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Comparison of Industrialized Late 20th Century Flowsheets for Reprocessing Used Nuclear Fuel

July 2025

Stuart T Arm

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Prepared for
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Richland, Washington 99354

Abstract

This study identified and compared three flowsheets for reprocessing used nuclear fuel (UNF) industrialized in plants in the United Kingdom (the Thermal Oxide Reprocessing Plant), France (UP2-800/UP3), and Japan (the Rokkasho Reprocessing Plant). The study also identified the major implications for a plant in the United States if it were initiated. All flowsheets employed the established Plutonium Uranium Reduction Extraction (PUREX) solvent extraction technology to separate uranium and plutonium from UNF dissolved in nitric acid. However, differences in the approaches to managing iodine-129, tritium and technetium were identified in the flowsheets. A US plant would also need to separate krypton-85 as well as iodine-129 and tritium for immobilization and disposal.

Summary

US policy is focused on direct disposal of the ~86,000 MT of Used Nuclear Fuel currently accumulated at US power plant sites (both operating and closed), without reprocessing it for economic and political reasons. However, the US Department of Energy (DOE) continues to invest in new reprocessing technologies and there continues a national conversation on the benefits and disadvantages of reprocessing UNF. For example, in May of this year, the President issued an Executive Order seeking to improve domestic fuel cycle infrastructure, including waste recycling and disposal infrastructure. The primary report directed by this order is a joint report by various government departments, that covers subjects around planning for and developing infrastructure to recycle, reprocess and dispose of UNF. The report is intended to set new policy and to identify regulatory and legislative changes needed to affect such policy. Therefore, longstanding US policy is being challenged.

In that context, this report describes a comparison of flowsheets industrialized in plants intended for reprocessing commercial or civilian oxide UNF in Europe and Japan. These plants were constructed and started operations in the late 20th century and continued operating into the 21st century. Flowsheet concepts and less mature processes are considered but only in helping to understand the implications for a US plant based on the industrialized flowsheets. Since no reprocessing plant has been constructed this century, this report describes industrialized state-of-the-art flowsheets for reprocessing UNF as standards against which those less mature demonstrated at laboratory or pilot scale or existing as concepts can be compared at least in qualitative terms.

Flowsheets from four plants in three countries are considered:

- The Thermal Oxide Reprocessing Plant (THORP) at Sellafield, United Kingdom.
- The UP2-800 and UP-3 plants at La Hague, France. The flowsheets from these two plants are broadly similar and considered together with differences articulated.
- The Rokkasho Reprocessing Plant (RRP) at Rokkasho, Japan.

At the summary level, the three head-end flowsheets are very similar in that they consist of disassembly, pin shearing, dissolution, clarification of the solution and dissolver off-gas management. Probably the larger differences between the flowsheets concerns volatile fission product management. Both THORP and UP2-800/UP3 employ caustic scrubbers to remove the bulk of the iodine, which is discharged to sea after treatment of the liquid effluent. There is no caustic scrubber in RRP, and instead silver impregnated media serves as the primary means of separating iodine from the off-gas. Therefore, no iodine is discharged to the sea from RRP. A US reprocessing plant will also likely need to separate krypton-85. Cryogenic distillation is, notwithstanding its complexity, likely the closest to what could be considered as an industrialized state of the art technology for krypton-85 separation.

There are several similarities between the THORP and UP2-800/UP3/RRP flowsheets for primary separations, including the use of uranium(IV) for adjusting the valence of plutonium to facilitate its separation in pure form. The major difference between the flowsheets concerns technetium management and where it is separated. Technetium is problematic because it catalyzes the destruction of hydrazine, which is used with uranium(IV) to facilitate the separation of plutonium. Technetium management has a profound effect on the flowsheets implemented in

the reprocessing plants under consideration. In THORP, the effect of technetium on hydrazine is minimized through equipment and chemistry adjustments whereas in UP2-800/UP3 and RRP it is separated ahead of introducing hydrazine. Likely the most important implication for a US plant concerns plutonium recovery assuming it is desired. Non-proliferation policies would likely mean pure plutonium should not be separated anywhere within a US plant. In this regard, the COEX™ flowsheet developed in France is applicable and could be considered nearest to an industrialized state-of-the-art. There is little to separate the uranium and plutonium purification flowsheets between the plants. A US plant would necessarily have to purify a uranium-plutonium product, which is accounted for in the COEX™ flowsheet.

Tritium is difficult to manage because it is essentially manifested as water and so, without some form of management, is historically permitted for discharge to the sea as wastewater. There is an explicit tritium management approach in the UP2-800/UP3 and RRP flowsheets. In THORP, most of the tritium was routed with the HA raffinate due to the limited solubility of water in the solvent but there is no further attempt to control its downstream migration. Discharging tritium to the sea will likely prove unacceptable if not impractical if a US plant is located away from the ocean or large river. There are several technical management strategies for tritium that could be implemented in any one of the industrialized head-end and separation flowsheets. Additionally, tritiated wastewater could be immobilized and dispositioned as low level waste especially if combined with a water management approach that includes recycle to minimize waste volume. Alternatively, several technologies have become available and industrialized this century for removing tritium from nuclear power plant wastewater, although none have been demonstrated with liquid effluent arising from a reprocessing plant. All these options should be evaluated in the context of water and liquid effluent management. The evaluation should aim to understand the advantages and disadvantages of each solution by themselves or in combination.

