

URANIUM-PLUTONIUM PARTITIONING BY PULSED COLUMN IN THE FIRST CYCLE OF THE THREE CYCLE THERMAL OXIDE REPROCESSING PLANT

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ABSTRACT

The Thermal Oxide Reprocessing Plant (THORP) is currently being commissioned at the Sellafield, England site of British Nuclear Fuels Plc, and will use the Purex process to reprocess irradiated oxide fuel from British, European and Japanese reactors. Careful initial design of the chemical flowsheet, combined with extensive small and full scale, fully active and inactive development work resulted in an efficient three cycle flowsheet with the minimum number of liquid waste streams. The use of salt-free reagents allows these wastes to be evaporated and vitrified for long term storage. The effect of technetium on the uranium-plutonium partitioning process and of neptunium on the purification of the uranium product received particular attention during the development work.

INTRODUCTION

The Thermal Oxide Reprocessing Plant (THORP) is currently being constructed and commissioned at the Sellafield, England reprocessing site of British Nuclear Fuels Plc, and will reprocess irradiated oxide fuel from British, European and Japanese reactors using the Purex solvent extraction process. Chemical flowsheet and process equipment design for the solvent extraction cycles of THORP was governed by three main factors.

First, it was required to minimize the environmental impact of the new plant and, in particular, to reduce the amount of activity discharged from the plant in liquid wastes. This was achieved by replacing the normal reagents added to the process with "salt-free" reagents which do not restrict the ability to concentrate and encapsulate waste streams, and by employing three solvent extraction cycles instead of the more normal five, thus reducing at source the number of waste streams.

Second, it was desired to minimize the extent, size and complexity of the process equipment in contact with radioactive material. This helps to provide a low operator radiation dose and minimizes both capital and operating costs. This led to the adoption of an "early split" chemical flowsheet, with uranium and plutonium separated in the first cycle of solvent extraction, and was supported by the use of single subsequent uranium and plutonium purification cycles in the three-cycle process (1).

Third, the relatively high plutonium and fission product content of irradiated oxide fuel led to the use of pulsed, plate columns as the solvent extraction contactors, instead of mixer settlers that are used at Sellafield for Magnox Uranium metal fuel reprocessing. The high surface area to volume ratio of pulsed columns allows the higher plutonium concentrations to be handled with criticality safety, whilst their shorter aqueous and solvent phase residence times minimizes the degradation of the solvent by the fission products in the aqueous phase.

The Chemical Separation Plant flowsheet, thus developed, with three cycles of solvent extraction is shown in Fig. 1.

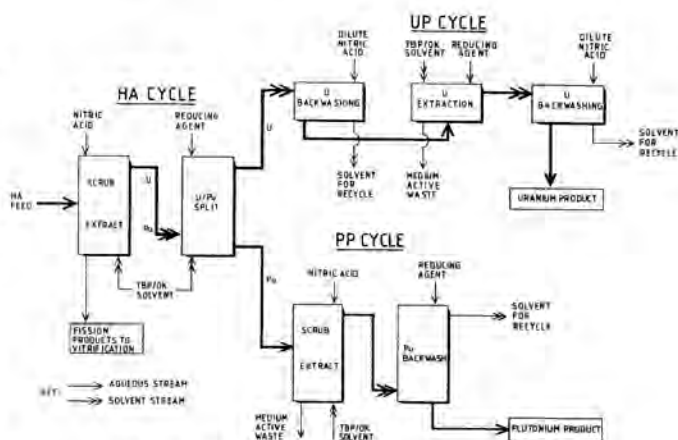


Fig. 1. Thorp chemical separation plant.

The HA Cycle separates the bulk of the fission products from the uranium and plutonium and then partitions the uranium from the plutonium. The single UP and PP Cycles further purify the uranium and plutonium nitrate product streams respectively, before these pass on to the finishing sections where they are converted to uranium trioxide and plutonium dioxide. Pulsed columns are used in the HA and PP Cycles, whilst mixer settlers are employed in the UP cycle where plutonium concentrations and activity levels are low.

