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THOREX PROCESS BY PRECIPITATION TECHNIQUE

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60	<i>Abstract :</i>	A sequential precipitation technique is reported for the separation of uranium and thorium present in the uranium product stream of a single cycle 5% TBP Thorex Process. It involves the precipitation of thorium as oxalate in 1M HNO ₃ medium at 60-70°C and after filtration, precipitation of uranium as ammonium diuranate at 80-90°C from the oxalate supernatant. In order to meet the varying feed conditions, this method has been tested for feeds containing 10 g/l uranium and 1-50 g/l thorium in 1-6M HNO ₃ . Various parameters like feed acidities, uranium and thorium concentrations, excess oxalic acid concentrations in the oxalate supernatant, precipitation temperatures, precipitate wash volumes etc. have been optimised to obtain more than 99% recovery of thorium and uranium as their oxides with less than 50 ppm uranium losses to ammonium diuranate filtrate.
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ABSTRACT

A sequential precipitation technique is reported for the separation of uranium and thorium present in the uranium product stream of a single cycle 5% TBP Thorex Process. It involves the precipitation of thorium as oxalate in 1M HNO₃ medium at 60-70° C and after filtration, precipitation of uranium as ammonium diuranate at 80-90°C from the oxalate supernatant. This technique has several advantages over the ion-exchange process normally used for treating these products. In order to meet the varying feed conditions, this method has been tested for feeds containing 10 g/l uranium and 1-50 g/l thorium in 1-6M HNO₃. Various parameters like feed acidities, uranium and thorium concentrations, excess oxalic acid concentrations in the oxalate supernatant, precipitation temperatures, precipitate wash volumes etc. have been optimised to obtain more than 99% recovery of thorium and uranium as their oxides with less than 50 ppm uranium losses to ammonium diuranate filtrate. The distribution patterns of different fission products and stainless steel corrosion products during various steps of this procedure have also been studied. For simulating the actual Thorex plant scale operation, experiments have been conducted with 25g and 100g lots of uranium per batch.

SEPARATION AND PURIFICATION OF URANIUM PRODUCT FROM THORIUM IN
THOREX PROCESS BY PRECIPITATION TECHNIQUE

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1. INTRODUCTION

The solvent extraction processes widely employed for the separation of U233 from irradiated thorium, (such as Thorex process) utilize tributyl phosphate (TBP) as extractant in kerosene like diluents. Depending upon whether U233 alone or both U233 and thorium are to be recovered, the process conditions and TBP concentrations employed differ in each of these processes. When U233 alone is to be recovered from irradiated thorium, 1-5% TBP in kerosene type diluents is used as extractant for preferential extraction of U233(1-6). In this process, the loaded organic phase containing U233 is scrubbed with nitric acid to remove the co-extracted thorium and then the U233 is stripped from the organic phase with water. Because of the various constraints encountered while processing, the uranium product thus obtained often contains significant amounts of thorium as contaminant and requires additional TBP extraction or ion exchange steps for further purification from thorium.

In the pilot plant at Trombay (7), the final purification of uranium from thorium was carried out by anion exchange in hydrochloric acid medium in lead-shielded glove boxes.

In 8M HCl medium, uranium forms a strong anionic chloro complex which absorbs strongly on the anion exchange resin

Dowex 1x4 whereas thorium is not absorbed under the same conditions. In this case, nitrate ions interfere in the formation of chloro complex and hence the feed U233 solution to the column should be free from nitrate ions. This involves a number of process steps such as pre-concentration of the product solution, precipitation of U233 and thorium with ammonium hydroxide, washing of the precipitate to remove nitrate ions and finally, dissolution of the precipitate in hydrochloric acid to obtain the feed solution for ion exchange. Though a good decontamination from thorium could be had employing this procedure, the use of hydrochloric acid resulted in the corrosion of the process equipment and gas formation in the resin bed. The decontamination from iron was poor as iron also forms anionic chloro complex in concentrated hydrochloric acid medium.

As an alternative, anion exchange in acetic acid medium was also considered (8) as uranium forms anionic complexes with acetate ions. Here again, the preparation of feed solution in acetate medium was equally cumbersome though the corrosion problems were less. Subsequently, a cation exchange procedure was studied in detail (9) which involved the preferential sorption of thorium from 0.5 M nitric acid feed containing U233 and thorium (at 1:1 ratio) by cation exchanger, Dowex W 50x8 in H⁺ form. This procedure yields an effluent and washing stream containing >99% U233 which is almost free from thorium. As the medium of operation is nitric acid, this method has several advantages and the uranium product solution from the process can be directly fed to the column. A satisfactory separation of uranium from

thorium is achieved in this technique by careful manipulation of feed and wash acidities and by controlling the thorium loading to within 60-80% of the total column capacity. For feeds with fluctuating Th/U ratios and acidity the design and routine operation of this cation exchange technique can pose some problems as the thorium loading pattern and feed and wash acidities are required to be rigidly controlled. Further, after the separation of uranium, the complete removal of the loaded thorium from the column is difficult with nitric acid alone as eluting agent and requires complexing agents such as ammonium acetate-acetic acid buffer (pH : 5.5) in the final stages, generating large waste volumes. The resin would also require periodic replacement.

Considering these points, an alternate procedure has been developed as described in the present paper for the removal of thorium from uranium product employing a precipitation technique. It involves the precipitation of thorium as thorium oxalate in 1M nitric acid medium at about 70 C and after filtration, precipitation of uranium from the oxalate supernatant as ammonium diuranate at 80-90 C. This technique has several advantages over ion exchange process and can be used for feeds containing varying amounts of thorium and uranium at different acidities. The liquid wastes generated contain very little thorium or uranium and can be disposed off without difficulty.

This report summarizes the results obtained on the purification of uranium product from thorium using the above precipitation route under a wide variety of conditions that can

be envisaged during the recovery of U233 from irradiated thorium after a single cycle 5% TBP process.

2. EXPERIMENTAL

2. 1. Reagents

Nuclear grade uranium dioxide obtained from Uranium Metal Plant, BARC, Trombay was used to prepare a stock solution of uranyl nitrate by dissolution of the oxide in nitric acid.

Thorium nitrate stock solution in water was prepared by dissolving LR grade thorium nitrate obtained from Indian Rare Earths Ltd., Trombay.

A 10% solution of oxalic acid (BDH/LR) in water was used for precipitating thorium as oxalate.

Ammonia solution (25%) obtained from BDH/LR was used without any dilution for ammonium diuranate precipitation. Ammonium nitrate and nitric acid were of AR grade.

For precipitation studies, feed solutions with different ratios of U/Th were prepared in 1M nitric acid by mixing appropriate quantities of uranium and thorium stock solutions and nitric acid. Wherever required all these solutions were preanalysed for relevant components before use.

2. 2. Procedure for Precipitation of Thorium as Oxalate

The feed solution was heated to about 70° C (and after taking into account the thorium content of the feed), a calculated quantity of 10% oxalic acid in water was slowly added with constant stirring so as to bring the free/excess oxalic acid concentration to approximately 0.1 M. After 1-2 hours settling,

the precipitate was separated by filtration through a Whatman No. 542 filter paper and washed with 0.5% hot (60° C) oxalic acid solution. The filtrate and washings were collected together for the subsequent ammonium diuranate precipitation step.

After drying under infra red lamp, the oxalate cake was heated for 4 hrs at 750° C for its conversion to oxide and weighed as ThO₂. Then thorium content was calculated. The supernatant was analysed for uranium and thorium wherever required.

2. 3. Procedure for Precipitation of Uranium as Ammonium Diuranate

The filtrate after thorium oxalate separation together with washings was mixed with ammonium nitrate at the rate of 4 g of ammonium nitrate/100 ml feed uranium and heated to 90° C. To the hot solution, concentrated ammonia (25%) solution was added with constant stirring till the ammonium diuranate (ADU) precipitation was complete and the supernatant attained a pH of 9.5 +/- 0.3.

After allowing a settling time of 15 min. the ADU precipitate was separated by filtration under hot condition through Whatman No. 541 filter paper and washed with 2% hot ammonium nitrate solution containing a few drops of ammonium hydroxide. During precipitation and filtration care was taken to avoid interference from carbon di oxide.

After drying under infra red lamp, the ADU cake was heated for 4 hrs at 750° C for its conversion to oxide and weighed as U₃O₈. The uranium recovered was calculated from the weight of U₃O₈ and confirmed by wet analysis. The ADU supernatant was

analysed for thorium and uranium.