Uranium finishing processes are essentially the same across all three plants and use the well-established thermal denitration technology. The plutonium finishing process in THORP and UP2-800/UP3 employ the same oxalate precipitation technology. In RRP a portion of the uranium product is mixed with the plutonium product ahead of finishing. Therefore, the RRP plutonium finishing flowsheet is different in denitrating a mixture of uranium and plutonium by microwave heating to satisfy concerns with proliferation risk. US non-proliferation policies will likely require that no pure plutonium be produced in the plant, which has implications for product finishing. There are a number of technical options to finish the mixture but only that deployed in RRP is industrialized.

The flowsheets evaluated for this report are recommended as industrialized baselines against which improvements expected from research initiatives should be qualitatively measured. Only a qualitative measurement can be made because material balances are not available although they could be modeled with some assumptions.

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Acronyms and Abbreviations

BNFL	British Nuclear Fuels Limited
DOE	US Department of Energy
HA	High Active
HAN	HydroxylAmine Nitrate
HEPA	High Efficiency Particulate Air
HS	High Active (or Hot) Scrub
JNFL	Japan Nuclear Fuel Limited
LLW	Low Level Waste
LWR	Light Water Reactor
NOx	Nitrogen Oxides
OK	Odorless Kerosene
PP	Plutonium Purification
PUREX	Plutonium Uranium Reduction Extraction
RRP	Rokkasho Reprocessing Plant
TBP	Tri-Butyl Phosphate
THORP	Thermal Oxide Reprocessing Plant
UNF	Used Nuclear Fuel
UP	Uranium Purification

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1.0 Introduction

1.1 Background

The US has a long history of reprocessing used nuclear fuel (UNF) starting with the Manhattan Project and subsequently during the Cold War until 1990. Then, over 200,000 MT of UNF had been reprocessed at Hanford and Savannah River to recover plutonium for defense purposes. However, from a civilian standpoint, only a small quantity of commercial power plant UNF (640 MT) was reprocessed at West Valley between 1963 and 1972 when operations were terminated. Other commercial reprocessing plants have been constructed in the US (e.g., at Barnwell, SC) but never operated. Instead, civilian reprocessing of UNF has been mainly pursued in Europe, notably in the United Kingdom and France and more recently in Japan. However, it's been 30 years since a reprocessing plant was designed, built and commissioned in Europe and the Japanese plant is yet to process UNF.

In the United Kingdom (UK), the main reprocessing plant, the Thermal Oxide Reprocessing Plant (THORP) at Sellafield reprocessed 9,331 MT of UNF from a variety of international and British customers since startup in 1994. Another reprocessing plant intended to reprocess UNF from Magnox reactors reprocessed approximately 55,000 MT of UNF. Both THORP and the Magnox plants ceased reprocessing operations in 2018 and 2022, respectively. Meanwhile, in France, there are two main reprocessing plants, UP2-800 and UP3 at La Hague that together have reprocessed over 63,000 MT of SNF. Knowledge and experience of industrial reprocessing of UNF has, therefore, increasingly shifted from the US to Europe since the end of the Cold War.

For economic and political reasons, over the last four decades US policy has focused on direct disposal of the ~86,000 MT of UNF currently accumulated at power plant sites (both operating and closed), without reprocessing. However, the US Department of Energy (DOE) continues to invest in new reprocessing technologies and there continues a national conversation on the benefits and disadvantages of reprocessing UNF. For example, in May of this year, the President issued Executive Order 2025-09801, 'Reinvigorating the Nuclear Industrial Base' establishing US policy to 'maximize the efficiency and effectiveness of nuclear fuel through recycling, reprocessing, and reinvigorating the commercial sector'. Further, the primary report directed by this order is a joint report by the DOE, Department of Defense, Department of Transportation and Office of Management and Budget, due January 18th, 2026, that covers various subjects around planning for and developing infrastructure to recycle, reprocess and dispose of UNF and high-level nuclear waste. The report is intended to set new policy and to identify regulatory and legislative changes needed to affect such policy. Therefore, longstanding US policy is now being challenged. The subject of this report is intended to inform that debate in terms of what can be accomplished in the near term for reprocessing US commercial UNF.

1.2 Scope

The scope of this evaluation is limited in several respects:

1. The evaluations consider only flowsheets industrialized in plants intended for reprocessing commercial or civilian oxide UNF. These plants were constructed and started operations in the late 20th century and continued operating into the 21st century. Flowsheet concepts and less mature processes are considered but only in helping to understand the implications for a US plant based on the industrialized flowsheets. Only

the process flowsheets are described, no mechanical operations are considered except as they relate to the process flowsheet.

2. This report does not describe in detail the technology and chemistry underpinning the flowsheets except as they facilitate comparison and understanding the implications for a US plant. The reader is encouraged to obtain the reference material for details on the underpinning technology and chemistry.
3. Finally, this evaluation is intentionally limited to the use of published information. Providing anecdotal or experiential information is avoided.