This flowsheet, and the process equipment to operate it, has undergone extensive development and proof testing at Sellafield over the last 10 years using a range of pilot plants, including a full size uranium-active replica of the HA cycle (the Pulsed Column Test Rig or PCTR), a series of small and intermediate scale alpha-active pilot plants and a small-scale fully active pilot plant (the Miniature Pilot Plant or MPP) which used irradiated oxide fuel as its feed material. Full details of these pilot plants and the development programs that were carried out are published elsewhere (2).

This paper outlines the HA and UP cycle flowsheets and process equipment, shows how the influence of the contaminant technetium was allowed for in the HA cycle uranium-plutonium partitioning step design and indicates how the

chemistry of the contaminant neptunium influenced the design of the single UP cycle.

THE THORP HA AND UP CYCLES

The THORP HA Cycle consists of 4 main pulsed columns, two mixer settlers and equipment to remove solvent from the waste and plutonium product streams (Fig. 2).

The HA and HS columns extract the uranium and plutonium in the dissolved nuclear fuel feed into 30% tri-butyl phosphate in odorless kerosene diluent (TBP/OK), and scrub out partially extracted fission products using nitric acid. The aqueous highly active waste stream flows via a steam strip column to remove TBP traces and then onto the vitrification plant and storage. The 1BX column and 1BXX mixer settler separate plutonium from uranium in the solvent product from the HS column by chemically reducing the plutonium so that it is no longer extractable and passes into the aqueous phase. The reducing agent is salt-free uranium IV, stabilized using hydrazine against re-oxidation by the nitrous acid present in plant liquors. The plutonium-in-aqueous stream flows to the 1BS column, where uranium traces are removed by extraction with TBP/OK before passing to the kerosene wash column, to remove traces of TBP and then on to the PP cycle. The uranium-in-solvent stream flows to the 1C mixer settler where it is backwashed into dilute acid before passing to the UP Cycle.

The UP Cycle consists of feed pre-conditioning equipment, three mixer settlers and a product evaporator (Fig. 3). The UP1 mixer settler extracts uranium into 20% TBP/OK and, because of neptunium valency pre-conditioning and the use of salt free aqueous hydroxylamine nitrate to reduce the plutonium, most of these two contaminants are rejected into the aqueous waste stream. Further hydroxylamine nitrate re-

duction is used in the UP2 mixer settler to complete the removal of the plutonium, whilst the UP3 mixer settler back-washes the uranium into the aqueous phase prior to the evaporator.

THORP FLOWSHEET REQUIREMENTS

The THORP flowsheet is designed for the reprocessing of uranium oxide fuels irradiated up to 40 GW days per ton and 5 years after discharge from reactor. It has been further demonstrated capable of dealing with proportions of mixed uranium and plutonium oxide fuels with irradiation up to 60 GW days per ton. The uranium product specification is shown in Table I, together with the Decontamination Factors (DF's) necessary to achieve this specification with reference fuel.

For the uranium stream contaminants plutonium, neptunium and technetium, initial alpha-active trials indicated the DF's that were likely to be required from the HA and UP cycles if the uranium product specification was to be achieved (Table II). A large Pu DF was required and most of this would need to be achieved in the HA Cycle, leaving a DF of a few hundred to be achieved in the UP Cycle.

For neptunium, although a smaller overall DF was needed, it was known that the feed to the HA Cycle contains predominantly the extractable Np VI state and that the 1BX reducing conditions would produce extractable Np IV. Hence, only a small DF could be expected in the HA Cycle, with the bulk DF therefore needing to be achieved in the UP Cycle.