2. 4. Precipitation Experiments

Most of these experiments were conducted with 100 ml of U/Th feeds in 1M nitric acid with a fixed uranium concentration level of 10g/l (ie, 1g U/Expt) and with thorium concentration level varying from 1g/l to 50g/l (ie, 0.1 to 5g Th/Expt) as per requirement in each experiment.

To assess the reliability of the standard procedure under a wide variety of abnormal feed conditions, experiments were also conducted with feeds having different acidities (upto 5M) and free oxalic acid concentration, high salt content (4M NH₄NO₃) and high uranium and thorium content. Details of these experiments are given at appropriate Tables.

For studying the distribution pattern of fission products during the precipitation steps, the feed solution containing uranium and thorium was spiked with fission product activity at appropriate concentration levels using solutions drawn from high active streams of the Purex process. As trace level organic impurities from degradation of TBP is likely to be present in the uranium product, the above results were again confirmed with feeds prepared using uranium solution drawn from 2EPCON tank of the Purex process after necessary spiking with fission products. In both cases, spikes contained some plutonium as well and hence its distribution pattern was also assessed.

For studying the distribution pattern of corrosion products during the precipitation steps, a 304L stainless steel sample was dissolved in conc. HCl and after repeated evaporation with nitric

acid, a known amount of this solution containing all the relevant components of stainless steel was spiked into U/Th feed such that the final concentration of Fe(III) in the feed amounted to 1% of uranium present. Cr and Ni were present at correspondingly lower levels.

Based on the procedure standardized at 1 g uranium scale, experiments were extended to 25 g and 100 g uranium/batch containing equal amount of thorium, at respective feed volumes of 2.5 and 10L to assess the various requirements for routine plant scale operation. Such experiments were also done for abnormal feeds with high acidity and thorium content and these are described at appropriate places. Material balance problems were inherent in these large scale experiments as measuring cylinders were used for large volume measurements.

2. 5. Analysis

Uranium in the feed solutions and in the product oxides was determined by titrimetry using modified Davies and Gray method(10). The product oxide was dissolved in nitric acid for this purpose. In these cases, the titrimetric values agreed well with the values calculated from the weight of U3O8 taken for dissolution.

Thorium in the original stock and other feed solutions was estimated by titration (11) with standard EDTA solution using xylenol orange as indicator. In the product oxides, the thorium content was calculated from the weight of thorium oxide (ThO₂).

Trace level uranium and thorium in various supernatant solutions, impurities in uranium and thorium oxide products and

distribution pattern of corrosion products in various streams were estimated by spectrographic techniques (12,13).

The fission product analysis was done using a 62 cc high purity germanium detector coupled to a 4K MCA. Wherever required, the plutonium estimation was carried out using HTTA extraction procedure(14).

3. RESULTS AND DISCUSSION

The precipitation scheme developed is mainly applicable for treating the concentrated uranium product obtained after one cycle of Thorex process employing 5% TBP flow sheet. This is expected to have an acidity in the range of 1-2M and uranium concentration of 8-10 g/l. Depending on the scrub column performance and the no. of stages provided for, the thorium content in the final uranium product is expected to vary. Keeping this in view, the scheme developed was tested over a wide range of Th/U ratios at concentration and acidity levels normally encountered in the process. After testing the scheme at 1g U scale, experiments were carried out at 25g and 100g U scale. A typical Th/U separation scheme at 1 g U scale from 1M HNO₃ with 10 g/l uranium and 10 g/l thorium is given in Fig.1. The data on the thorium - uranium recovery at 1 g U scale having 10 g/l uranium and 1-50 g/l thorium at an acidity of 1M are presented in Table 1 and the same are discussed below.

3. 1. Precipitation of Thorium as Oxalate

3. 2. Thorium Separation

The thorium oxalate precipitation conditions recommended in the procedure have been evolved from the literature data (15-17)

on precipitation of thorium and plutonium as oxalates. The plutonium product in many Purex plants is subjected to oxalate precipitation step for its final conversion to oxide. In these cases, an excess oxalic acid concentration of 0.05 to 0.2 M in the final solution over and above the stoichiometric requirement is usually maintained during precipitation, which is carried out at acidities 1-4 M HNO₃ and at 50-60°C. In the present study with thorium the above conditions were optimised for achieving good quality thorium oxalate precipitate, rapid settling and filtration, good DF from fission products and maximum recovery of Th (>99%) and minimum loss to supernatant (<1%). These were then incorporated in the scheme for thorium oxalate precipitation, after suitable modification to meet the additional requirement of recovering uranium from the oxalate supernatant through ADU route. Under the acidity, temperature and excess oxalic acid concentration levels recommended, the precipitation of thorium oxalate was near quantitative as revealed by spectrographic and other analyses of oxalate supernatant and the product oxide in blank experiments with thorium alone.

In the procedure, 0.1M excess oxalic acid concentration is recommended in the final solution during oxalate precipitation. The results given in Table 1 indicate that this scheme can be employed for the precipitation and removal of thorium from 1M HNO₃ feeds having 10 g/l uranium and 1 to 50 g/l thorium (Th/U 0.1 to 5). In all the cases, the thorium recovery is better than 99%.

The results obtained for the same feeds with free oxalic acid concentration in the final solution ranging from 0.01 to 0.23M are given in Table 2. In these experiments, the excess oxalic acid concentration in each case amounts to about 100% excess over and above the stoichiometric requirement of thorium. It is seen in the case of feeds with less than 10 g/l thorium (Th/U ratio less than one) that 100% excess oxalic acid is sufficient to give a satisfactory recovery of thorium as oxalate and adjusting the solution to 0.1M in oxalic acid is not necessary. Further, maintaining a lower concentration (< 0.1M) of oxalic acid as excess in these cases (Th/U < 1) is helpful in reducing the possibility of precipitation of uranium as oxalate from the supernatant as discussed later on in this report. For the same reason, the excess oxalic acid concentration was restricted in the standard procedure even for feeds with thorium concentration higher than 10 g/l. At 50 g/l thorium concentration level the excess oxalic acid concentration works out to about 40%. For routine operational convenience a fixed excess oxalic acid concentration of 0.1M has been used in all the experiments.

After thorium oxalate precipitation, a settling time of 1-2 hours was adequate. While filtering, the supernatant was decanted first through the filter before transferring thorium oxalate slurry on the filter. The washing with dilute hot oxalic acid was continued till the cake and the wash filtrate were free of yellow colour due to uranium. The wash volume could be varied depending on the quantity of thorium oxalate cake to be washed and uranium decontamination required for the cake. This step is very

important for a good recovery of uranium as well as for removing the last traces of uranium from the thorium oxalate cake.

The feed acidity of 1M and temperature conditions used were helpful in preventing the precipitation of uranium as oxalate. The possibility of precipitation of uranium as oxalate can be further minimized by employing higher feed acidities and temperatures but this would entail handling increased waste volumes after ADU precipitation. To verify the behaviour of high acid feeds, acidities upto 5M HNO₃ were tried as feed acidities for thorium oxalate precipitation step. No significant enhancement in thorium loss to the supernatant was observed upto 6M feed acidity when the excess oxalic acid concentration was 0.1M. The results are presented in Table 3.

3. 3. Behaviour of Uranium During Thorium Oxalate Precipitation

In all the experiments, uranium remained in solution under the conditions employed for precipitation of thorium as oxalate. However, the uranium concentration in feed solution was never allowed to exceed 10 g/l and the feed acidity was maintained at 1M HNO₃ or more, as higher uranium concentrations and lower acidities could lead to precipitation of uranium as oxalate alongwith thorium (18). As mentioned above, to avoid the possibility of precipitation of uranium as oxalate, the excess oxalic acid concentration level in the supernatant after thorium precipitation should not be high (0.1M).

Blank experiments were conducted with feeds having 10g/l U in 1M HNO₃ in the absence of thorium by adding 10% oxalic acid to adjust the oxalate ion concentration in the solution to about

0.1M. The procedure followed was the same as described for Th-oxalate precipitation. It was seen that the solution remained clear upto 8 hours and no ppt of uranium oxalate was observed. The same solution after 24 hours of settling under uncontrolled ambient temperature conditions developed some sediments which however were found to dissolve on slight warming.

In the procedure recommended, normally as the feed Th/U ratio is above 1, the precipitation of thorium by oxalic acid solution would increase the volume of the final solution, thus decreasing the actual concentration level of uranium to a value much below 10 g/l. The thorium oxalate precipitate is allowed to settle for 1-2 hours only. Further, after filtering the cake it is washed with hot dilute oxalic acid to minimise losses due to entrainment of uranium in thorium oxalate cake. The increase in the volume of the filtrate because of the washings would help to keep the uranium in solution in the filtrate.