1.3 Purpose

The evaluation described in this report serves several purposes:

1. Since no reprocessing plant has been constructed this century, this report describes industrialized state-of-the-art flowsheets for reprocessing UNF. These plant flowsheets represent standards against which less mature methods that are conceptual or have only been demonstrated at laboratory or pilot scale can be compared, at least in qualitative terms.
2. The plants described in this report employed flowsheets matured in the 1980s and early 1990s. Therefore, the publications describing the technology and chemistry underpinning the flowsheets are not readily available and are not identified by performing broad internet searches. However, this report's author has reasonable knowledge of the contemporary conferences and workers in the field to know where to look for published, albeit 'lost', technical information. The reference list in this report represents the key publications describing the technology and chemistry underpinning the subject flowsheets and are thereby rescued from 'becoming lost to history'.
3. Related to the second purpose, this report and its reference material informs early and mid-career scientists and engineers working in the field in providing context for research and a technical baseline.
4. Consideration of the industrialized flowsheets in identifying the implications for a new US reprocessing plant informs the national technical and potentially social and political conversation for recycling UNF.

2.0 General Descriptions of Considered Reprocessing Plants

2.1 Thermal Oxide Reprocessing Plant, Sellafield, United Kingdom

THORP is the third reprocessing plant constructed at the Sellafield site in the UK (Figure 2-1). The first was built in the late 1940s to separate plutonium for weapons purposes and used a now obsolete solvent extraction technology. The second plant was constructed in the early 1960s and operated from 1964 to 2022 to reprocess metal UNF from the UK's Magnox reactors. The Magnox Reprocessing Plant used the Plutonium Uranium Reduction Extraction (PUREX) technology to separate uranium and plutonium from the UNF.

As explained by Burrows et al (2006), British Nuclear Fuels Limited (BNFL) used its experience from the Magnox Reprocessing Plant to develop, design and construct a plant to reprocess oxide UNF from the UK's Advanced Gas-Cooled Reactors and German and Japanese Light Water Reactors (LWRs). Like the Magnox Reprocessing Plant, THORP used the PUREX technology as its basis but with improvements. The plant started radiological operations in 1994 with a maximum capacity of 5 MTU/day or 1,200 MTU/year. THORP closed its reprocessing operations in 2018 given falling demand for reprocessing and the relatively low cost of uranium.



Figure 2-1. The Thermal Oxide Reprocessing Plant, Sellafield, UK

2.2 UP2-800 and UP3, La Hague, France

According to Schneider and Marignac (2008) and the CEA (2008), the first reprocessing plant operated in France was at Marcoule. Termed UP1 (Usine de Plutonium, or 'Plutonium Factory'), it started operating in 1958 with a capacity of up to ~1000 MTHM/year initially to recover plutonium from gas graphite reactor UNF for weapons but later reprocessed UNF from other sources. UP1 terminated reprocessing operations in 1993.

At La Hague, UP2, originally designed to reprocess gas graphite reactor UNF, commenced operations in 1966. In 1976, UP2 was adapted to reprocess LWR UNF and termed UP2-400 given its intended throughput was 400 MTHM/year. A second La Hague plant, UP3 with a capacity of 800 MTHM/year, started operations in 1989 and was almost entirely financed by German and Japanese contracts. Focused on French LWR UNF, another reprocessing plant, UP2-800, started up in 1994 and shared common facilities with UP2-400. With closure of UP2-400 in 2004, the licensed capacities of UP2-800 and UP3 were revised to 1,000 MTHM/year

each with an overall site limit of 1,700 MTHM/year. Both plants use the PUREX technology with improvements similar to those in THORP.

2.3 Rokkasho Reprocessing Plant, Rokkasho, Japan

The Rokkasho Reprocessing Plant (RRP) is the last of the reprocessing plants considered in this report with construction starting in 1993 by Japan Nuclear Fuel Limited (JNFL). RRP was originally scheduled to start operations in 2008. Startup has been frequently delayed but is now in the final stages of active commissioning. Nonetheless, JNFL have announced full operations will not start until late 2026 or early 2027 due to issues raised by Japan's Nuclear Regulation Authority, particularly with the 'ground model' used in designing the plant's earthquake resistance. The RRP is designed to annually reprocess 800 MT of UNF and is heavily based on UP2-800/UP3 technology with some incorporation of THORP and others' technologies.

3.0 Comparison of Head-End Flowsheets

The head-end of the reprocessing plants under consideration broadly consists of fuel assembly break down, shearing of fuel pins to lengths of ~50 mm, dissolution of the fuel in nitric acid, clarification of the UNF solution and treatment of the off-gas from dissolution. In this respect, all the flowsheets of the subject plants are the same although they differ in some important details.

3.1 THORP Head-End Flowsheet

The flowsheet for the THORP head-end is shown in Figure 3-1. Key references for the technical details summarized in this report include Phillips (1993), Arm and Butcher (2009), Hudson and Buckley (1996) and Hudson and Jeapes (1989).

