Recovery Of Uranium From Primary Radioactive Liquid Waste Generated In Uranium Purification Process

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Abstract

Uranyl nitrate raffinate (UNR) is generated in the purification step of UO_2 production process which is a liquid effluent. Since this effluent contains residual uranium, its direct disposal is not permissible and hence it is first fixed in sollid form as uranyl nitrate raffinate cake (UNRC) by suitable treatment method. Later this ‘U’ recovered at the Uranium mill. The filtrate from effluent treatment process contains sodium nitrate and other salts. This ‘U’ free filtrate is analysed for uranium and disposed off, for recovery of the valuable salts.

The present process is manpower intensive, requires large storage space, and involves material handling work, transportation etc. In order to overcome these problems, the need for avoiding the generation of UNRC was felt. A new process resulting in avoidance of UNRC generation was studied in detail and demonstrated successfully at plant scale.

The superiority of this process compared to the other options lies in the fact that no new reagents are required. The same solvents at the same concentrations are used, thus making the process more amenable for using on-line by dove-tailing into the existing set-up.

The details of the process developed are presented in this paper.

1.0 INTRODUCTION

The Uranium di-oxide (UO_2) powder production process involves dissolution of raw material magnesium di-uranate(MDU) in nitric acid to obtain crude uranyl nitrate solution (CUNS) followed by solvent extraction to produce nuclear grade uranyl nitrate solution (UNS).The UNS is precipitated with liquid NH_4OH to produce ammonium di-uranate(ADU) which is subsequently filtered, dried, calcined, reduced & stabilized to produce UO_2 powder (Refer Fig. 1).

The most important step in the above mentioned flow sheet is the purification process step, wherein all the impurities associated with the raw material are removed to obtain nuclear grade uranyl nitrate solution meeting stringent specifications with respect to purity. In Nuclear Fuel Complex(NFC), Hyderabad, India the purification process is carried out using solvent extraction technique employing tri-butyl phosphate(TBP) diluted with kerosene (33% TBP, 67% kerosene). The CUNS obtained in the dissolution step is adjusted to a concentration of about 250 g/l 'U' & 2.5 N FA and is then extracted with the solvent by admitting it counter currently in a 10 stage slurry extractor unit, at a organic / aqueous(O/A) ratio of 2 : 1 without resorting to filtration & washing etc. of CUNS. The loaded extract is subsequently stripped with de-mineralized water in a 12 stage Combined Air lift Mixer Settler unit (CALMIX) at a O/A ratio of 1 : 1.2.

2.0 EXISTING PROCESS

The solvent extraction process is so developed as to handle aqueous slurries directly and also to avoid scrubbing step. However, the uranyl nitrate raffinate(UNR) leaving the process contains about 0.5 to 1.0 g/l residual uranium which makes its direct disposal difficult due to the presently applicable disposal limits. (The disposal limit is 1 Bq/g of salt. This corresponds to about 10 mg'U'/l of raffinate). Presently, therefore, this effluent is subjected to a chemical treatment process to make it amenable for disposal by bringing down the uranium content in the effluent to below acceptable limits. The process involves neutralization of the UNR with caustic lye (NaOH) followed by filtration of the resultant slurry using a pre-coat rotary drum filter.

The entire uranium gets precipitated and gets fixed in the uranyl nitrate raffinate cake(UNRC) from which it is recovered by leaching and ion-exchange route. The filtrate containing sodium nitrate but free of uranium is disposed off for recovery of valuable salts. This process is manpower intensive, requires extra chemicals, large storage space and involves material handling work etc.

A new process has therefore been developed to recover the valuable uranium and also to avoid all the manpower intensive works.

3.0 NEW PROCESS

The new process developed involves two cycles of solvent extraction. The UNR generated in the1st cycle solvent extraction step is treated in 2nd cycle solvent extraction to recover the last traces of uranium from the 1st cycle UNR having initial uranium concentration of about 0.5 – 1.0 g/l. This 2nd cycle UNR containing less than 10 mg/l is amenable for direct disposal.

The process developed essentially consists of two major steps added to this existing process.

1. Solvent treatment / conditioning : Presently solvent conditioning is being carried out as a routine. However, in the modified process developed now, the solvent treatment is so improved as to bring down the uranium concentration in the solvent to as low a level as less than 0.1 g/l.

