THE THERMAL OXIDE REPROCESSING PLANT AT SELLAFIELD: Four Years of Successful Treatment of Irradiated Nuclear Fuel

C. Phillips, International Technology Manager, Thorp Group
British Nuclear Fuels Plc, B570/4, Sellafield, CA20 1PG, UK

ABSTRACT

The Thermal Oxide Reprocessing Plant at British Nuclear Fuels' Sellafield site is designed to treat irradiated fuel from UK Advanced Gas-Cooled Reactors and European and Japanese Light Water Reactors, so as to separate recyclable uranium and plutonium from the 3-4% fission product waste. The plant started operating in March 1994 with the shearing and dissolution of its first irradiated fuel in the Head End Plant. In January 1995 the Chemical Separation Plant commenced processing this dissolved irradiated fuel feed solution and by late 1998 over 1800t of irradiated fuel had been reprocessed. The plant is now being steadily and successfully ramped up to its normal operating throughput. Following the completion of the baseload fuel Thorp will be able to reprocess fuel from worldwide nuclear reactors

The performance of Thorp has been excellent, with both the mechanical Head End and the three-cycle Purex solvent extraction process and equipment operating better than predicted. In particular the uranium-plutonium separation stage, which received intensive development to deal with the effects of the fission product technetium, has given an overall separation performance well in excess of the minimum flowsheet requirement. Decontamination of the uranium and plutonium products from fission products has in general been better than flowsheet requirements and the solvent extraction equipment has operated stably under the automatic controls developed during the R&D programme.

The uranium and plutonium products from Thorp have routinely met international specifications for the recycle of these materials as new nuclear fuel. Losses of uranium and plutonium into waste streams have been in line with expectation and each amount to about 0.2% of the feed at most.

The "salt free" flowsheet design for Thorp allows all Head End and nearly all Chemical Plants Wastes to be vitrified or encapsulated in cement, and the operation of these processes with the Thorp liquid wastes has been shown to be both effective and efficient. The small amounts of liquid wastes that are discharged off site contain at most no more than 4% of the Sellafield Annual Discharge Limit and typically much less than 1% of this limit.