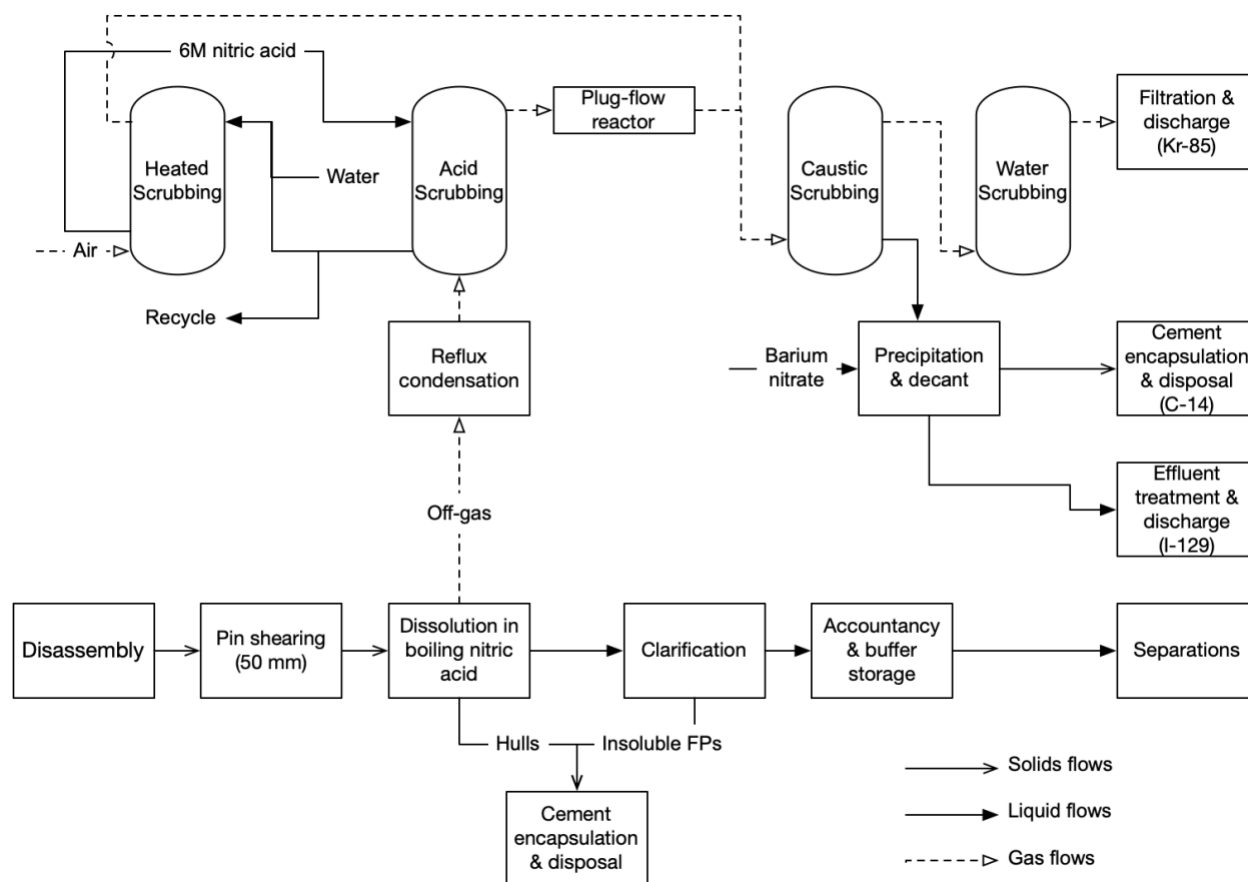


Figure 3-1. The THORP Head-end Flowsheet

With reference to the flowsheet, fuel pins are extracted from the assemblies and sheared to lengths of 50 mm. The sheared pins fall into baskets, which are inserted into one of three batch dissolvers of hot nitric acid. As described by Mayson and Gunston (1999), gadolinium nitrate is added as a neutron poison. During the first few years of operation, no burnup credit was taken in calculating the required concentration of poison. However, Mayson and Gunston (1999) describe a burnup credit method to reduce the poison concentration, which was submitted to the regulators. The outcome of the submission is not known. The dissolver temperature is raised to

reflux when a complete batch is charged. The product solution is transferred from the dissolver upon completion. Any coarse insoluble particles are removed from the dissolver and washed. The basket of empty cladding hulls is washed with the next batch of fresh acid and subsequently encapsulated for disposal. The product solution contains insoluble constituents of the fuel (primarily noble metals) and these are separated in suspended bowl centrifuges with the cake encapsulated with the cladding hulls. The product solution then goes through nuclear material accountancy and held in storage for subsequent separations.

The off-gas from the dissolver is treated in a condenser and a series of countercurrent scrub operations to separate nitrogen oxides, iodine (particularly iodine-129) and carbon (particularly carbon-14) but notably not radioactive noble gases such as krypton-85. Nitrogen oxide gases are mainly removed with 6M nitric acid, and the product liquor is scrubbed with hot air to desorb any iodine. Nitric acid is periodically purged and recycled while water is used to maintain the acid concentration at 6M. An empty vessel serves as a plug flow reactor wherein any nitric oxide is provided sufficient residence time to convert to nitrogen dioxide by the oxygen in the air. The gas from the reactor and heated scrubber is treated in a caustic scrubber that removes the nitrogen dioxide, iodine and carbon. Iodine-129 and carbon-14 are each removed to a DF of approximately 100 in the caustic scrubber. A subsequent water scrub (some references say a weak nitric acid scrub) removes any entrained drops of sodium hydroxide. Any remaining entrained particles are filtered before the treated off-gas is discharged to the atmosphere. A portion of the caustic scrubber liquor is periodically purged and the carbon precipitated by addition of barium nitrate. The precipitated barium carbonate (containing the carbon-14) is encapsulated in cement for disposal while the remaining solution is treated before release to the sea. The iodine-129 is thereby discharged to the sea.

3.2 UP2-800 and UP3 Head-End Flowsheet

The flowsheet for the UP2-800 and UP3 head ends are shown in Figure 3-2. Key references for this flowsheet are CEA (2008), Bernard et al (1993) and Saudray et al (1991).