Thus, the above observations emphasise the importance of restricting the uranium concentration to 10g/l and acidity to above 1.0M HNO₃ in the feed to the oxalate precipitation step. It also emphasises the need for restricting the excess oxalic acid concentration to 0.1M.

3. 4. Thorium Oxide Product

The thorium oxide products obtained from these experiments were tested for uranium content by dissolving a small portion of the sample (200 mg) in nitric acid containing small amounts of fluoride and aluminium nitrate and subjecting the resulting solution to spectrographic analysis (19) for uranium. The results

obtained are included in Table 1 which indicate low losses of uranium in this step.

From the process point of view, the thorium oxide can either be disposed off as such or recycled to the process after dissolution depending on its uranium content. As the thorium oxalate precipitation would carry all the Th228 activity generated from the decay of U232 present as contaminant in U233, the radiation level on the thorium oxide would increase gradually due to the decay of Th228 and its daughter products. This dose rate would depend on the U232 content in the feed and the time lapsed before processing.

3. 5. Precipitation of Uranium as Ammonium Diuranate (ADU)

The uranium bearing oxalate supernatant was subjected to ADU precipitation step using the standard procedure (20,21). The solution was heated to about 90 C and uranium was precipitated as ADU by the addition of ammonia to a final pH of 9.3 to 9.5. The addition of NH4NO3 is not necessary if the nitrate concentration of the solution is high. The precipitate settled fast (usually within 15 minutes) and the solution was filtered hot. The clear supernatant was decanted through the filter first before the transfer of slurry. The ADU cake was washed adequately with hot 0.5% NH4NO3 solution containing a few drops of NH4OH before air drying. Usual precautions were taken to avoid the interference from CO2 during precipitation and filtration. It is essential that the ADU should be filtered off immediately under hot conditions. It has been observed that if the ADU precipitate is allowed to remain in solution over long periods (eg. overnight

settling), it slowly redissolves in the solution. Under the conditions recommended, the uranium recovery by ADU precipitation is near quantitative as can be seen from the results in Tables 1&2. Free Oxalate ion concentrations upto 0.2M do not seem to affect the ADU step. The ADU supernatant had less than 50 ppm of uranium and thorium in all the cases as determined by spectrographic analysis.

3. 6. Treatment of Ammonium Diuranate Supernatant for the Recovery of Uranium and Thorium

The ADU supernatant can be sent for waste treatment and final disposal as the uranium content would be very low in these streams. However, if some uranium losses to the ADU supernatant do occur due to mal-operation and the presence of carbon dioxide it can easily be recovered using co-precipitation/scavenging techniques using Fe(III) as carrier. The scheme suggested for treating such ADU supernatant waste is given in Fig.2. Using this scheme test experiments were done. To the ADU supernatant (100 ml) obtained from one of the earlier experiments, about 100 mg of uranium was added alongwith 4 g of $(NH_4)_2CO_3$. The resultant clear yellow solution was subjected to the co-precipitation step suggested in the scheme. It is seen that the uranium escaping to the ADU supernatant can be recovered almost quantitatively by this scheme thus rendering the final filtrate safe for disposal.

3. 7. Uranium Oxide Product

The product uranium oxide (U3O8) was assayed for uranium by wet analysis and for impurities by spectrography. The results show that a good quality product could be obtained using this

separation procedure.

3. 8. Distribution Pattern of Fission Products

As any information regarding the distribution pattern of different fission products during the various steps of the procedure would be of interest to Thorex process, experiments were conducted with fission products spiked feeds of natural uranium as well as with uranium from product streams of Purex process. The later experiments, with Purex uranium product were necessary to check the influence of dissolved organic impurities normally encountered in a TBP process, on the fission products distribution pattern. The distribution pattern observed for relevant fission products at different stages of the precipitation scheme is given in Fig.3A & 3B and the decontamination factors obtained are given in Table 4A & 4B. No significant differences in fission product behaviour could be observed in the results obtained with feeds of natural uranium and Purex uranium product.

The trend of the results indicates that while Ce144 and Zr95 follow the thorium oxalate precipitate almost quantitatively, Cs137 and a part of Ru106 remain in the oxalate supernatant. During ADU precipitation, a part of the Ru106 is carried by ADU precipitate while a major part of the Cs137 activity tends to remain in the ADU supernatant. The washing of the ADU cake with the recommended reagent helps to remove the contamination from the cake. This can be seen from the plots of individual fission products and gross beta, gamma activities in the washings of the ADU cake against the wash volume used as shown in Fig. 4A & 4B

Depending on the fission product contamination of the cake, the wash volume can be either increased or decreased. Plutonium, if present, gets carried along with the thorium oxalate precipitate.

Further decontamination from Cs137 and Ru103 can be achieved during the ignition of ADU cake to get U3O8 as these fission products have a tendency to volatilize.

Depending on the U232 content, the radiation dose levels of U233 product would keep building up on long storage due to short lived decay products of U232 chain. The activity and dose levels due to these decay products would assume more significance in comparison to that of residual fission product activities. The U233 is usually purified from these daughter products of U232 by a cation exchange procedure wherein Th228, the long lived daughter of U232, is sorbed on the exchanger thus breaking the decay chain. Significant amount of Th229, a decay product of U233 would also be sorbed on the cation exchanger. This step should also help in removing the trace level contamination of natural thorium, if present, in the U233 product.

The above cation exchange procedure may be replaced by the precipitation procedure using natural thorium as carrier during oxalate precipitation step.

3. 9. Distribution Pattern of Corrosion Products

The distribution of corrosion products like Fe, Cr, and Ni during the various steps of this precipitation scheme is given in Fig. 5 and the DF values obtained for the uranium product with respect to these elements are given in Table 5. It is seen that a good DF values for Fe, Co and Ni is observed in ADU. Part of Cr

and Mn present in the feed follows uranium. However, it is expected that all hydrolysable cations present in the oxalate supernatant would follow uranium during ADU precipitation.

3.10. Large Scale Precipitation Experiments

In order to simulate the actual Thorex Plant scale operation which envisages the processing of 100g lots of U233, experiments were carried out using the conditions tested above at 25g (2.5L) and 100g(10L) uranium scale. The schemes with stream values obtained are given in Fig. 6 & 7. The volume quantities mentioned are actually measured volumes in each case. These data would be useful in sizing of the equipment and for assessing the final volume of ADU supernatant wastes that would be generated.

Results obtained with 25g uranium lot (Fig.6) indicate recoveries better than 99.5% for uranium as well as thorium with negligible losses to ADU supernatant.

Similar results with 100g uranium lot(Fig.7) also show negligible losses of uranium and thorium to the ADU supernatant. However, the uranium recovery could not be fully assessed as Hastelloy container had to be used for ignition and the oxide had to be transferred from it for weighing in analytical balance. As mentioned earlier, volume of these solutions were measured using 1L measuring cylinder, which might contribute to the errors. This scheme has been successfully implemented by FRDL, IGCAR, Kalpakkam in its recent Thorex campaign for the reprocessing of irradiated thorium rods (22).

3.11. Experiments with Non Standard Feeds

Feeds with higher acidities and significant thorium

content are often encountered in uranium products generated in process recycling and in cation exchange cycle effluent concentrates. In order to test the applicability of this scheme to such feeds, few experiments were conducted with feeds having 8-10 g/l uranium and 30-40 g/l thorium along with acidities upto 5M nitric acid. One of the experiments was done at 4g U scale (instead of the usual 1g U scale) to assess the volume of wastes generated. The experimental scheme used and the thorium and uranium recoveries obtained are summarized in Fig.8 and Table 6 respectively. As an alternate option to process such high acid feeds, the possibility of partly neutralising the excess acid present in the feed was also considered. To test this, in one experiment, the feed to the oxalate precipitation step was adjusted to 1M nitric acid and 4M ammonium nitrate. Though thorium could be precipitated satisfactorily under these conditions, the precipitate obtained was bulky in nature, probably due to the formation of salts other than $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. No further efforts were made to characterize this precipitate. The Table also includes results and the recoveries obtained with feeds having 2g/l uranium and thorium in 1M HNO_3 . All the results indicate that the procedure works satisfactorily even under these adverse conditions with good recoveries for uranium and thorium.