2. Extraction of uranium from UNR after acidification in a 2nd cycle of solvent extraction using treated / conditioned solvent generated in the above step.

3.1 Solvent Treatment:

Tri-Butyl Phosphoric acid(TBP) used as solvent in the solvent extraction process, reacts as a typical ester, hydrolysing in either an alkaline or acid medium. The hydrolysis proceeds in steps, splitting off one alkoxy group in each step, successively forming di-butyl phosphate (DBP), mono-butyl phosphate (MBP) and phosphoric acid.

The hydrolysis reaction proceeds as follows :

$$\underset{\text{TBP}}{(C_4H_9O)_3\,PO} + H_2O \longrightarrow \underset{\text{DBP}}{(C_4H_9O)_2\,(OH)\,.\,PO} + \underset{\text{Butyl alcohol}}{C_4H_9OH}$$

$$\underset{\text{DBP}}{(C_4H_9O)_2\,.(OH)\,.\,PO} + H_2O \longrightarrow \underset{\text{MBP}}{(C_4H_9O)\,(OH)_2\,.\,PO} + \underset{\text{Butyl alcohol}}{C_4H_9OH}$$

$$\underset{\text{MBP}}{(C_4H_9O)\,(OH)_2\,PO} + H_2O \longrightarrow \underset{\text{Phosphoric Acid}}{H_3PO_4} + \underset{\text{Butyl alcohol}}{C_4H_9OH}$$

One of the important properties of TBP and its degraded products is the solubility of these materials in aqueous medium. The solubility of TBP in aqueous phase is low and is decreased even further in the presence of uranium. However, DBP has an appreciable solubility in aqueous solution and during extraction step, part of this DBP remains in each phase i.e. in organic & aqueous phase. MBP is much more soluble in the aqueous phase and is removed almost completely in the raffinate of extraction process. If the hydrolysis product DBP is allowed to accumulate in the solvent, stripping of uranium from the solvent in the stripping process (Re- extraction) becomes incomplete. As this solvent is recycled to extraction unit, incomplete stripping leads to excessive uranium loss in the raffinate in the solvent extraction process.

The objective of the solvent treatment process is to completely remove the degraded products of solvent and to bring down the concentration of uranium in the lean solvent(LS) to as low level as possible (close to that of freshly prepared solvent).

3.2 Uranium Extraction from Uranyl Nitrate Raffinate (UNR)

Nitric acid acts as a typical salting agent, it increases the distribution coefficient of uranyl nitrate at all concentrations, but especially at low 'U' concentrations, where the self salting and solvent saturation effects are absent. When the aqueous phase contains less than 10 g/l 'U' the distribution coefficient increases by a factor of 300 or more by increasing the nitric acid concentration in the aqueous feed to about 3.0 – 6.0 N. The positive effect of nitric acid / nitrates on the distribution coefficient of uranium has been favorably exploited in the present trials.

4.0 TRIALS

The solvent treatment as well as UNR extraction from UNR trials were carried out in a 2.5 KL cylindrical tank with conical bottom, having four baffles and two stage pitched turbine type agitator. The batch size of the trials is 1.0 KL.

A part (25%) of the lean solvent stream from the stripping unit of 1st cycle is taken out and is subjected to sodium carbonate solution washes and acidified with nitric acid. The lean solvent from the stripping unit normally contains about 10 – 12g/l 'U' and DBP concentration up to about 0.5%. The solvent is first washed with dilute alkaline solution. DBP an acidic compound, readily dissolves in the alkaline solution, forming soluble salts. The uranium dissolves in aqueous (sodium carbonate solution) forming soluble uranyl tricarbonate complex. The solvent stream which is free of uranium and degraded products is then washed with water and finally acidified with nitric acid to break up any emulsions and neutralize any residual alkalinity. The loaded alkaline solution is recycled a few times and both the alkaline & acidic wash solutions are sent to dissolution section for recycle.

Several trials were carried out using different concentrations of alkaline solution and at different ratios of solvent to alkaline solution(O/A) in soda wash stage and solvent to acid solutions in acidification stage, in order to minimize the quantity of wash solutions generated.