With reference to the flowsheet, fuel pins are extracted from the assemblies and sheared to lengths of 35 mm as broadly similar to other reprocessing plants. Dissolution also occurs in hot nitric acid but using a continuous, rather than batch, dissolver. The continuous rotary dissolver consists of a zirconium slab (for criticality safety) tank into which a wheel is partially immersed. The wheel contains twelve enclosed compartments. The compartments are loaded with the chopped pins and immersed in nitric acid for sufficient time to dissolve the fuel as the wheel moves around on its axis. The compartments are unloaded at the top of the wheel after draining the acid. The dissolved fuel solution is continuously withdrawn while recycled acid is added to the tank.

The dissolved fuel solution passes to a vessel where it is sparged with nitrogen oxides (NO_x) to drive any iodine into the off-gas. The solution is then clarified using suspended bowl centrifuges before passing to the separations portion of the plant.

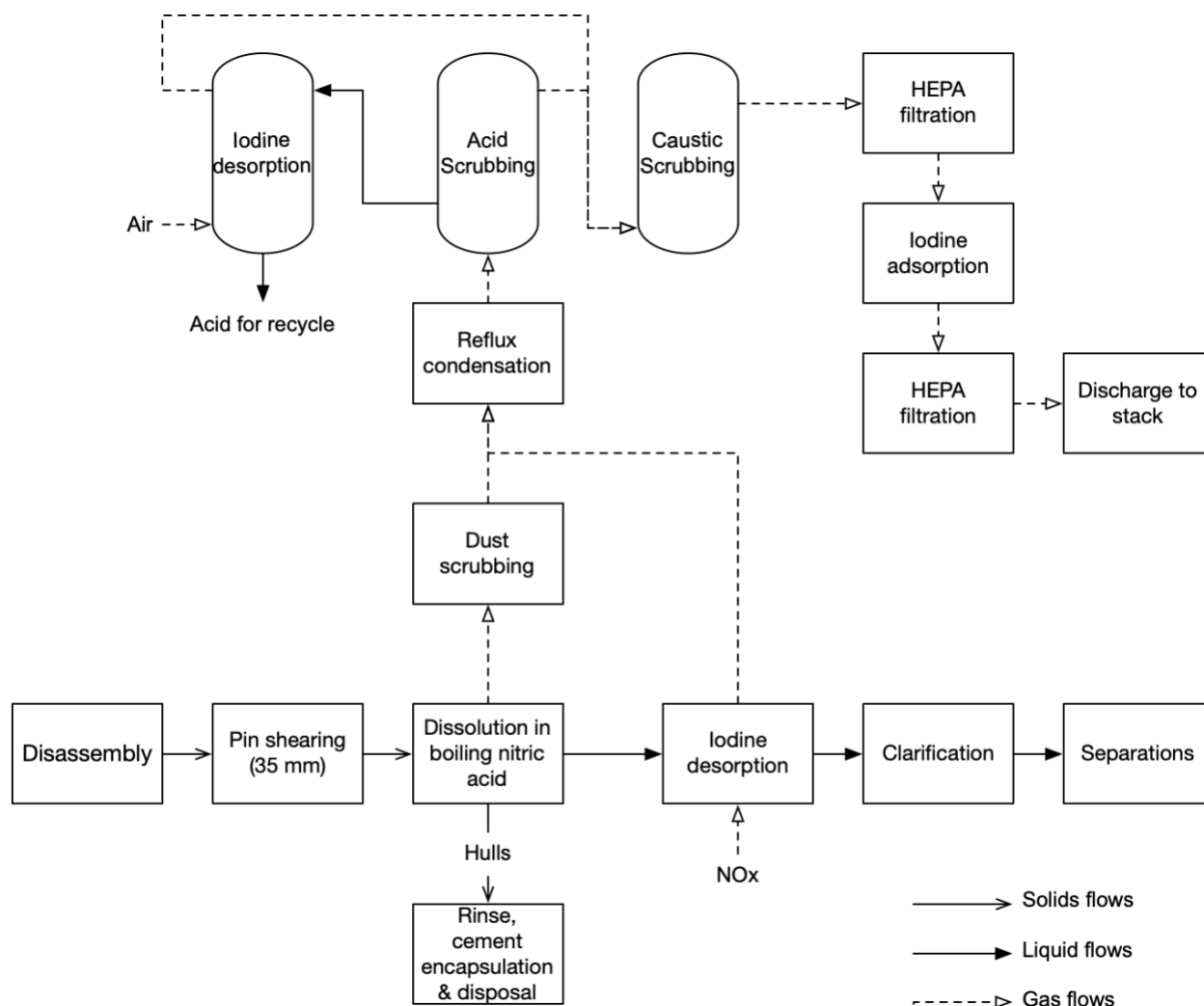


Figure 3-2. The UP2-800 and UP3 Head End Flowsheet

Off-gas treatment consists of a dust scrubber, a reflux condenser and acid scrubbers to capture the NO_x. The nitric acid formed in the off-gas system is recycled into the dissolution process after iodine is desorbed using air in a packed column. The subsequent caustic scrubber captures most of the iodine while the iodine adsorber (a mineral, silica- or alumina-based substrate, impregnated with silver nitrate) after High Efficiency Particulate Air (HEPA) filtration acts as a polish. The off-gas passes through further HEPA filters before discharge to the environment. The iodine captured in the caustic scrubber is discharged to the sea.