4. CONCLUSION

The concentrated U233 product from a single cycle 5% TBP extraction step of Thorex process containing thorium in the ratio $\text{Th}/\text{U} = 0.1$ to 5 can be separated from thorium in a satisfactory

manner using the oxalate precipitation procedure described above. The uranium and thorium recoveries above 99% are possible. The optimum feed acidity should be about 1M with feed uranium concentration less than 10g/l. However, acidities upto 5M HNO₃ could be tolerated in the feed. The excess oxalic acid concentration was restricted to 0.1M. The fission product distribution pattern indicates that among the fission products, Ru106 partly follows the ADU cake. Further improvement in decontamination is possible by prolonged washing of the ADU cake. The corrosion products' behaviour has also been assessed.

The thorium thus separated, can either be disposed off as oxide or recycled back to the process after dissolution. The ADU supernatant can be disposed off as such or after scavenging the residual traces of U233 with Fe(III) as carrier in ammoniacal medium. The U308 obtained has good product purity.

Large scale experiments with 25g and 100g lot uranium have yielded good results confirming the applicability of the method. This method has several advantages over anion and cation exchange procedures used so far.

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Table 1

Separation of Thorium as Oxalate and Uranium as ADU at 10 g/l U and 1-50 g/l Th levels

Feed composition : U = 1.0 g H₂C₂O₄ = 0.1 M excess in oxalate supernatant

Th = 0.1-5.0 g

HNO₃ = 1.0 M

Vol. = 100 ml

S.No.	Feed		Recovery of thorium as oxalate			Recovery of uranium as ADU		Losses to ammoniacal supernatant				Material balance	
	U/Th Ratio	Th g	Th g	Th %	U in Th, mg	U g	U %	Th μ g	Th %	U mg	U %	U g	Th g
1.	1:0.1	0.106	0.105	99.1	0.616	0.991	99.1	80	0.075	3.2	0.32	0.995	0.105
2.	1:0.5	0.529	0.528	99.8	0.629	0.991	99.1	130	0.025	2.5	0.25	0.994	0.528
3.	1:1	1.058	1.051	99.3	0.685	0.989	98.9	130	0.012	4.3	0.43	0.994	1.051
4.	1:2	2.012	2.007	99.8	1.662	0.990	99.0	120	0.006	2.3	0.23	0.994	2.007
5.	1:5	4.970	4.970	100.0	5.104	0.987	98.7	300	0.006	3.1	0.31	0.995	4.970

Table 2

Separation of Thorium as Oxalate and Uranium as ADU at 10 g/l U and 1-50 g/l Th levels
with Varying Excess Oxalic Acid Concentrations.

Feed composition: U = 0.997 g & 1.004 g H₂C₂O₄ = 0.01 - 0.23 M excess in Oxalate

Th = 0.1 - 5.0 g

Supernatant

HNO₃ = 1.0 M

Vol. = 100 ml

S.No.	Feed		Excess Oxalic Acid M	Recovery of Thorium as oxalate		Recovery of Uranium as ADU		Losses to ammoniacal supernatant		Material balance	
	U g	Th g		Th g	Th %	U g	U %	U mg	Th g	U g	
1.	0.997	0.106	0.01	0.106	100.0	0.989	99.2	6.0	0.106	0.995	
2.	0.997	0.529	0.04	0.528	99.8	0.990	99.3	3.0	0.528	0.993	
3.	1.004	1.088	0.08	1.087	99.9	1.032	102.8	6.0	1.087	1.038	
4.	0.997	2.117	0.13	2.125	100.4	0.981	98.4	4.0	2.125	0.985	
5.	0.997	5.293	0.23	5.274	99.6	0.983	98.6	12.0	5.274	0.995	

Table 4 A

Distribution Behaviour of Fission Products During the Separation
of Thorium as Oxalate and Natural Uranium as ADU

Feed Composition: U = 1.012 g H₂C₂O₄ = 0.1 M Excess in Oxalate
 Th = 1.075 g Supernatant
 HNO₃ = 1.0 M
 Vol. = 100 ml

Activity	Activity in feed	Activity in U product	DF
Po, μ g/g U	1.21	0.003	403
Gross β , μ C/g U	82.00	3.840	21
Gross γ , μ C/g U	27.70	2.260	12
Cs144, μ C/g U	39.20	0.140	280
Pu106, μ C/g U	8.35	0.520	16
Cs137, μ C/g U	4.07	0.050	81
Am241, μ C/g U	0.39	0.030	13
Pb210, μ C/g U	0.98	0.700	1

Table 6

Separation of Thorium as Oxalate and Uranium as ADU
under Non- standard Feed conditions

Feed composition: U = 0.0 - 4.0g H₂C₂O₄ = 0.02-0.20M Excess in Oxalate Supernatant
 Th = 0.2 - 17.5g
 HNO₃ = 1.0 - 5.0M

S.No.	Feed			Excess oxalic Acid M	Recovery of thorium as oxalate		Recovery of Uranium as ADU		Losses to ammoniacal supernatant		Material balance	
	U g	Th g	HNO ₃ M		Th g	Th %	U g	U %	Th µg	U mg	Th g	U g
1.	0.199	0.212	1.0	0.02	0.219	103.3	0.199	100.0	-	-	0.219	0.199
2.	0.997	3.992	4.0	0.20	3.950	98.9	0.987	99.0	32.0	11.0	3.95	0.998
3.	3.897	17.516	5.0	0.10	17.20	98.2	3.859	99.3	600.0	33.0	17.20	3.902
4.	NIL	1.030 (4M NH ₄ NO ₃)	1.0	0.10	1.042	101.2	NIL	-	2.4	NIL	1.042	-

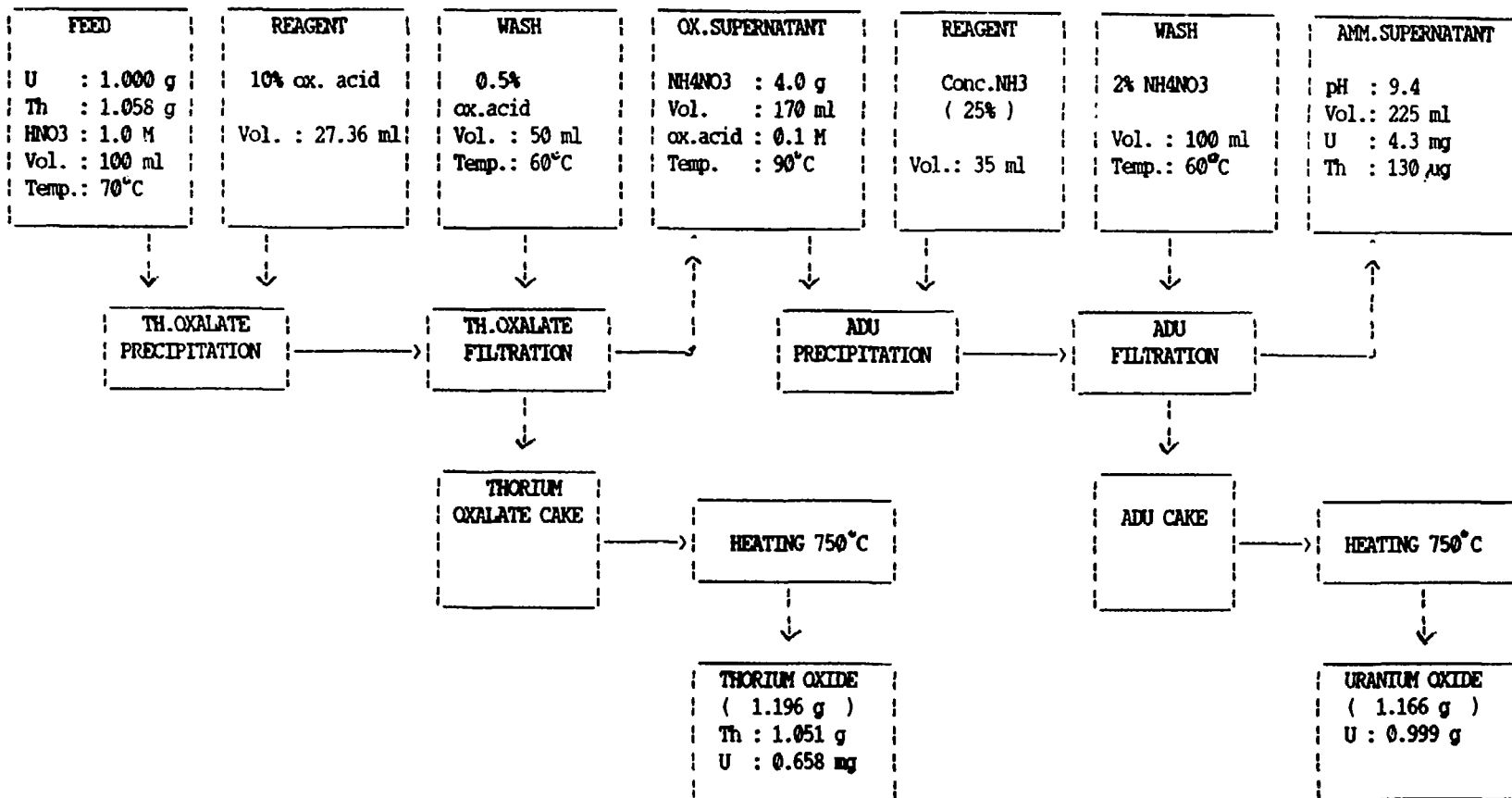
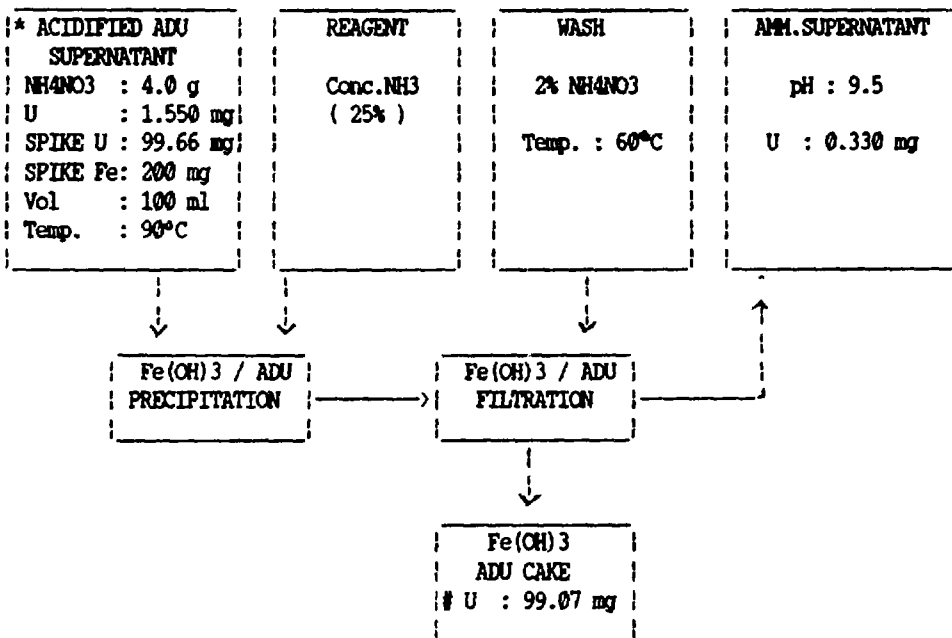