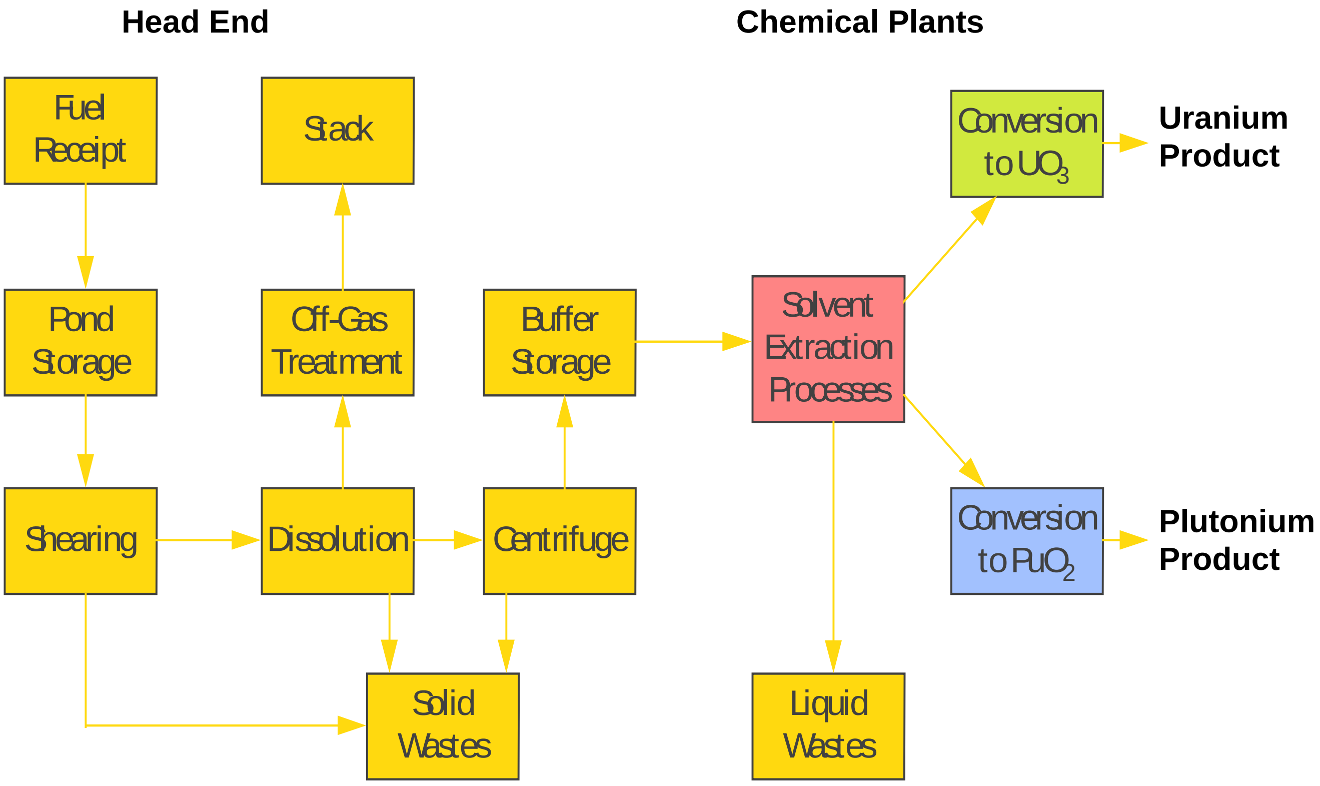
The paper compares with flowsheet predictions certain key fission product and transuranic decontamination factors achieved in Thorp, shows how waste stream discharges are a small fraction of Sellafield Site discharge limits, demonstrates how uranium-plutonium separation performance has compared with expectation and summarises the overall performance of Thorp. The paper concludes that Thorp has met or exceeded its design expectations, and is a successful and environmentally responsible way of treating irradiated nuclear fuel.

INTRODUCTION

The Thermal Oxide Reprocessing Plant (Thorp) is one of the services offered by British Nuclear Fuels Plc at its Sellafield UK site for the treatment of spent nuclear fuel. It reprocesses irradiated oxide nuclear fuel from British, Japanese and European Light Water and Gas Cooled Reactors. In the Head End Plant irradiated fuel is received, stored under water, sheared into 50mm lengths, dissolved in nitric acid and residual solids removed by centrifuge. In the Chemical Plant the Purex solvent extraction process with tri-butyl phosphate (TBP) in kerosene as solvent is used in a three-cycle process to separate uranium, plutonium and fission products (Fig 1). There are further facilities for the conversion of plutonium nitrate to plutonium dioxide by oxalate precipitation and uranyl nitrate to uranium trioxide by thermal denitration. These products are then suitable for recycle into fresh reactor fuel.

The Head End processes generate mainly intermediate level solid wastes and these are encapsulated in cement for long term storage. The Chemical Plants generate High Level and Intermediate Level liquid wastes which are vitrified, and a small amount of Low Level liquid waste which is floc-treated to remove residual activity before discharge to sea. The floc so formed is also encapsulated in cement. The Head End and Chemical Plants are integrated, with all process stages and services in one building.

FIGURE 1
Thorp Unit Processes



During the first 10 years of operation of Thorp there is a committed throughput of 7,000 tonnes based on irradiations up to 40 GW days per tonne and out-of-reactor cooling time of no less than 5 years. Subsequently, more highly irradiated fuels are planned to be reprocessed. A full account of the development, design and construction of Thorp is given elsewhere (1), (2), (3). With some 15,000 process vessels, 300,000 metres of pipe, 3 million metres of electrical and instrument cabling and 14,000 instrument loops contained in a building 500m long, 150 m wide and 50 m high, Thorp is one of the biggest and most complex chemical plants in the world.