It was observed that by using 5% sodium carbonate solution (w/v) and 3.0 N acid at O/A ratio of 3.0 & 6.0 respectively, the DBP concentration in the solvent could be brought down to less than 0.1% and 'U' concentration to less than 0.1 g/l from about 10 – 12 g/l. [Refer Table 1].

The UNR generated in the 1st cycle solvent Extraction step contains about 0.5 – 1.0 g/l and about 1.5 – 2.0 N FA. This UNR is further acidified to 3.0 N. The treated solvent generated in the solvent treatment step above, (having ‘U’ concentration of less than 0.1 g/l and solvent degraded products concentration less than 0.1%) is used for 2nd cycle solvent extraction. Several trails have been carried out in one, two and three cross flow stages (Refer Fig.2). In multistage extraction trials, the raffinate was successively contacted with equal quantity of fresh solvent. The entire operation was done in a batch mode. It was observed that at O/A ratio of 1:2 and with free acidity(FA) in UNR at about 3.0 N and with 3 cross flow stages the uranium concentration in 1st cycle UNR could be brought down from about 0.5 – 1.0 g/l to less than 10 mg/l [Refer Table 2]. The level of ‘U’ in UNR is so low that the solution is equivalent to a ‘U’ free salt solution suitable for direct disposal. The extract generated in the 2nd cycle solvent extraction step is mixed with the Lean solvent stream (75%) from the stripping process (Refer Fig.3) and is subsequently used in 1st cycle solvent extraction process.

5.0 BENEFITS

- The new process developed requires less chemicals compared to the existing process.
- The material handling works associated with respect to solid waste UNRC is avoided.
- The present trials are with batch operation for solvent treatment followed by batch-wise UNR treatment. However, this process can also be adopted online by introduction of treated solvent at the last stage and the untreated part of the solvent at a suitable intermediate stage in the 1st cycle extraction process. This would further reduce the number of process steps (2nd cycle solvent extraction step can be avoided).
- The addition of such a tail-end residual ‘U’ recovery process makes the ‘UO_2’ production process much more environment friendly by way of reducing uranium content in barren liquid in Ion-exchange process (Refer Fig. 4).

6.0 CONCLUSION

- The ‘U’ concentration in UNR could be brought down from about 0.5 g/l to less than 10 mg/l.
- Bringing down the ‘U’ concentration from the level of 0.5 g/l to less than 10 mg/l results in recovery of about 2 kg ‘U’ per tonne of UO_2 produced.

7.0 ACKNOWLEDGEMENT

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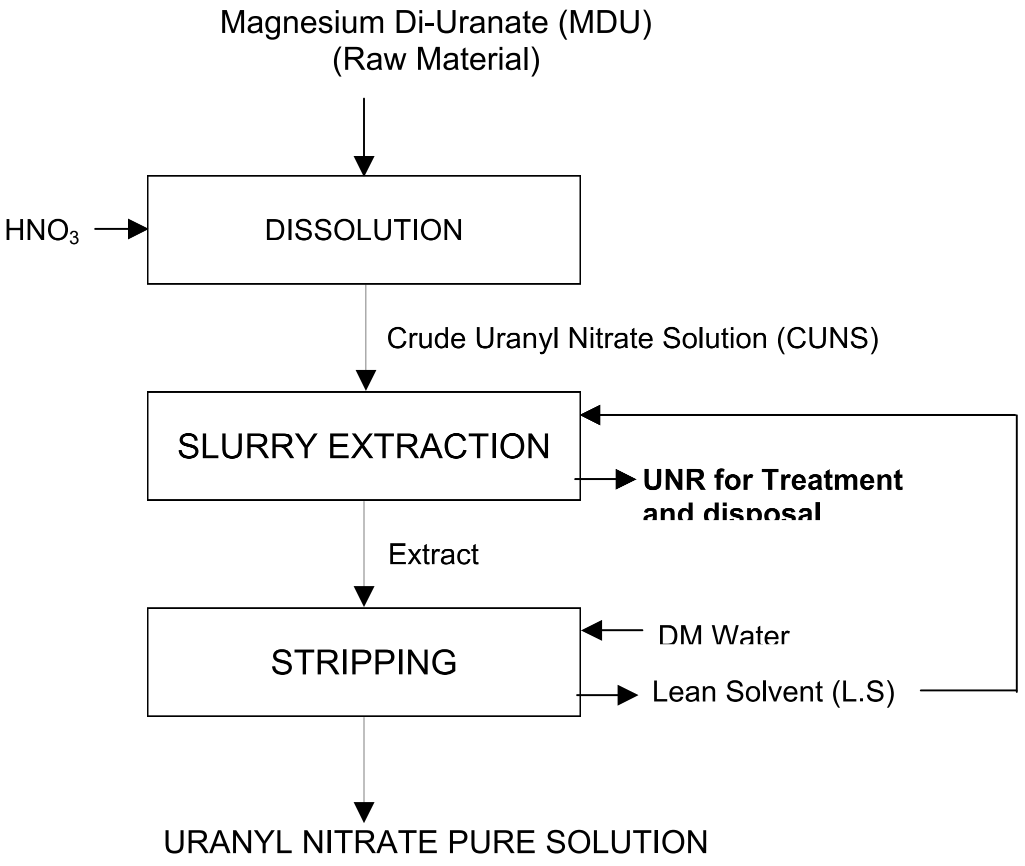

