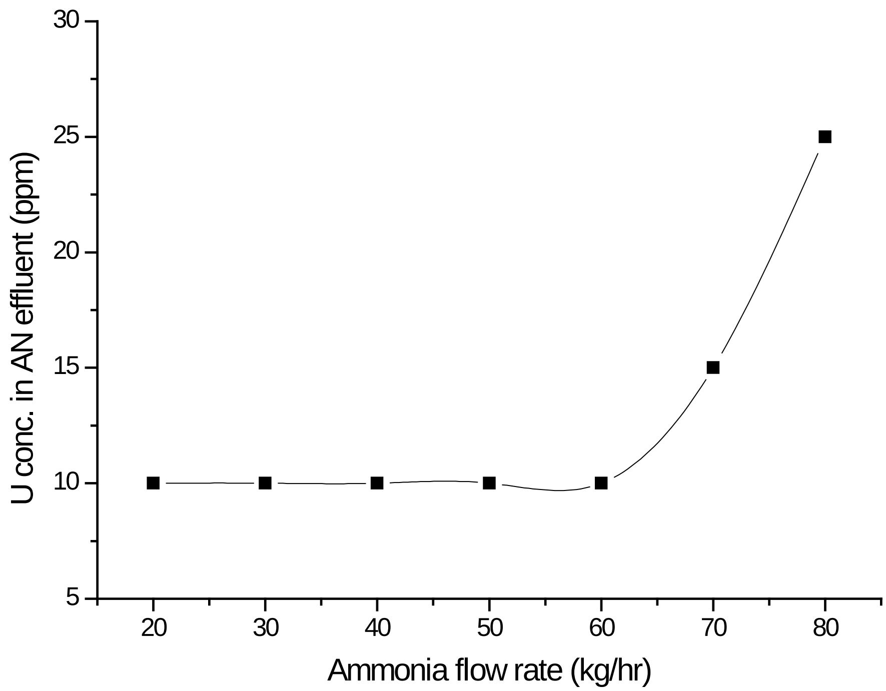



**Figure 4 Effect of ammonia flow rate on Uranium concentration of AN effluent.**

It is clear from the **Figure 4** that nochange was observed in concentration of uranium in AN effluent at initial increase of flow rate of ammonia. But after 60 kg/hrthere is appreciable increase in uranium concentration in AN effluent. Increased flow rate of ammonia leave high concentration of $NH_4^+$ ion into solution and results in large nucleation than particle growth [5]. Hence more fines are generated which are difficult to settle and results increased concentration of uranium in AN effluent. Thus 60 kg/hr of ammonia flow rate is chosen for further experimentation.

### 3.4 Effect of Temperature

To study the effect of temperature on uranium concentration trails were carried with mix ratio of 3/8, ammonia flow rate of 60 kg/hr and end pH 8. The mixed solution (UNR and AN from UNPS filtrate) is steam heated to raise its temperature to desired trial temperature. The neutralization reaction is an exothermic reaction wherein temperature continuously increases with time. The resulting uranium concentration in AN effluent with various initial temperatures is plotted in **Figure 5**.From the figure it is noticed that with increase of temperature, the uranium trace is coming down in AN effluent.