Construction of Thorp was completed to programme and budget in 1992, and commissioning with water, acid and uranium was finished during 1994. Irradiated fuel was introduced into the Head End in early 1994 and into Chemical Plants a year later. By late 1998, Thorp had processed a total of over 1806t of UK Advanced Gas-Cooled (AGR) fuel, Boiling Water Reactor (BWR) fuel and Pressurised Water Reactor (PWR) fuel from UK, European and Japanese customers.

THORP DESIGN PROVISIONS

Head End Plant

In the Head End the main design provisions were:

- **a)** The fuel shear is designed with a vertically acting shear blade and a series of different "gags" or clamps to hold the full worldwide range of oxide fuel assemblies. Sheared fuel, including all cladding material, falls by gravity into one of three batch dissolvers. Provision is made for the remote maintenance and replacement of the blade and gag assemblies, whilst the shear hydraulic ram, and fuel incremental feed ram, are situated outside the radiation shielding to allow hands-on maintenance.
- **b)** Batch dissolution of the fuel is employed using three dissolvers on a rotating basis. This allows full monitoring of the dissolver liquor before it is fed to the Chemical Plant, and provides for each batch of fuel cladding "hulls" to be monitored for undissolved material prior to encapsulation, and returned for re-dissolution if required. Batch dissolution also allows the amount of acid used for each batch to be adjusted in accordance with the differing uranium to cladding proportions of each type of fuel, so as to produce a consistent product concentration.
- **c)** Removal of undissolved solids is done using one of two suspended bowl centrifuges, with the motors and gear boxes situated outside the radiation shielding for ease of maintenance. Recovery of the solids from the centrifuge bowls is accomplished batch-wise by water jet and the resulting slurry sent direct to cement encapsulation. This system avoids the production of an additional spent filter waste stream.
- **d)** Gravity feed and no-moving part fluidic liquid pumps are used in the shielded active areas of the plant, to avoid the need for maintenance throughout the life of the plant
- **e)** Simple robust mechanical designs were developed using full size inactive pilot plants to prove reliability, and these allow process handling operations to be achieved by simple crane movements. Provision for remote maintenance was made where this was shown to be necessary.

Chemical Plant

Four main principles governed the design of the Chemical Plant solvent extraction cycles:-

- a) In order to minimise the amount of activity discharged in liquid wastes, the chemical reagents fed to the process to adjust valency states are "salt-free" so that they do not restrict the ability to concentrate and encapsulate waste streams.
- b) It was required to minimise the extent, size and complexity of the process equipment in contact with radioactive material, so as to minimise operator radiation dose, reduce capital and operating costs, and reduce the number of waste streams. This was achieved by using an "early-split" flowsheet with U-Pu separation in the first solvent extraction cycle. Careful flowsheet design, development and proving also allowed single cycles only to be used for the subsequent uranium

and plutonium purification stages. In particular, close attention was paid to the chemistry of neptunium (5) so as to direct it into the appropriate waste streams. This allowed a three-cycle flowsheet to be used rather than the previous typical five-cycle one, thus reducing at source the number of waste streams produced.

c) Pulsed, perforated plate columns are used as the solvent extraction contactors in the Highly Active (HA) and Plutonium Purification (PP) cycles (Fig 2) to allow critically safe operation with the higher plutonium concentrations of oxide fuel. Their relatively short aqueous-solvent contact time also minimises solvent degradation from the increased amounts of fission products in oxide fuel.
d) All equipment in contact with radioactive material is designed for minimum or no maintenance throughout the life of the plant. In the highly active parts of the Chemical Plant, no moving mechanical parts are used, and fluidic and compressed air devices are employed for liquid pumping and instrumentation.

Thorp Overall

Thorp is built on an existing nuclear site which contains a uranium metal fuel reprocessing plant, and its associated upstream and downstream plants. A major design target for Thorp was that it should contribute no more than 10% at most to the activity in discharged liquid wastes from the Sellafield site.