Fig. 1. URANYL NITRATE PURIFICATION PROCESS

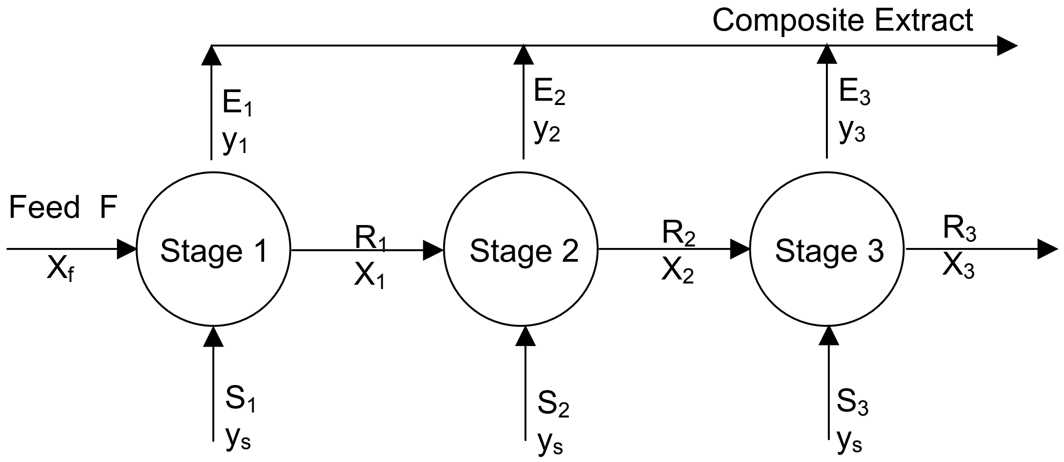

Fig. 2. 3-STAGE EXTRACTION OF 'U' FROM UNR ADOPTED FOR TRIALS

E_1, E_2, E_3 = Extract flow rate in Stage1, 2, 3 respectively
R_1, R_2, R_3 = Raffinate flow rate in Stage1, 2, 3 respectively
S_1, S_2, S_3 = Solvent flow rate in Stage1, 2, 3 respectively
X_1, X_2, X_3 = Concentration of 'U' in Raffinate in Stage1, 2, 3 respectively
y_1, y_2, y_3 = Concentration of 'U' in Extract in Stage1, 2, 3 respectively
X_f = Concentration of 'U' in Feed
Y_s = Concentration of 'U' in Solvent