3.3 RRP Head-End Flowsheet

The RRP head-end flowsheet is described by Saudray et al (1991) and Kawakatsu (1994) and is depicted in Figure 3-3 below.

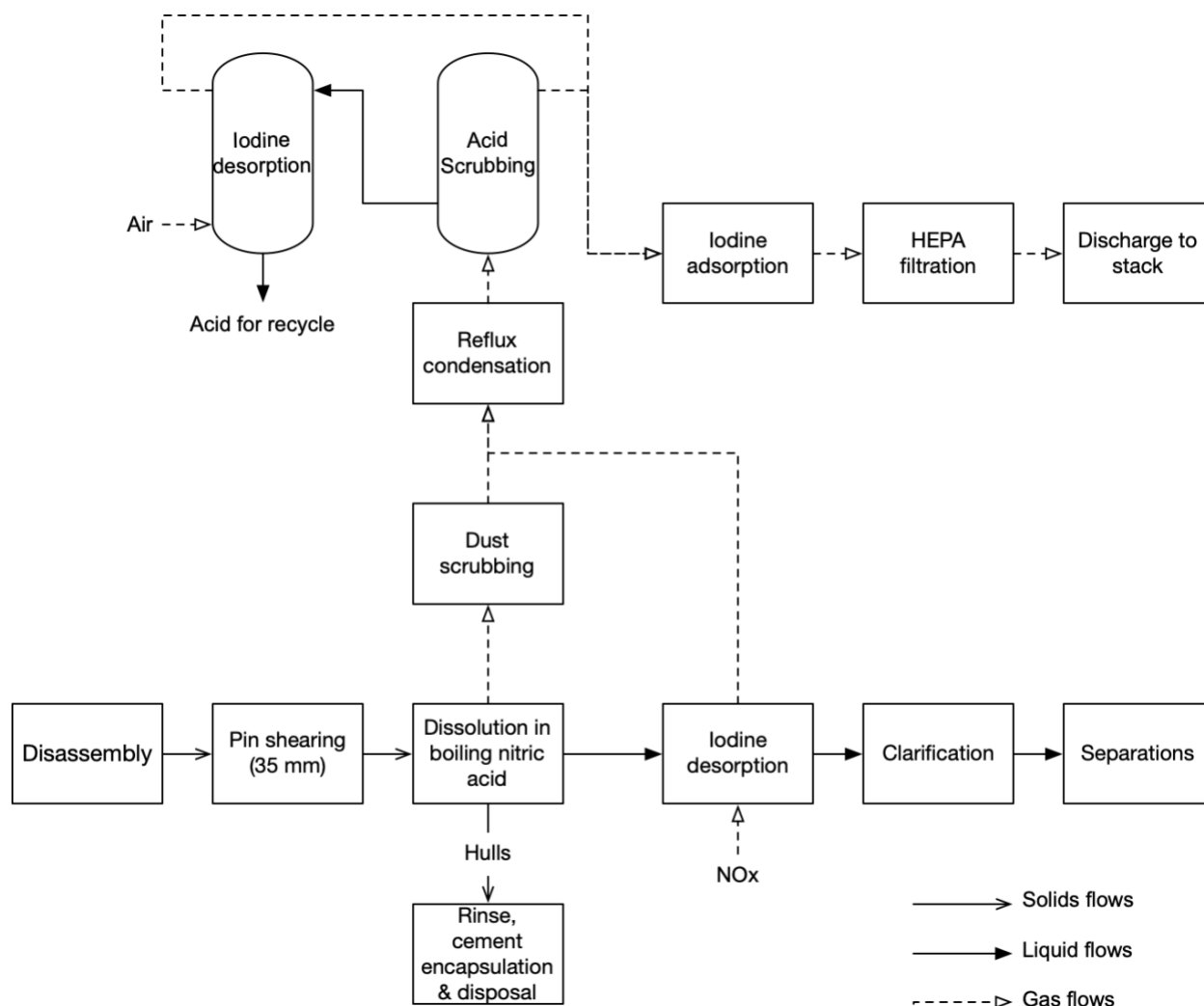


Figure 3-3. RRP Head-End Flowsheet

The flowsheet is essentially identical to that in UP2-800 and RRP including the use of the continuous dissolver. The one major difference is in the management of iodine. In RRP there is no caustic scrubber and, instead, iodine is adsorbed onto silver-impregnated adsorbents. Consequently, no iodine is discharged to sea.

3.4 Comparison of Head-End Flowsheets

At the summary level, the three head-end flowsheets are very similar in that they consist of disassembly, pin shearing, dissolution, clarification of the solution and dissolver off-gas management. The differences between the flowsheets are discussed below.

- In THORP, the use of batch dissolvers and the ability to effectively sparge means most of the iodine issues from the dissolver itself. In contrast, the continuous wheel dissolver employed in UP2-800/UP3 and RRP means a separate desorption step must be employed to route most of the iodine into the off-gas treatment system.
- A disadvantage with batch dissolvers is their geometry, meaning their window for criticality safety is narrower than the continuous dissolvers at UP2-800/UP3 and RRP.

While the literature is not explicit, it is apparent that a soluble neutron poison, such as gadolinium nitrate must be added for some UNF batches depending on their burnup for all dissolvers. However, the THORP batch dissolvers likely have a wider window wherein a neutron poison is needed. Addition of gadolinium nitrate would be consequential for further separation of trivalent actinides. This is because it would add to the trivalent lanthanide fission products, which can complicate trivalent actinide separation and lead to larger process equipment.