Development Work

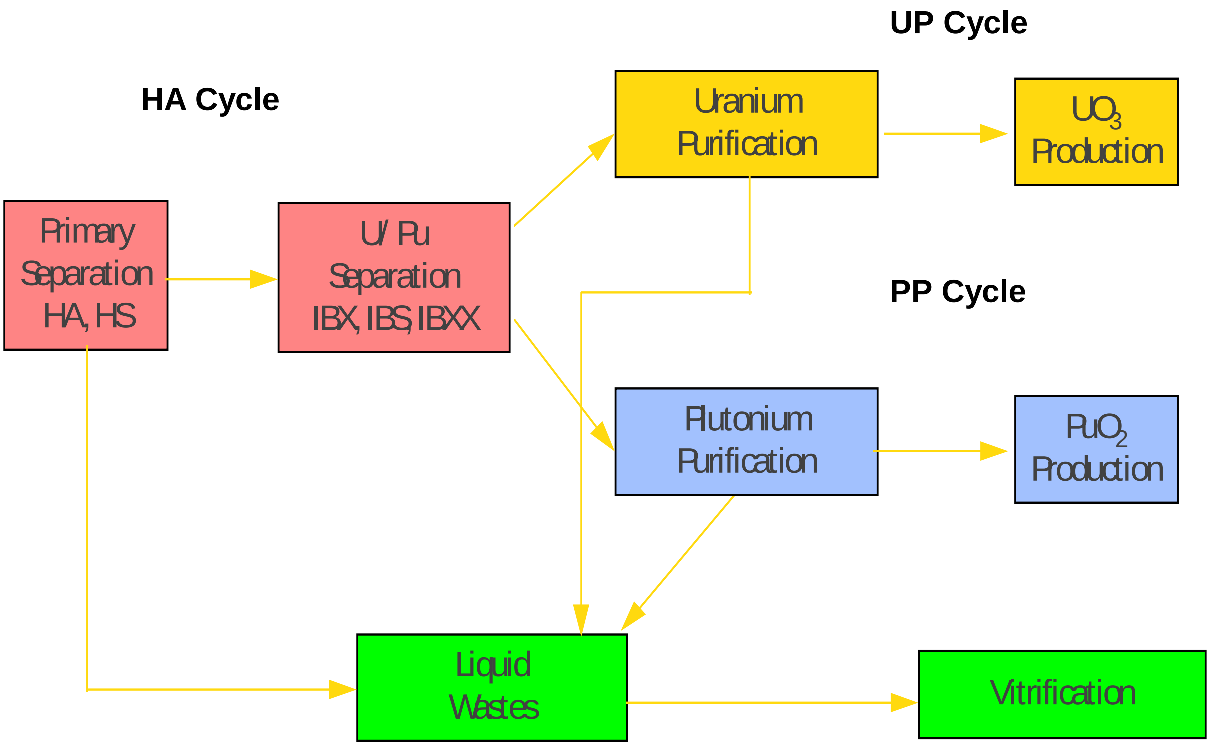
The realisation of these design provisions and principles necessitated a comprehensive research and development programme which was carried out during the period from the late 1970's to the late 1980's (3). An extensive series of pilot plants was designed, built and operated during this period, ranging from full size inactive replicas of major sections of Thorp, through intermediate scale plutonium-containing pilot plants operated in glove boxes, to small scale fully active replicas of most of Thorp using actual irradiated fuel. To underpin this pilot plant work and the extensive safety assessments that were required for Thorp, a range of fundamental studies was also done of the process chemistry and mechanical engineering of the Thorp processes.

CHEMICAL PLANT FLOWSHEET

The three-cycle Purex flowsheet is shown in Figure 2. The HA and HS pulsed columns in the HA cycle primary separation section extract the uranium and plutonium from the nitric acid solution of the fuel into the 30% TBP in kerosene solvent, leaving almost all the fission products in the acid aqueous phase, which flows to the Vitrification Plant. The uranium and plutonium are then separated in the 1BX and 1BS pulsed columns and 1BXX mixer-settler. This is done by chemically reducing the plutonium using salt-free uranium IV produced on site from uranium VI and chemically stabilising the resultant Pu(III). The presence of significant technetium, which is completely extracted in HA/HS, adversely affects the chemistry of plutonium reduction by reacting with the chemical stabiliser and causing re-oxidation of the plutonium. Extensive development work (4),(7) allowed this problem to be overcome by careful control of residence times and temperatures.