For technetium, it was found in initial trials that only about one third of the amount in the feed was extracted in the HA/HS system and that this was almost entirely reduced to the inextractable Tc VI in the 1BX column, this therefore following the plutonium stream. All the required technetium

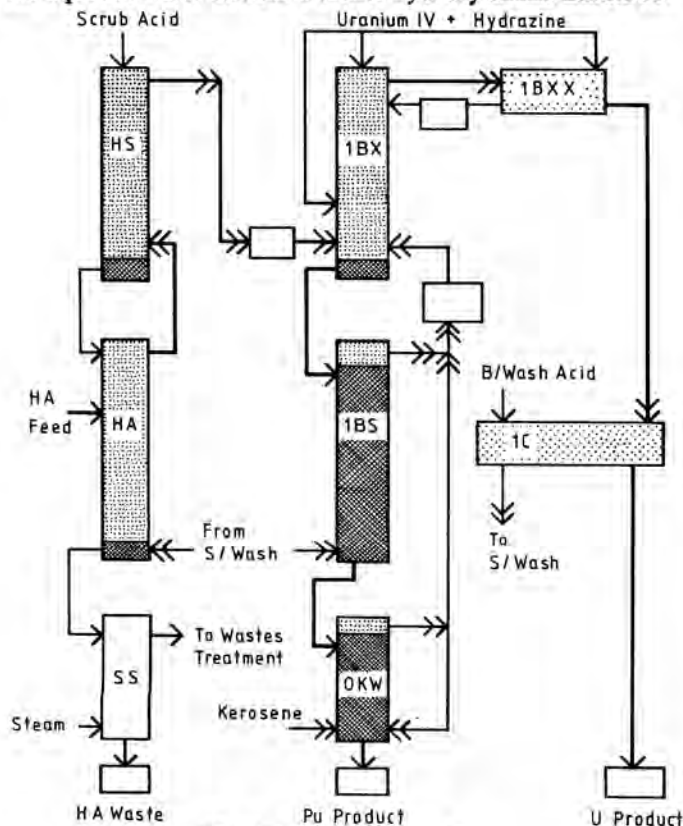


Fig. 2. Thorp HA cycle.

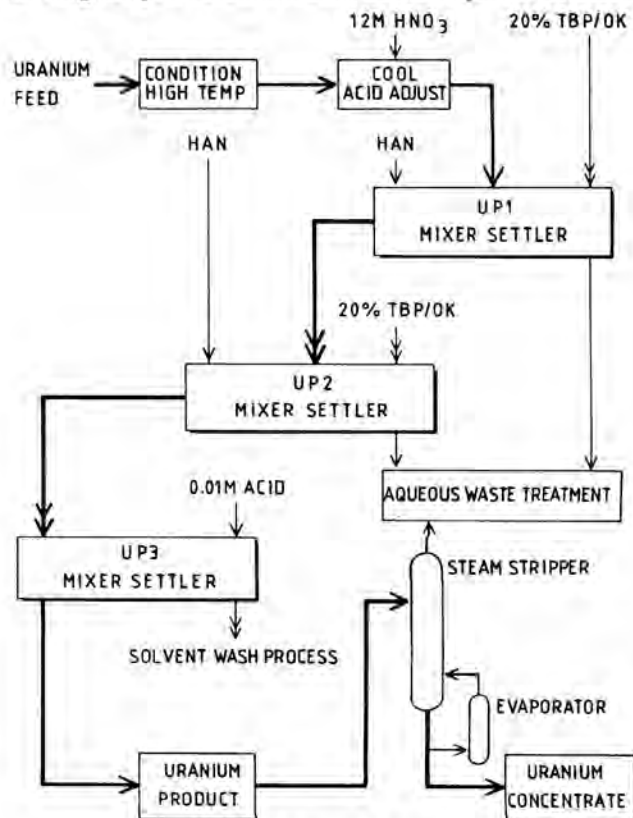


Fig. 3. Thorp UP cycle.