Fig. 1

Scheme of separation of thorium and uranium from 1M HNO3
 U concentration = 10 g/l Th concentration = 10 g/l



* Fe and U were spiked into original ADU supernatant in presence of (NH4)2CO3 before acidification.

Volumetric analysis value.

Fig. 2

Scheme for the recovery of uranium from ammoniacal supernatant

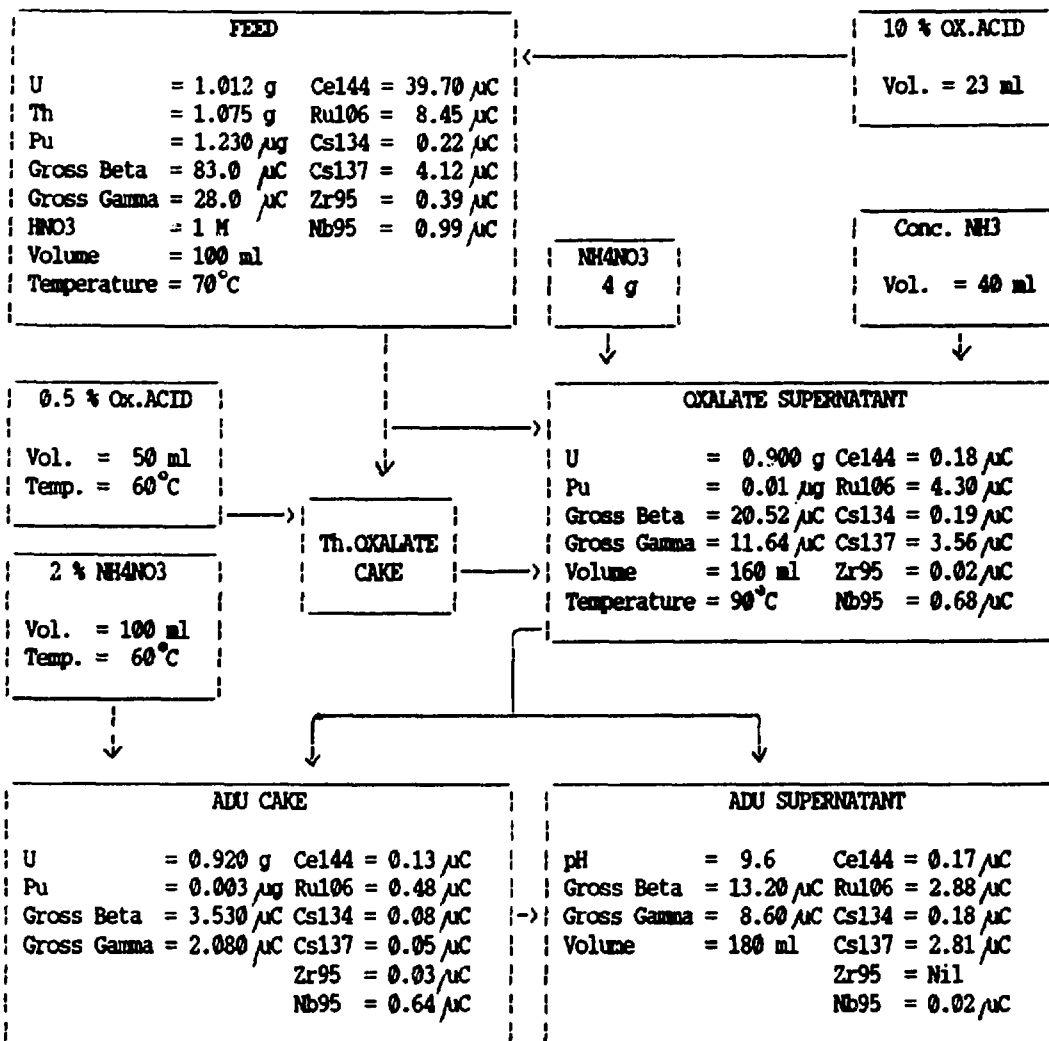


Fig. 3 A

Distribution of activities during the separation of thorium and natural uranium by precipitation