The plutonium stream passes to the single plutonium purification (PP) cycle where pulsed columns and 30% TBP/kerosene are again used to purify the plutonium product from the principal contaminant technetium and residual uranium, ruthenium, caesium and cerium. The single uranium purification (UP) cycle uses 20% TBP/kerosene and mixer-settlers to remove neptunium, plutonium, ruthenium, caesium and cerium from the uranium product. Careful valency conditioning of the neptunium and plutonium prior to solvent extraction, and the use of hydroxylamine nitrate reductant, achieves high simultaneous neptunium and plutonium decontamination (5) in a single solvent extraction cycle. Single Intermediate Level waste streams are produced by the UP and PP cycles, and because they are salt free, these streams can be routed to vitrification along with the High Level waste.

FIGURE 2
Thorp Chemical Plant Flowsheet



COMMISSIONING OF THORP

Commissioning of Thorp followed a logical sequence with five stages (6):

1. Water and mechanical equipment commissioning to set equipment to work, check liquid pumping devices and calibrate vessels.
2. Use of inactive solid simulants to test solids handling equipment in the Head End, Uranium Trioxide and Plutonium Dioxide areas.
3. Nitric acid and TBP/kerosene solvent commissioning to set up and test dissolution, the 2-phase solvent extraction equipment, and initially set up instrumentation and control devices.
4. Uranium, nitric acid and TBP/kerosene commissioning to obtain unirradiated fuel dissolution data, pulsed column and mixer settler mass transfer and maximum throughput data, and refine instrumentation and control.
5. Irradiated fuel, nitric acid and TBP/kerosene commissioning to prove the complete process with different fuels of steadily increasing irradiation and decreasing cooling time, to verify that uranium and plutonium product qualities are achieved, and to demonstrate that waste stream contents are at the predicted levels.

The commissioning work was generally straightforward and successful, with plant operation and performance following closely that predicted from the pilot plant development trials. All active commissioning tests were completed by mid 1997 to the satisfaction of the UK Nuclear Regulators

(Nuclear Installations Inspectorate and Environmental Agency) and Thorp received its full Operating Licence in August 1997. Ramp-up of the throughput of the Plant has been rapid, with 65, 208, 408 and over 750 tonne (pre-irradiated) reprocessing achieved in financial years 94/95, 95/96, 96/97 and 97/98 respectively.

PERFORMANCE OF THE CHEMICAL PLANT PROCESSES

A comparison of the irradiated fuels reprocessed in Thorp up to late 1998 with the fuel provided for in the reference design is given in Table 1.

TABLE 1
Comparison of Fuel Processed with the Design Provision

	Design Provision	Fuel Processed
Irradiation GWD/t	40	10 to 39
Cooling Time Years	5	5 to 19
Plutonium Content %	100	28 to 96
Neptunium 237 Content %	100	23 to 95
Technetium 99 Content %	100	23 to 85
Ruthenium 106 Content %	100	1 to 17
Caesium 134 Content %	100	1 to 22
Caesium 137 Content %	100	19 to 98
Cerium 144 Content %	100	1 to 14

It can be seen that, with the exception of ruthenium-106, caesium-134 and cerium-144, fuel characteristic of the design provision has been reprocessed. The exceptions arise because, thus far, the higher burn-up fuel processed has been the longer cooled, allowing these relatively short half-life species to decay significantly.

The plant has been operated at throughputs ranging from 3 to 5 tonne uranium per day and has been chemically and hydraulically stable throughout, showing the value of the extensive development work carried out on both the chemistry and engineering of process equipment. The performance of the Chemical Plant was studied by looking at fission product separation efficiency, uranium-plutonium separation efficiency, product qualities, losses of uranium and plutonium to waste streams, and the volumes and content of contaminants in waste streams.