F = Feed flow rate

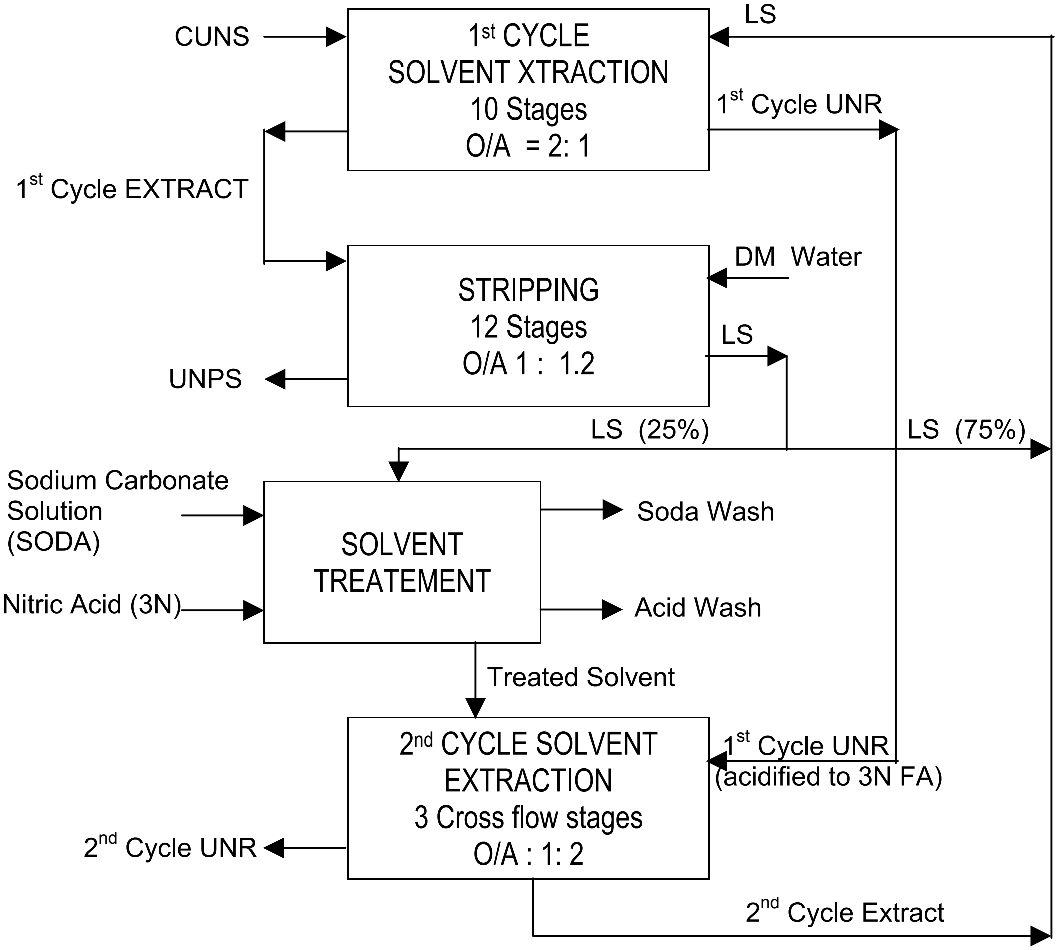

Fig. 3. FLOW DIAGRAM OF THE PROCESS FOR RECOVERY OF URANIUM FROM UNR

DETAILS OF PLANT-SCALE TRIALS

A) Solvent Treatment

Batch Size : 1000 ltrs

Batch Time : 12 hours

Alkaline solution concentration : 5% (w/v)

Nitric Acid concentration : 3.0 N

Solvent quantity : 1000 ltrs

Alkaline solution quantity : 330 ltrs

Acid quantity : 165 ltrs

O / A (solvent/Alkaline solution) : 3.0

O / A (solvent/acid) : 6.0

Table 1. ‘U’ REMOVAL IN SOLVENT BY TREATMENT

S. No.	‘U’ Concentration in Lean Solvent (g/l)	
	Before Treatment	After Treatment
1	12	< 0.1
2	8	< 0.1
3	10	< 0.1
4	5	< 0.1
5	7	< 0.1

B) UNR Extraction

Batch Size	: 1000 ltrs	Solvent quantity(Total)	: 500 ltr
Batch Time	: 6 hours	O/A (Solvent/UNR)	: 0.5
UNR quantity	: 1000 ltrs	‘U’ concentration in solvent	: <100 mg/l

Table 2. ‘U’ REMOVAL BY TREATMENT WITH CONDITIONED SOLVENT

S. No.	‘U’ Concentration in UNR				
	Before Treatment		After Treatment ‘U’ (mg/l)		
	‘U’ (mg/l)	F.A (N)	1 stage	2 cross flow stages	3 cross flow stages
1	370	3.6	84	23	7
2	380	3.2	93	31	9
3	490	3.1	65	24	10
4	500	3.7	50	15	6
5	680	3.9	41	19	9
6	700	4.1	24	9	4
7	980	3.7	140	36	10