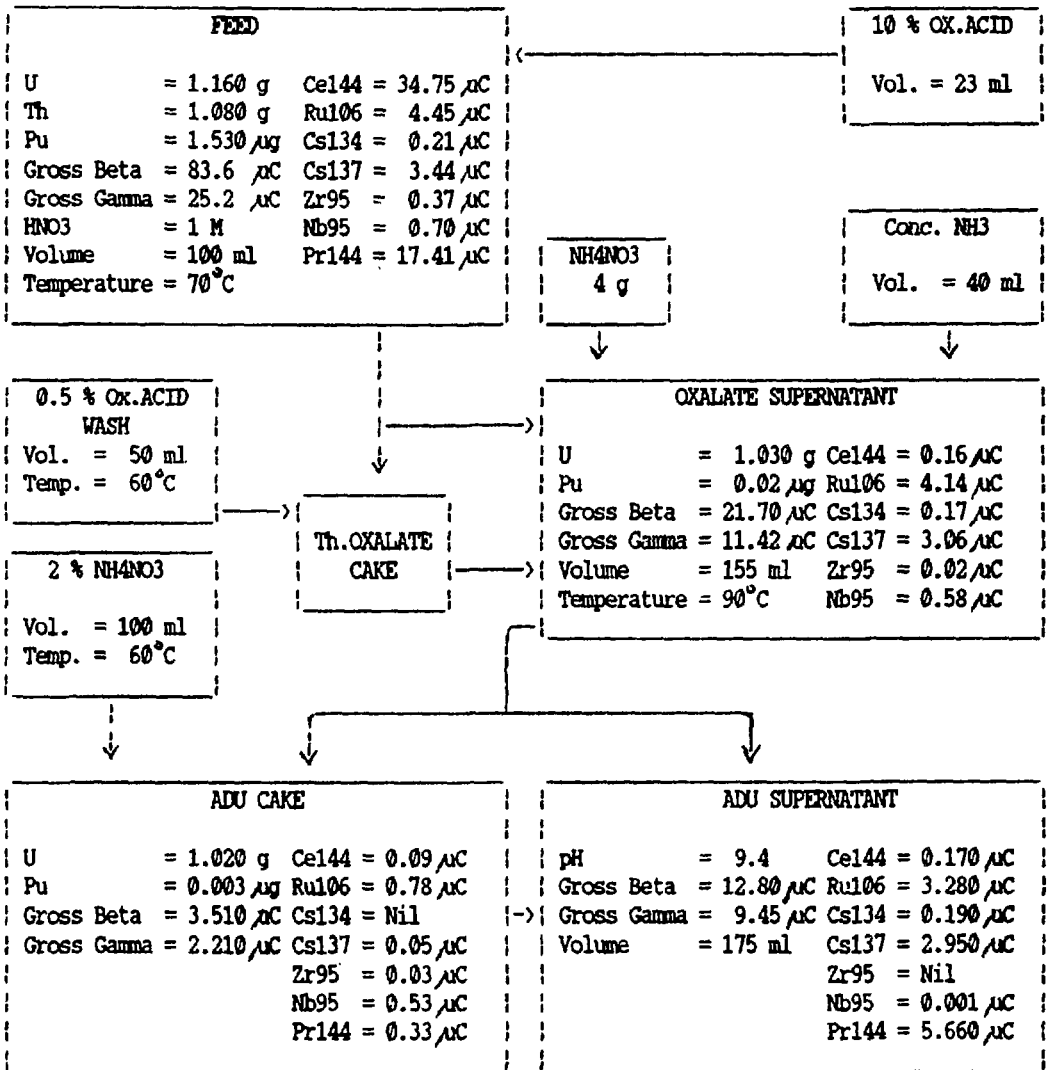


Fig. 3 B

Distribution of activities during the separation of thorium and processed uranium by precipitation.

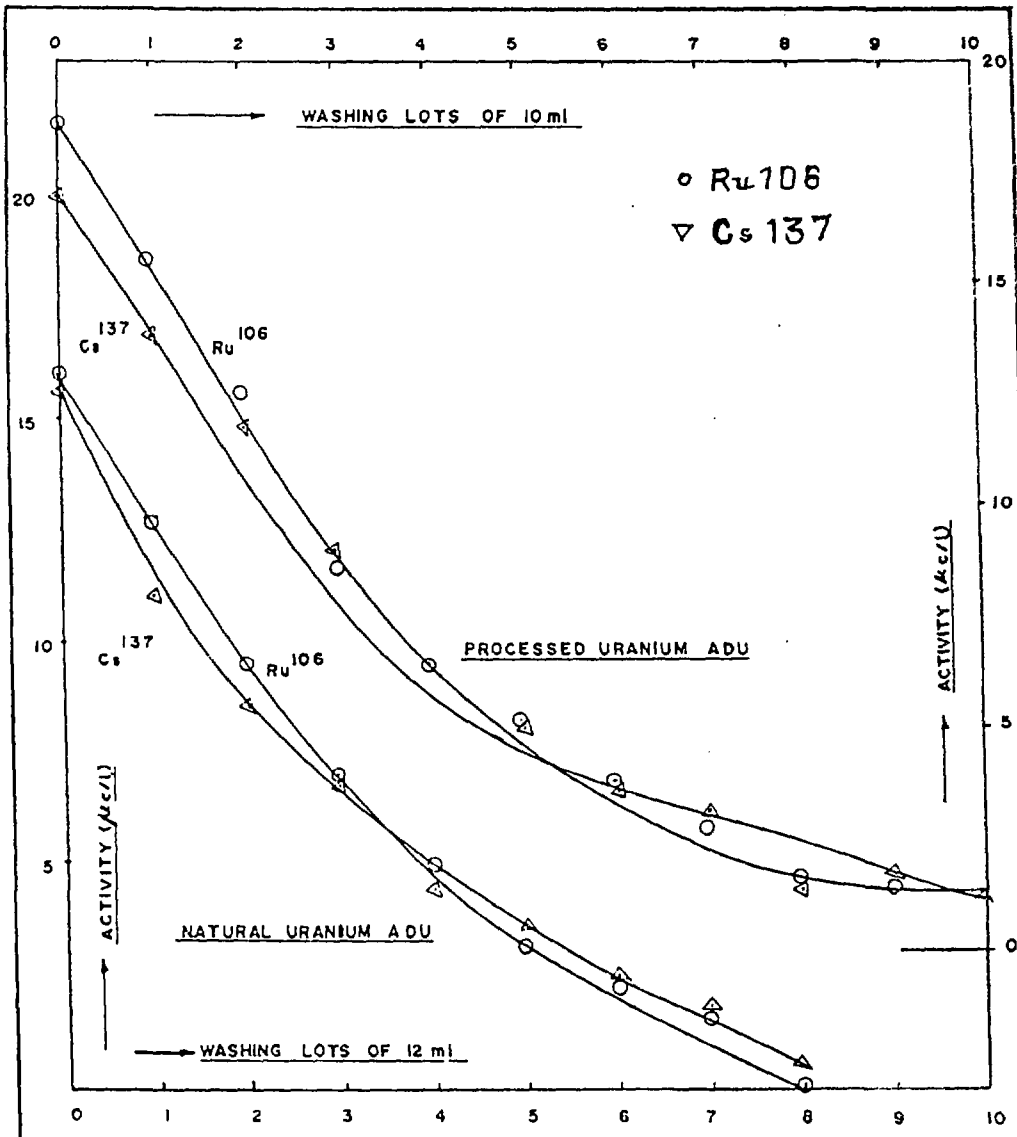


FIG: 4A FISSION PRODUCTS DECONTAMINATION OF
ADU BY WASHING

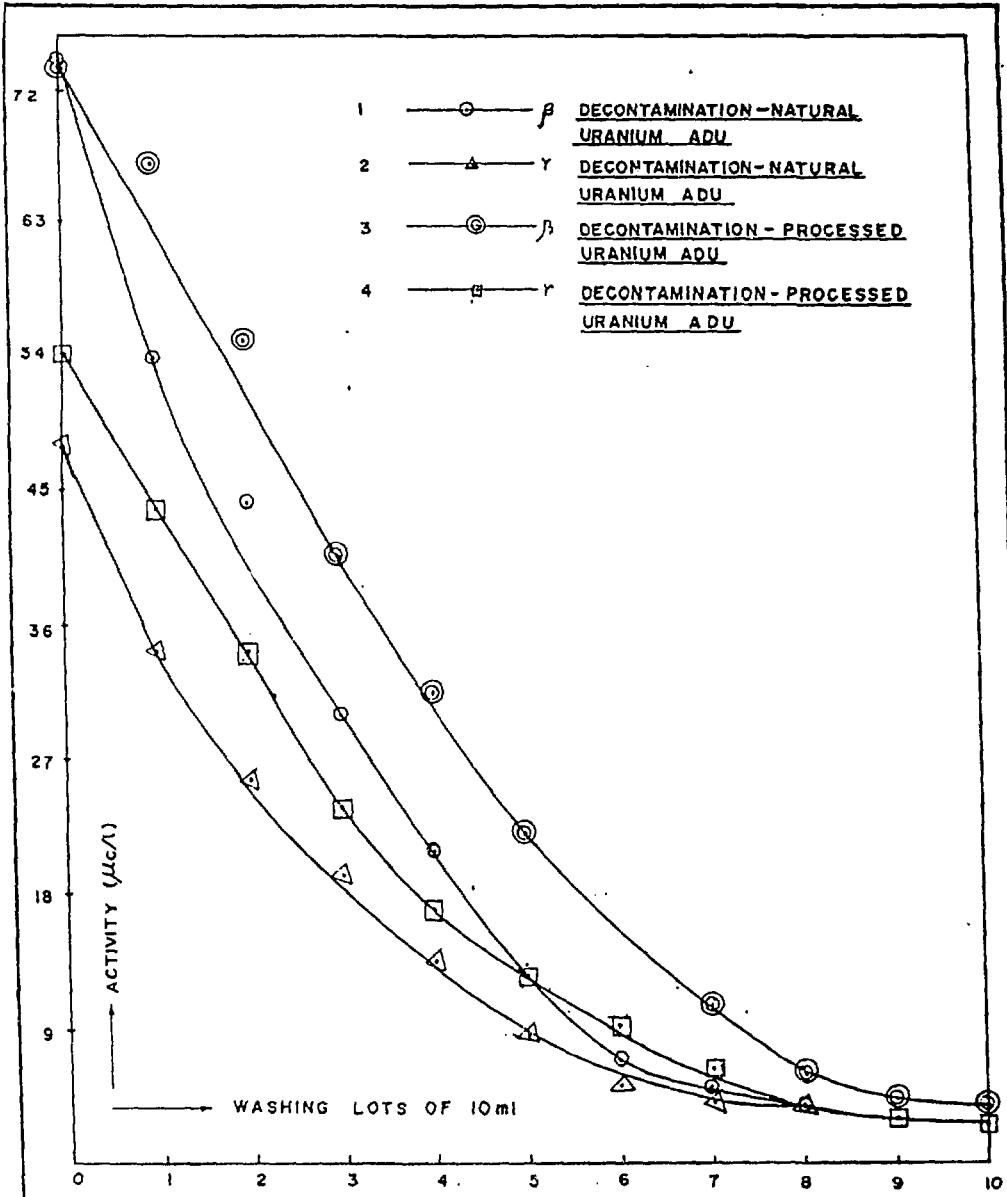


FIG. 4B β, γ DECONTAMINATION OF ADU BY WASHING

Feed: U = 0.997 g, Th = 1.060 g, HNO₃ = 1.0 M, S S = 16.00 mg, Vol. = 100 ml.