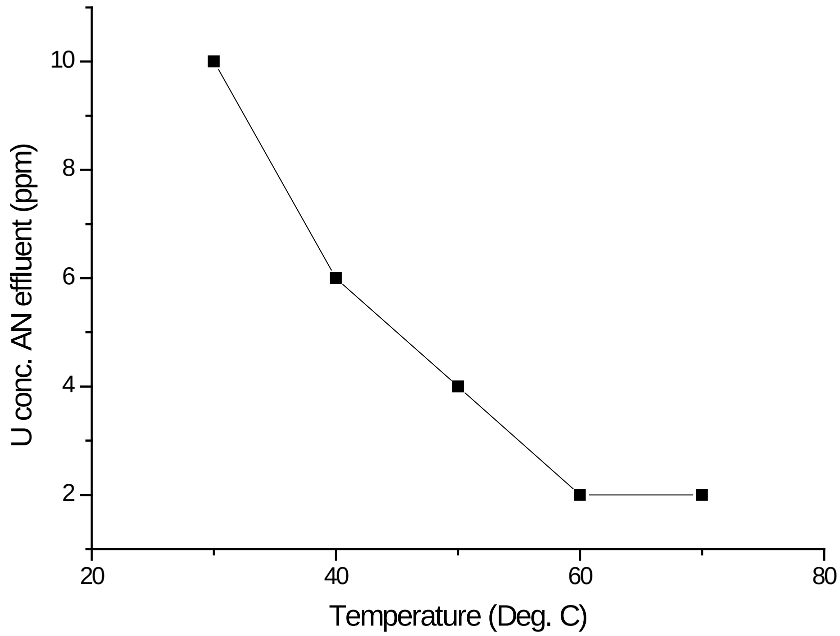



**Figure 5 Effect of temperature of solution on Uranium concentration in AN effluent**

## 4. The Modified Flow sheet for Effluent treatment and management

Base on above trials plant process flow sheet was modified for regular production. Pre-coat preparation operation for filtration of UNR slurry was totally eliminated. In the new modified process, UNR neutralization operation and chemical treatment of AU filtrate is combined into a single neutralization operation wherein, UNR is mixed with AU filtrate and neutralized by vapour ammonia. The resulting slurry is allowed to settle in gravity settler from 18 hr to 24 hr. The supernatant AN solution is transferred for treatment and further disposal. The settled slurry is pumped to Nutschfiltration unit for filtration. The retained cake on filter cloth is collected in polythene lined MS drums and resultant filtrate (AN effluent) is transferred for treatment and further disposal. The existing and modified process flow sheet is shown in **Figure 6**&**Figure 7**.

## 5. Advantage of the present development

The modified process flow sheet for management of effluent has fetched a number of direct and indirect benefits to the plant. The elimination of pre-coat preparation has resulted decrease in solid waste generation by 8 times. DE (pre-coat material), amorphous form of silica, also contains small

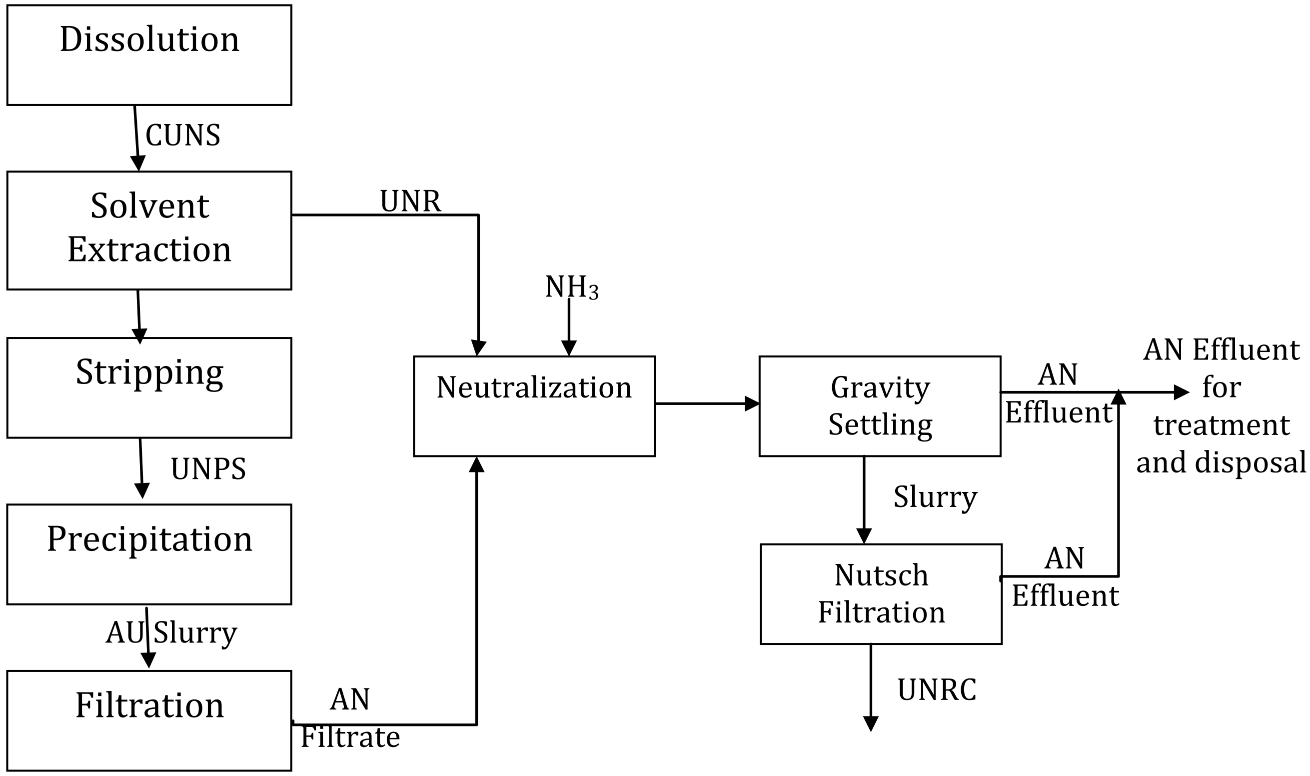
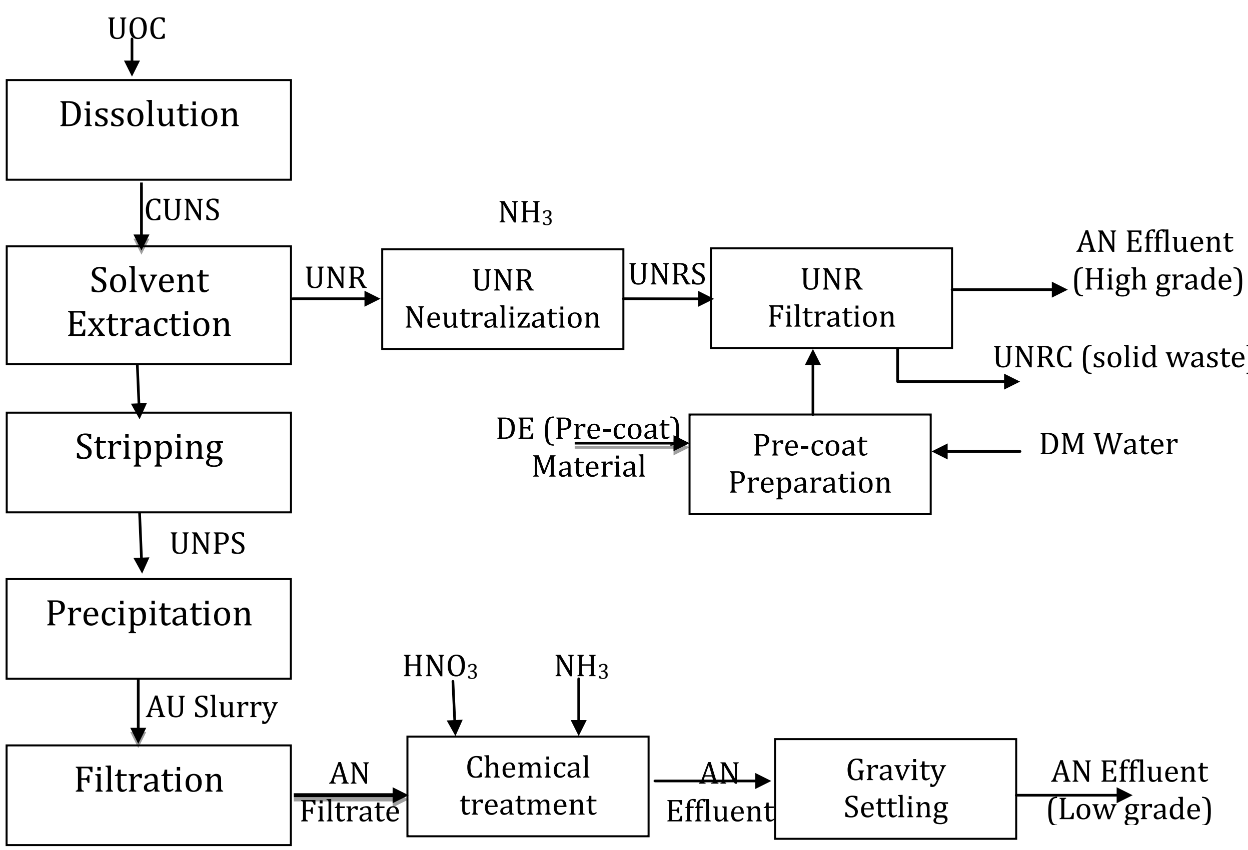