TABLE I

THORP Product Specification and Required Decontamination Factors

Species	Specification	Decontamination Factor Required*	
Total alpha (Bq g ⁻¹ U)	250	7.65 x 10 ⁻⁵	
Plutonium (Bq g ⁻¹ U)	208		
Neptunium (Bq g ⁻¹ U)	42		314
Technetium (ppm)	4		274
*Decontamination factor (DF) = $\frac{\text{Contaminant}/U \text{ in feed}}{\text{Contaminant}/U \text{ in product}}$			

TABLE II

Uranium Stream Decontamination Factors

	Pu	Np	Tc
DF Required across HA & UP	7.65 x 10 ⁵	314	274
DF Required across HA	3300	1.65	274
DF Achieved across HA	> 3300	1.67	> 300
DF Required across UP	232	190	1
DF Achieved across UP	> 560	> 3.7 x 10 ³	10

DF could therefore be achieved in the HA Cycle, with a DF of over 300 being found. Subsequent trials with a fully active irradiated fuel feed showed that, although the technetium continued to follow the plutonium stream from the 1BX column, all of it was extracted in the HA/HS system, because of the formation of an extractable technetium-zirconium complex (3). Furthermore, the technetium was found to react catalytically with the hydrazine stabilizer in the 1BX/1BS system so that the majority of the stabilizer was destroyed in this side reaction. The design of the 1BX column to provide the required plutonium DF therefore had to take the technetium effect into account and provide a means of reducing this undesirable side reaction.

URANIUM-PLUTONIUM PARTITIONING IN THE HA CYCLE AND THE EFFECT OF TECHNETIUM

The original design of the 1BX column had been aqueous-continuous, with droplets of solvent rising through a continuous aqueous phase to coalesce at a top phase interface. This followed conventional design practice in that it dispersed the phase with the highest flowrate, the solvent-aqueous flowrate ratio in 1BX being over 5. This mode of operation resulted in the filling of a relatively high fraction of the volume of the column (about 20-30%) with dispersed phase droplets (the dispersed phase hold-up or DPHU), giving a high surface area for mass transfer.

However, this mode of operation had three drawbacks. Firstly, the long aqueous phase residence time provided maximum time for the undesirable technetium-hydrazine reaction and secondly the low aqueous phase velocity produced unac-

ceptably high axial mixing which off-set the mass transfer advantage of the high solvent DPHU. Thirdly, full size PCTR trials of the aqueous continuous 1BX column showed it to be difficult to operate stably, with sudden transitions occurring between low and high DPHU's (4).

It was therefore decided to operate the 1BX column in the solvent-continuous mode, with solvent as the continuous phase flowing up the column, and aqueous droplets containing the U IV reductant falling down the column to coalesce at a bottom interface. This minimized aqueous residence time and substantially reduced the extent of the technetium-hydrazine reaction. The questions which then had to be answered were whether this new arrangement would (a) produce stable operation and an adequate DPHU, (b) give acceptably low axial mixing and (c) provide a plutonium DF that would meet flowsheet requirement. A program of development work was carried out to answer these questions.

Stability of Operation of Solvent Continuous 1BX Column

Trials on the PCTR with a full size replica of the THORP solvent continuous 1BX column produced DPHU profiles at three specific throughputs and pulse energy combinations as shown in Fig. 4.

DPHU's in the range 4-18% were achieved which are quite satisfactory for mass transfer, and there was no evidence of the unstable DPHU transitions experienced with aqueous-continuous operation.

1BX Column Axial Mixing

Axial mixing was measured in the full size column by injecting a pulse of solvent-soluble dye tracer into the solvent feed to the column and sampling at two points up the column over a time period, to measure how much the pulse is spread out between these points. A typical result is shown in Fig. 5 and it is clear that axial mixing is minimal, with calculated Peclet numbers as high as 140-200.

Uranium-Plutonium Partitioning Performance

Because the full size PCTR 1BX column could not use plutonium, a program of work was carried out comparing drop sizes, DPHU's, interfacial areas and axial mixing in the full size column with those in a 1:200 scale replica column, which did contain plutonium, under conditions that produced a satisfactory plutonium DF in the smaller column. Plutonium mass transfer coefficients could then be calculated from the