Product: U = 0.997 g

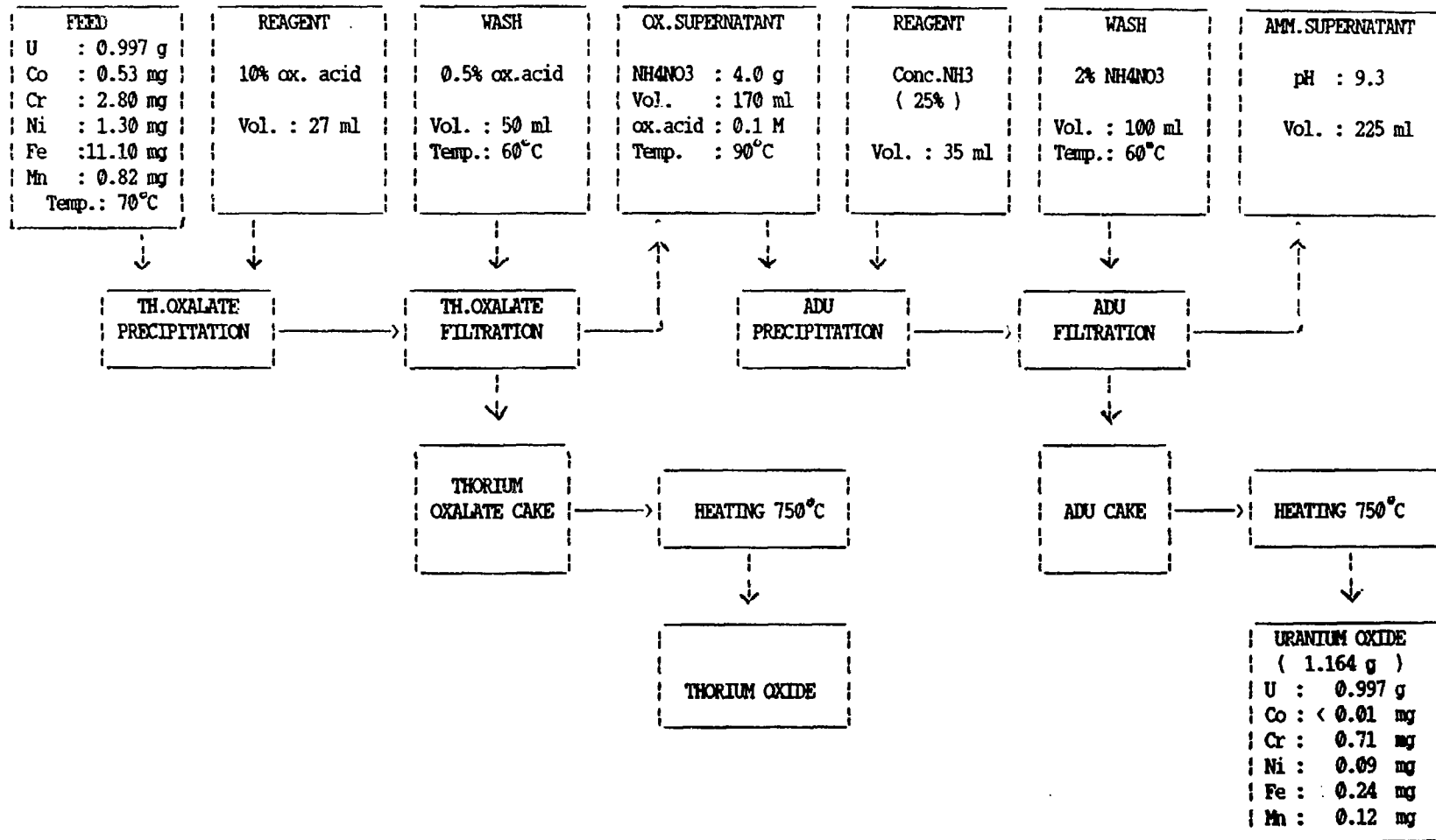


Fig. 5

Distribution of stainless steel corrosion products during the separation of thorium and uranium by precipitation

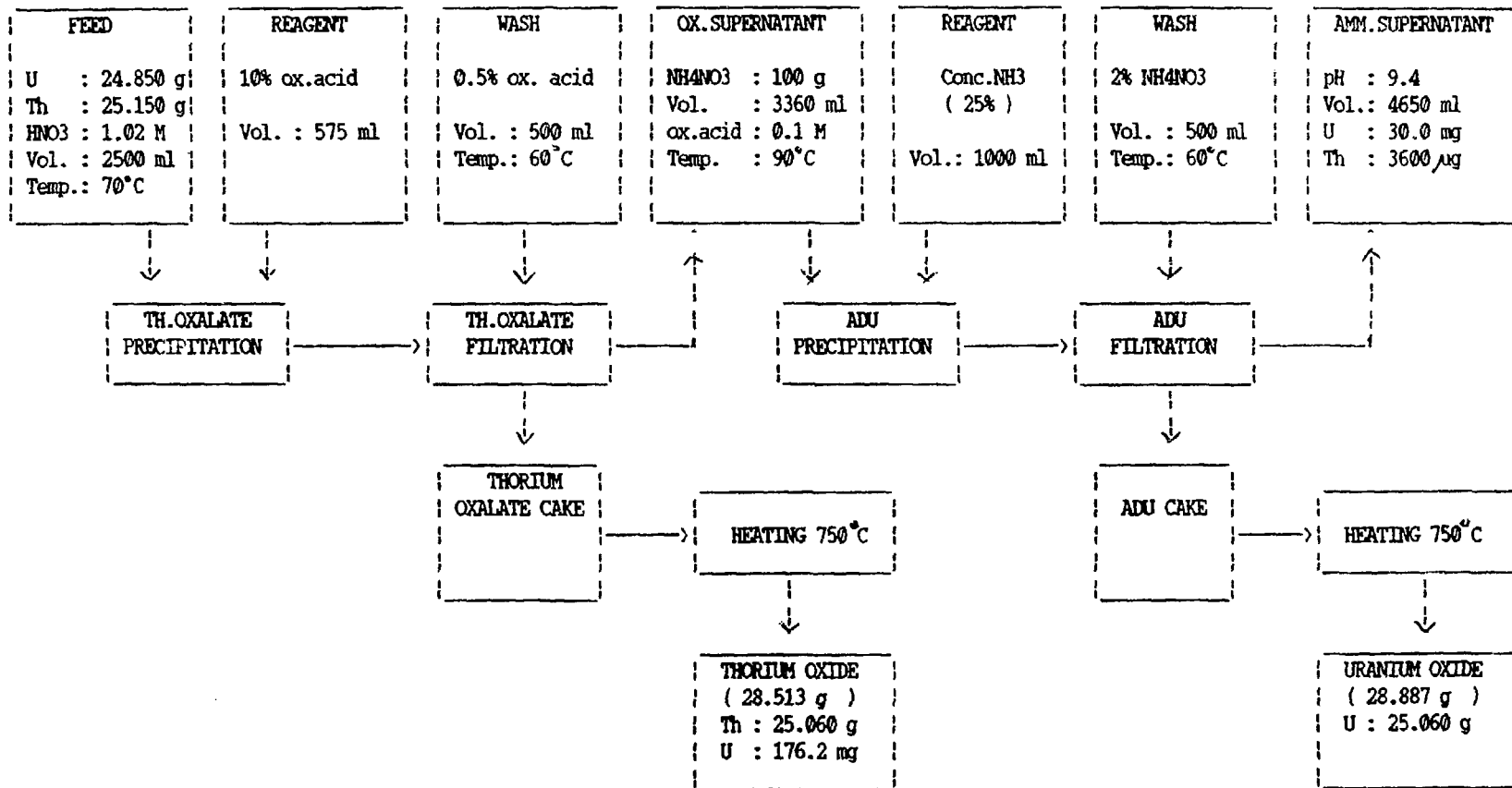


Fig. 6

Scheme of separation of 10 g/l thorium and 10 g/l uranium from 2.5 Ltrs. of 1 M HNO₃