Chemical Plant Separation Efficiency

Table 2 illustrates typical fission product decontamination factors (DF's) across the HA and HS pulsed columns for technetium, ruthenium, caesium and cerium, compared with the THORP reference flowsheet.

TABLE 2
Comparison of Observed Fission Product DF's with Flowsheet (HA&HS)

Fission Product	Ref Flowsheet DF (HA & HS)	Observed DF (HA & HS)
Technetium 99	1.0	1.0 to 1.3
Ruthenium 106	1.0 e 3	1.2 e 3 to 7.0 e 3
Caesium 134+137	4.5 e 3	6.9 e 4 to 1.9 e 5
Cerium 144	3.3 e 3	1.1 e 4 to 1.7 e 5

DF is $\dfrac{\textit{Amount of FP in Feed per g of Uranium}}{\textit{Amount of FP in Product per g Uranium}}$

Tables 3 and 4 show the overall DF's for fission products, neptunium, uranium and plutonium through to the uranium and plutonium products.

TABLE 3
Comparison of Observed Contaminant DF's with Flowsheet
(Whole Plant to UO_3 Product)

Contaminant	Ref Flowsheet DF	Observed DF to UO_3 Product
Technetium 99	4.0 e 3	8.17 e 3 to 1.16 e 4
Ruthenium 106	8.7 e 5	4.32 e 6 to 1.33 e 7
Caesium 134+137	6.5 e 8	5.66 e 9 to 1.38 e 10
Cerium 144	3.3 e 7	9.36 e 5 to 4.96 e 6
Neptunium 237	1.5 e 4	3.31 e 4 to 6.76 e 4
Plutonium	5.0 e 6	8.60 e 6 to 2.03 e 7

DF is $\dfrac{\textit{Amount of Contaminant in Feed per g of Uranium}}{\textit{Amount of Contaminant in Product per g Uranium}}$

TABLE 4
Comparison of Observed Contaminant DF's with Flowsheet
(Whole Plant to Plutonium Nitrate and PuO_2 Products)

Contaminant	Ref Flowsheet DF	Observed Average DF to Plutonium Nitrate Product	Observed DF to PuO_2 Product
All fission products	2.8 e 8	-	3.37 e 8 to 7.06 e 8
Technetium 99	1.0 e 2	1.00 e 2	-
Ruthenium 106	3.2 e 5	1.04 e 6	-
Caesium 134+137	5.0 e 6	1.31 e 8	-
Cerium 144	3.7 e 6	2.10 e 7	-
Neptunium 237	4.5 e 1	6.60 e 1	-
Uranium (to nitrate)	4.2 e 3	4.62 e 4	-
Uranium (to PuO_2)	2.1 e 5	-	5.80 e 6 to 5.55 e 8

$$\textit{DF is} \quad \frac{\textit{Amount of Contaminant in Feed per g of Plutonium}}{\textit{Amount of Contaminant in Product per g of Plutonium}}$$

Tables 2,3 and 4 demonstrate the excellent performance of the solvent extraction plant. Fission product decontamination factors (DF's) in the HA cycle have been consistently better than the flowsheet expectation. Across the whole plant to the UO_3 and PuO_2 products the achieved DF's for fission products and other radioactive contaminants have also been higher than design prediction, resulting in products well within International Specifications.

An apparent exception to this is the cerium-144 DF to the UO_3 product. However, the cerium content in the fuel feed to the plant has, up to present, been much lower than the reference flowsheet, leading to analytical limit-of-detection restrictions for the low levels that are therefore present in the uranyl nitrate product. That this is an analytical artefact is supported by the overall gamma activity of the UO_3 product, which is well within the Specification (Table 6).

The overall neptunium DF for the UO_3 product is seen to be higher than the already large flowsheet expectation. This shows the effectiveness of the specially developed flowsheet (5) for the simultaneous removal of neptunium and plutonium in the UP Cycle.