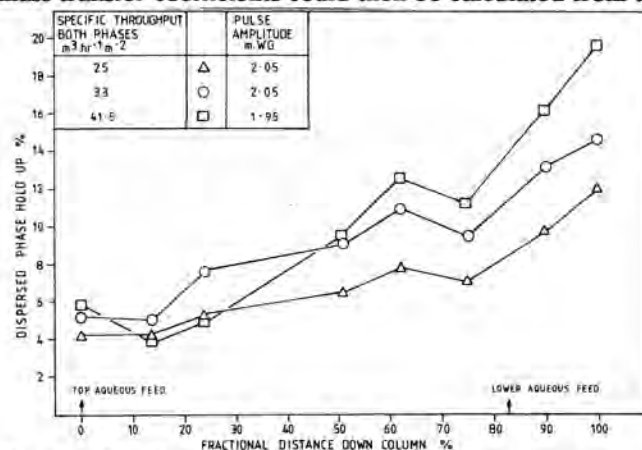


Fig. 4. 1BX column DPHU profiles solvent continuous operation.

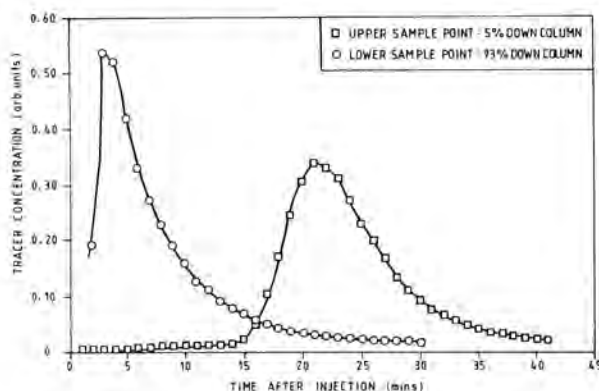


Fig. 5. Full size IBX pulsed column axial mixing by tracer injection.

1:200 scale column data and used with the full size DPHU, drop size and interfacial area data to estimate the partitioning performance of the full size column. For this calculation process to be reliable, it was necessary to demonstrate that mass transfer conditions in both sizes of column were similar.

It was not possible to measure DPHU profiles in the 1:200 scale column, but spot checks showed that average DPHU's of 6-10% were achieved at specific throughputs and pulse amplitudes similar to those used in the full size column. These compare well with the full size DPHU profiles. Axial mixing in the 1:200 scale column was measured by the same pulse injection technique as used in the full size column and similarly high Peclet numbers of 110-290 found, confirming low axial mixing.

Drop size distributions were measured at 3 positions in the 1:200 scale column and a single position in the full size column by photographing the dispersion, counting the drops and measuring them against an internal calibrated wire. An analysis of drop sizes by number and by surface area is shown in Fig. 6.

Although there are differences between the two columns in the number of smaller diameter (less than 1mm) drops present, the proportion of the surface area contributed by each drop diameter range is very similar in each column. It is also clear that in both columns the greatest proportion of the surface area is contributed by the relatively fewer drops of above 1mm diameter. The Sauter mean diameters for the dispersions (the diameter that drops of a uniform size would need to be to have the same interfacial area as that observed for the drop population) were calculated as 1.7mm and 1.9mm for the full size and 1:200 scale columns respectively. When these values were combined with the measured DPHU's, the specific interfacial area profiles for each column were found, as shown in Fig. 7. It can be seen that the full size and 1:200 scale results are very similar.

It was thus possible to use the mass transfer coefficients calculated from the 1:200 scale data with full size DPHU and interfacial area profile data to calculate the change in plutonium concentration with height up the full size THORP 1BX column. This gave plutonium DF's over the full height of the THORP column well in excess of the 3,300 required, thus achieving the required flowsheet performance whilst minimizing the effect of technetium on the system.

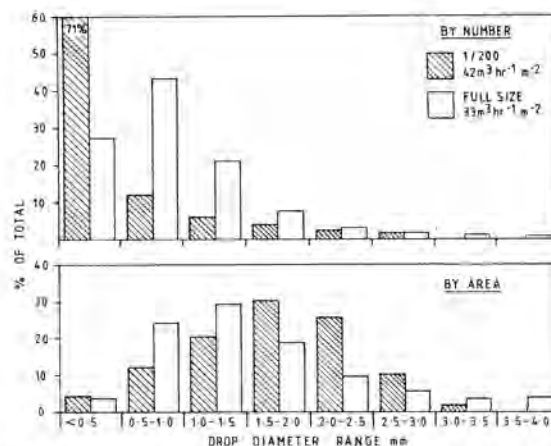


Fig. 6. Drop size distributions: full size & 1/200 IBX columns.