- Probably the larger differences between the flowsheets concerns volatile fission product management. Both THORP and UP2-800/UP3 employ caustic scrubbers to remove the bulk of the iodine, which is discharged to sea after treatment of the liquid effluent. In UP2-800/UP3 the caustic scrubber is followed by an adsorber to remove further iodine which is dispositioned as solid waste. In THORP, there was no additional adsorber, but carbon-14 was separated from the off-gas and dispositioned as solid waste. That could have resulted from negotiations with the UK environmental agency, i.e., a tradeoff between additional iodine separation versus carbon-14 separation. There is no caustic scrubber in RRP, and instead silver impregnated media serves as the primary means of separating iodine from the off-gas. Therefore, no iodine is discharged to the sea from RRP.
- There is notably no separation of noble gas fission products such as krypton-85 from the off-gas of any plant. However, at least known to the author, BNFL was required to identify appropriate technology and make provision for such a capability if later considered required by the regulator.

3.5 Implications for the Head End Flowsheet of a US Material Recovery Plant

The primary implications for a US plant concern off-gas management. Separation of iodine-129 will be required with the use of solid media since none of the fission product could be discharged to the sea. One option would be to grout the effluent from a caustic scrubber although using a solid absorbent such as a silver-impregnated media would likely produce a smaller volume for disposal. The low-level waste (LLW) limit for iodine-129 is sufficiently low (0.08 Ci/m³) that the most volume-efficient disposal route would be as Greater-Than-Class-C LLW although a geologic repository would likely be needed.

Krypton-85 will also likely need separation. No industrialized state-of-the-art technology exists for krypton-85 but extensive research was conducted in the Federal Republic of Germany supporting the proposed reprocessing plant at Wackersdorf. A process for removing krypton-85 was not required for the plant but the regulator required a technology be demonstrated at pilot scale. Furrer and Weinlander (1990) identified selective absorption in Freon-12 as the preferred technology for which a pilot plant was planned. Whether a pilot plant was operated is not known. The technology is described by Heinrich et al (1985). In any case, the manufacture of FREON-12 is now banned due to its deleterious impact on the ozone layer in Earth's atmosphere, so that it cannot be considered for a new reprocessing plant. Another technology significantly developed to pilot scale in the Federal Republic of Germany was cryogenic distillation and is described by von Ammon (1978). This technology, notwithstanding its complexity, is likely the closest to what could be considered as an industrialized state of the art for krypton-85 separation.

4.0 Comparison of Separations Flowsheets

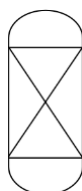
Like the head-end flowsheets, the separations flowsheets of the three plants are very similar at a high level but differ in important details, primarily in how they manage technetium, zirconium, and neptunium. What is termed primary separations here consists of separation of plutonium and uranium from the dissolver product solution and then separation of the plutonium from the uranium. The separated plutonium and uranium are then ready for purification.

The following notes apply to all flowsheets in this section:

- Solid lines indicate aqueous streams and dashed lines organic.
- Pulsed columns are indicated as below. Where publicly known, the primary interface position is indicated by a horizontal line (top or bottom). Top interfaces form when the organic phase is dispersed and vice versa.



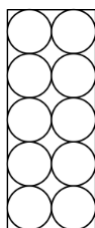
- Packed columns, where publicly known, are indicated as below.



- Mixer-settlers, where publicly known, are indicated as below. Note that the number of vertical lines is not intended to show the number of stages.



- Centrifugal contactors, where publicly known, are indicated as below. Note that the number of circles is not intended to show the number of stages.



4.1 Primary Separations Flowsheets

4.1.1 THORP Primary Separations

The THORP primary separations flowsheet is shown in Figure 4-1. Key references for the flowsheet include Garraway (1984), Denniss and Phillips (1990a), Denniss and Phillips (1990b), Phillips (1991), Phillips (1992), Phillips (1993) and NEA (2018).