Uranium - Plutonium Separation Performance

Table 5 shows the typical uranium-plutonium separation performance of the 1B (1BX, 1BXX, 1BS) system compared with reference flowsheet expectations.

TABLE 5

Comparison of Observed U-Pu Separation Performance with Flowsheet

	Ref Flowsheet DF	Observed DF
Removal of Pu from U product*	3.3 e 3	1.4 e 4 to 6.5 e 4
Removal of U from Pu product#	2.1 e 3	4.5 e 3 to 8.4 e 4

*DF is $\frac{\textit{Amount of Pu in feed per g of U}}{\textit{Amount of Pu in U product per g of U}}$ #DF is $\frac{\textit{Amount of U in feed per g of Pu}}{\textit{Amount of U in Pu product per g of Pu}}$

It can be seen that removal of plutonium from the uranium stream has been an order of magnitude higher than the design requirement and flowsheet expectation. The fuel processed so far has contained up to 85% of the flowsheeted amount of technetium and, with no technetium removal in the HA/HS system, the stability and reductive capacity of the 1B system has thus been fully tested and found to be satisfactory. This demonstrates the benefits of the extensive process chemistry and process equipment pilot plant development work that was carried out on the 1B system (4),(7). This work was done when initial fully active pilot plant trials showed that there would be no technetium DF across the HA/HS system when zirconium was also present in the feed, and that technetium destabilised the chemical reduction of plutonium (8). The very satisfactory operation of the Thorp 1B system shows the value of this work and vindicates the decision not to modify the plant design to insert a technetium removal step prior to the 1B system.

The removal of uranium from the plutonium stream has also exceeded original expectations. This excellent performance of the 1BS uranium re-extraction pulsed column is achieved. despite the presence of the less extractable UIV, and a lower operating temperature in the column to limit the adverse effects of technetium. Further uranium removal occurs across the oxalate precipitation production process for plutonium dioxide, resulting in the very high uranium DF's shown in Table 4.

Quality of Uranium and Plutonium Products

Tables 6 and 7 compare the amounts of some major contaminants in the UO_3 and PuO_2 products with the International Specifications.

Thorp's uranium and plutonium products are clearly shown to be fully suitable for recycle into fresh reactor fuel. Already initial amounts of plutonium have been used in Mixed Oxide (MOX) fuel in a demonstration facility at Sellafield, and a full production facility for producing MOX fuel is in an advanced stage of commissioning.

For the uranium, studies nearing completion have demonstrated the suitability of the Thorp product for producing fresh fuel for the UK Advanced Gas-Cooled Reactors, and such use will take advantage of the residual enrichment of the reprocessed uranium.

Uranium and plutonium losses to Thorp waste streams amount to no more than 0.19% and 0.22% respectively, so that Thorp is shown to be an efficient recycling process for these valuable sources of energy.

TABLE 6
Quality of Thorp Uranium Trioxide Product

Contaminant	Uranium Trioxide Composition	
	Typical Measured Value	ASTM Specification for UF_6: C 787-96*
Trans-U alpha activity: Pu+Np Bq/gU	4.0	$\leq$ 25
Non-U gamma activity: Bq/gU	35.0	$\leq$ 524#
Technetium microg/gU	0.03	$\leq$ 0.5

***** Same as BNFL specification

Derived from ASTM specification of $\leq 1.1 \times 10^5$ MeV Bq/kgU on "worst case" basis of all activity being due to Ru-106

TABLE 7
Quality of Thorp Plutonium Dioxide Product

Contaminant	Plutonium Dioxide Composition		
	Typical measured Value	BNFL Specification	ISO Specification TC85/SC5WG3 Rev 2, 1996
Uranium microg/gPu	12	$\leq$ 1000	Report
Fission Products Bq/gPu	650	$\leq$ 3 e 5	Report
Non Volatile Oxides microg/gPu	170	$\leq$ 5000	$\leq$ 5000

THORP WASTE STREAMS

In Table 8, some typical volumes and radioactive contents of High Level, Intermediate Level and Low Level wastes from Thorp are shown.