NEPTUNIUM AND PLUTONIUM DECONTAMINATION IN THE UP CYCLE

Neptunium is present in the feed to the UP Cycle as extractable Np IV and would therefore follow the uranium product in UP1 and UP2 if left untreated. Plutonium is present in the feed as extractable IV and this would also follow the uranium product.

The only inextractable state of neptunium is Np V (5), and it had been reported (6) that heating Np IV at low acidity would form Np V. A series of alpha-active trials at low acidities and high temperatures allowed the optimum conditions for maximum Np V production to be established, and hence a conditioning process for the UP1 feed liquor to be designed. For efficient uranium extraction in UP1, the feed liquor so produced needed to be re-acidified, and further trials showed that this could be achieved without destroying the Np V by suitable reduction in the liquor temperature before re-acidification took place.

To produce a plutonium DF in UP1 it was clear that chemical reducing conditions were needed to convert extractable Pu IV to inextractable Pu III. However, simultaneous conversion of Np V to extractable Np IV had to be avoided and, since U IV was known to reduce neptunium in this way, the use of this reductant in the UP Cycle was rejected. Experimental trials showed that plutonium reduction could be achieved without neptunium also being reduced by the use of

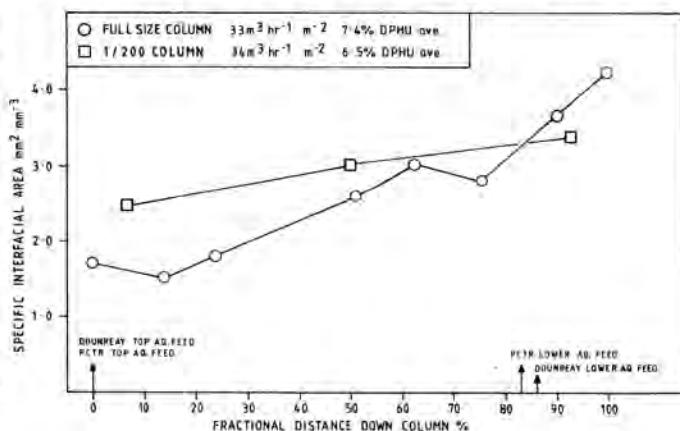


Fig. 7. Specific interfacial area profiles.

hydroxylamine nitrate reductant under optimized temperatures and acidities in UP1 and UP2.

Alpha-Active and fully active trials of the UP cycle flowsheet designed in this way gave plutonium and neptunium DF's comfortably in excess of requirements (Table II) and also showed a good technetium DF.

OVERALL HA AND UP CYCLE PERFORMANCE

A series of fully active Miniature Pilot Plant trials of the combined HA and UP Cycle flowsheets allowed the uranium product quality achieved to be compared with the specification and this showed that the THORP uranium product quality could be met comfortably with only the two cycles of solvent extraction (Table III).

CONCLUSIONS

This paper has showed how a combination of careful initial flowsheet design, chemical flowsheet development under alpha and fully active conditions, and equipment development at full and intermediate scale has produced an efficient THORP flowsheet with the minimum number of cycles and waste streams. The use of salt-free reagents allows these wastes to be evaporated and vitrified for long-term storage.

Important factors in the success of this development work were the ability to test flowsheets under fully radioactive conditions and the close integration between the chemical flowsheet and equipment development programs, with results in one area quickly influencing the work program in the other.

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TABLE III

Compositions of Uranium Product from Miniature Pilot Plant (Corrected To Basis Of Reference Fuel, 40 GWD/tU Burn-up, 5 Year Cooled)

Uranium Product	Pu Alpha Bq/g U	Np 237 Bq/g U	Tc 99 ug/g U
Pilot Plant	<2	<1	<1
Specification	208	42	4

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