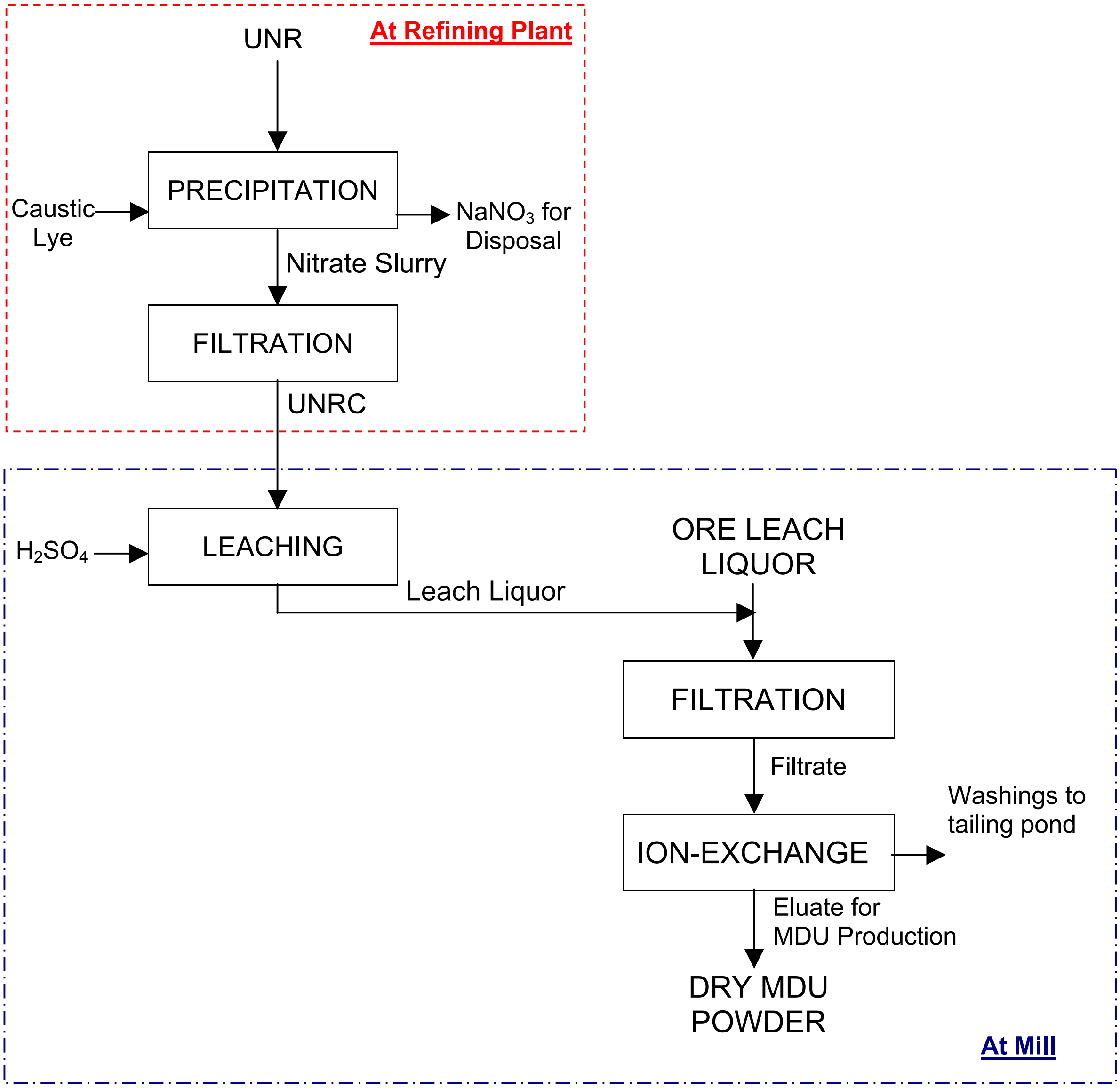

Fig. 4. EXISTING PROCESS FOR RECOVERY OF RESIDUAL URANIUM FROM

UNR & RESULTING UNRC