It can be seen that in excess of 98.4% of the activity in the waste is concentrated into the very small volume of the vitrified product, which is straightforward and safe to store indefinitely. Nearly all the remaining activity is contained in the cement encapsulate which occupies less than $0.5m^3$ per tonne uranium reprocessed and is also satisfactory for long term storage

TABLE 8
Volumes and Activities of Thorp Waste Streams

Waste Stream	Final Conditioned Volume	Alpha Activity	Beta Activity	Gamma Activity
	m^3/t (U)	GBq/t (U)	GBq/t (U)	GBq/t (U)
Vitrified high/intermediate liquid waste	0.05	5.3 e 4	6.2 e 6	
Cement encapsulated Head End intermediate level waste	0.49	99	1.0 e 5	
Cement encapsulated floc from treating low active salt-containing wastes	0.01	3.3	172	
Discharged low level liquid waste	--	0.05	2.43	Nil

The discharged low level waste activity amounts to less than 4 e -5 % of the total activity in the reprocessed fuel. For the calendar years 1997 and 1998, Table 9 shows the main constituents of these activity discharges as a percentage of the Sellafield Site yearly limits, and it can be seen that they form a small fraction of them and are, in general, well within the design target of less than 10%. The cobalt-60 discharge in 1997 was just over this target; this was due to a particular pond storage issue which was resolved by 1998.

TABLE 9
Liquid Effluent Discharges from Thorp Head End and Chemical Plant in 1997

Contaminant	Activity Discharged as Percentage of Site Limit	
	1997	1998*
Uranium	3.27	3.79
Total alpha activity	3.75	1.71
Total beta activity	0.54	0.31
Technetium 99	0.08	0.03
Ruthenium 106	0.35	0.22
Caesium 134	0.64	0.35
Caesium 137	1.12	1.12
Cerium 144	0.81	2.19
Americium 241	8.77	2.82
Carbon 14	3.75	1.67
Cobalt 60	10.8	3.25

*****Scaled up from January to June 1998 measurements

CONCLUSIONS

The design, construction and commissioning of THORP has been the most challenging single project ever undertaken by BNFL. The plant was commissioned and set to work without significant difficulty and has quickly ramped up to expected throughputs. This has been in large part due to extensive development work and close liaison between developers, designers and the commissioning teams during design, construction and commissioning.

The plant uses well established reprocessing technology in an innovative way so as to minimise the number of processing steps needed to meet product quality specifications, and minimise the number of waste streams produced. Product qualities are excellent and allow ready recycle into fresh reactor fuel, preserving separative work and allowing considerably more energy to be extracted from the original fuel. The plant produces only three types of waste stream and nearly all the radioactivity is concentrated into the small volume vitrified waste material. Activity discharges from Thorp are a small fraction of the overall discharge limits for the Sellafield site.

Thorp has thus met or exceeded its design intentions, has operated safely and efficiently, and is an advantageous and environmentally responsible method of treating spent irradiated fuel from the world's nuclear reactors.

REFERENCES

(1) Phillips, C, 1989. Atom, No394, 13-20
(2) Harrop, G, Phillips, C, 1992. Spectrum, Boise, USA
(3) Phillips, C, 1993. Trans. I. Chem. E. 71(A), pp132-142
(4) Phillips, C, 1992. Proc. WM99, Tucson, USA, pp1041-1045
(5) Denniss, I.S, Phillips, C, 1992. Proc. ISEC '90. Elsevier, pp549-554
(6) Phillips, C, Hamilton, C, 1993. Proc. ISEC '93. SCI London, pp1463-1470
(7) Phillips, C, 1991. Int. Symp. on Reprocessing and Waste Management, A. I. Chem. E, Pittsburgh,USA
(8) Garraway, J, 1984. I Chem E Symp Series No.88, pp47-56