**Figure 6Modified flow sheet for single grade of AN effluent**



amount of microcrystalline material. The crystalline form is a suspicious carcinogen and inhalation need to be avoided during handling. The complete removal of DE has also slightly reduced the consumption of scantly available DM water.

The management of generating single grade AN effluent has reduced the manpower and chemical consumption and reduced the effluent generation. In the modified flow sheet addition of nitric acid and ammonia is completely eliminated because of which nitric acid consumption has reduced by 20% (0.5 MT / ton of $UO_2$ production). The equivalent amount of ammonia consumptionis also reduced by 13.5% (80 kg / ton of $UO_2$ production). Furthermore 4% reduction of AN effluent (liquid effluent) has been observed. Apart from above direct benefits, there are many indirect benefits like availability of space due to removal of few unused equipment like drum filter unit, precoat preparation tanks, pipelines , trimming of process flow sheet, reduction of process time etc.

## 6. Conclusion

Development of vapour ammonia neutralization has improved the settling characteristics of UNR slurry which necessitated the removal of DE addition during its filtration. The removal of DE has also reduced the solid effluent (UNRC) generation by 8 times. Mix ratio of 8/3 was found suitable for easy disposal of single grade of AN effluent. Increase of temperature, decrease of flow rate of ammonia addition and increase of pH result in lower trace of uranium in AN effluent. The modified process flow sheet has enabled plant to reduce chemical consumption (20% nitric acid, 13.5% ammonia), liquid effluent generation (AN 4%) and manpower saving (67%).

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