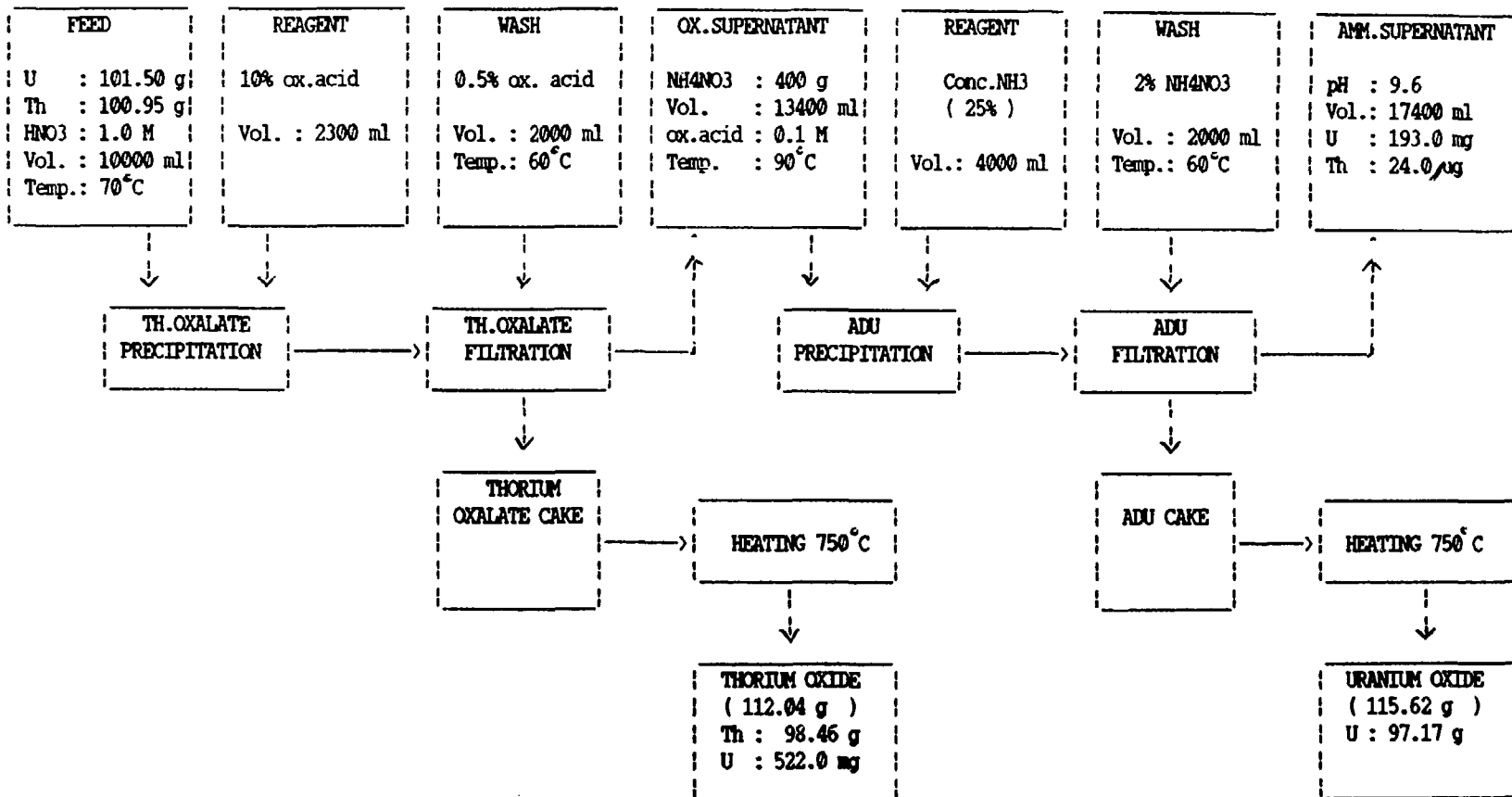


Fig. 7

Scheme of separation of 10 g/l thorium and 10 g/l uranium from 10 Ltrs. of 1M HNO₃

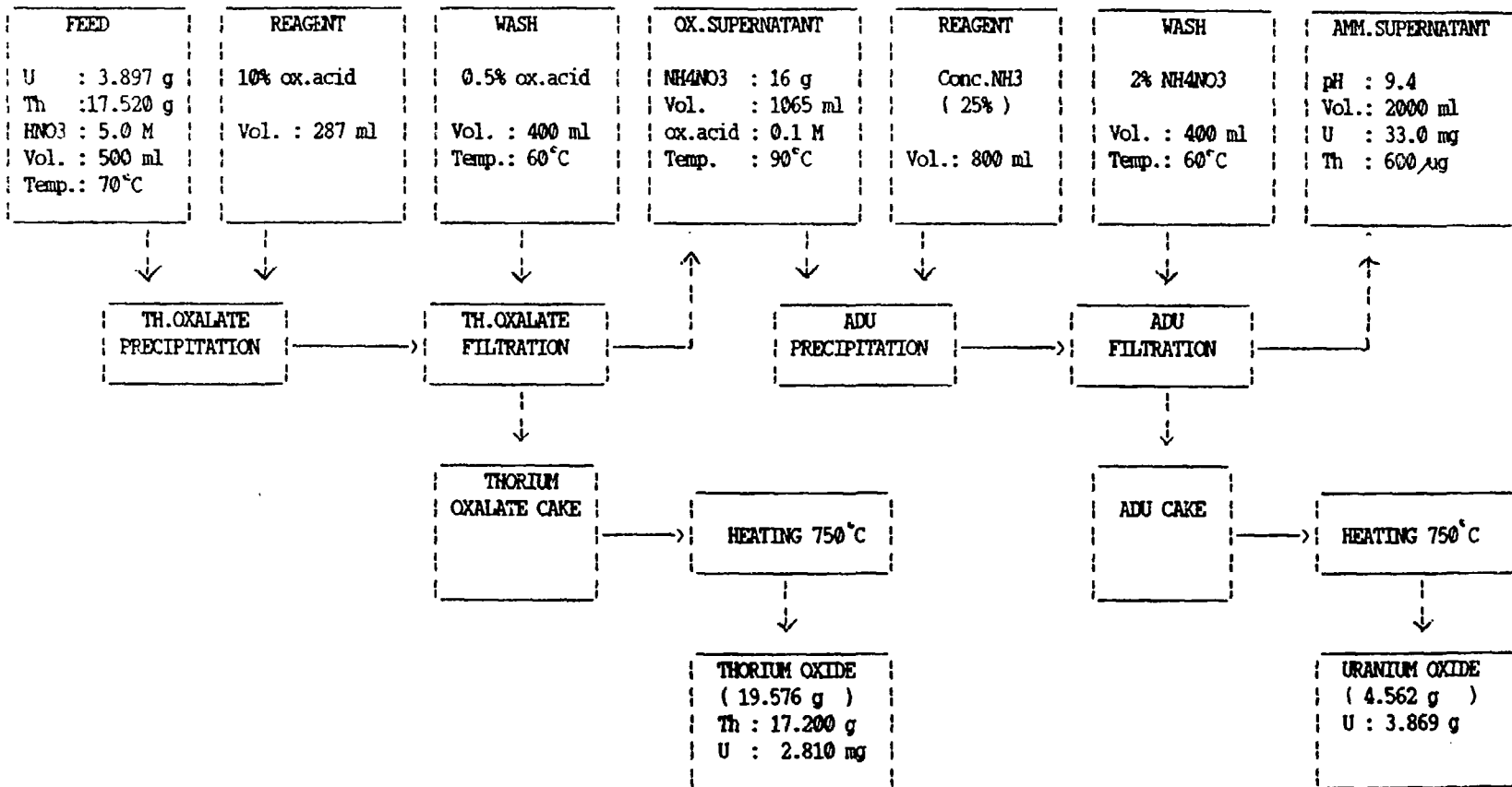


Fig. 8

Scheme of separation of 35 g/l thorium and 8g/l uranium from 500 ml of 5 M HNO3