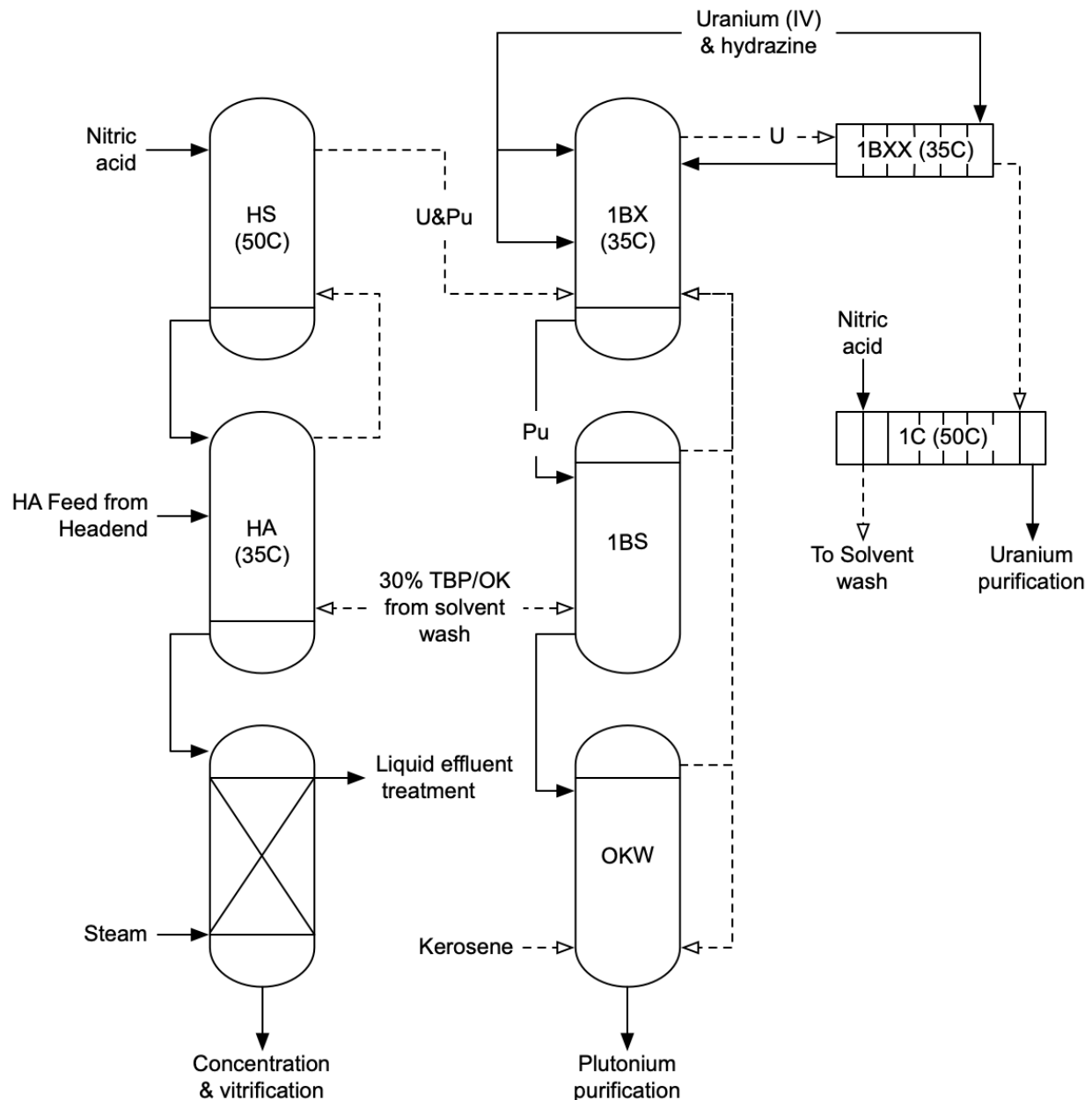


Figure 4-1. THORP Primary Separations Flowsheet

Here, high active (HA) feed from the head-end buffer storage is contacted with 30% tri-butyl phosphate (TBP) in odorless kerosene (OK) in the HA pulsed column at 35°C. Uranium and

plutonium as well as neptunium and technetium complexed with zirconium are extracted into the organic phase and pass to the high active (or hot) scrub (HS) column operated at 50°C. The hot scrub is intended to remove partially extractable fission products such as ruthenium and zirconium, which suggests the acid concentration is low. The raffinate from the HA column is treated with steam in the packed column to remove any entrained organic phase before it is concentrated by evaporation and vitrified.

The solvent product of the HS column therefore primarily contains uranium, plutonium, neptunium, and technetium and passes to the 1BX column at 35°C. Here, the solvent is contacted with uranous [(U(IV))] nitrate in nitric acid to reduce plutonium(IV) to inextractable plutonium(III). A stabilizer, hydrazine, is added to react with any nitrous acid that would otherwise re-oxidize the plutonium and uranium. Early development work by BNFL indicated the technetium reduces to the inextractable +4 valence such that it follows the plutonium. However, technetium was found to catalyze the destruction of the hydrazine stabilizer leading to undesirable quantities needing to be added in excess. BNFL therefore worked to limit the reaction between hydrazine and technetium by reducing the aqueous residence time in the 1BX column. The most satisfactory means of doing this was to operate the 1BX column with the organic phase as continuous, counter to conventional wisdom to operate a pulsed column with the phase at higher flow rate as continuous. The development and design of the 1BX column and flowsheet testing at several scales was a major endeavor. Notably, BNFL rejected early scrubbing of technetium with highly concentrated nitric acid because of the additional mechanical complexity and production of an additional waste stream.

The aqueous product from the 1BX column therefore contains primarily plutonium and technetium. This aqueous product is scrubbed of any uranium or neptunium in the 1BS column with 30% TBP/OK before passing to a the OKW column where any dissolved TBP is removed by contact with OK.

Meanwhile the neptunium is reduced by the uranous nitrate to the extractable +4 valence state such that it follows the uranium into the 1BXX mixer-settlers at 35°C where any residual plutonium is scrubbed. Uranium and neptunium are stripped into nitric acid in the 1C mixer-settlers operated at 50°C.

4.1.2 UP2-800 and UP3 Primary Separations

The high active extraction and scrub portions of the UP2-800 and UP3 primary separations flowsheet are shown in Figure 4-2. Key references for this flowsheet are Bernard et al (1991), Fournier et al (1992), Bernard et al (1993), Baron et al (1993), Drain et al (1991), Drain et al (1997), Drain et al (2003) and CEA (2008). The UP2-800 and UP3 flowsheets are essentially identical except where noted in the figures.

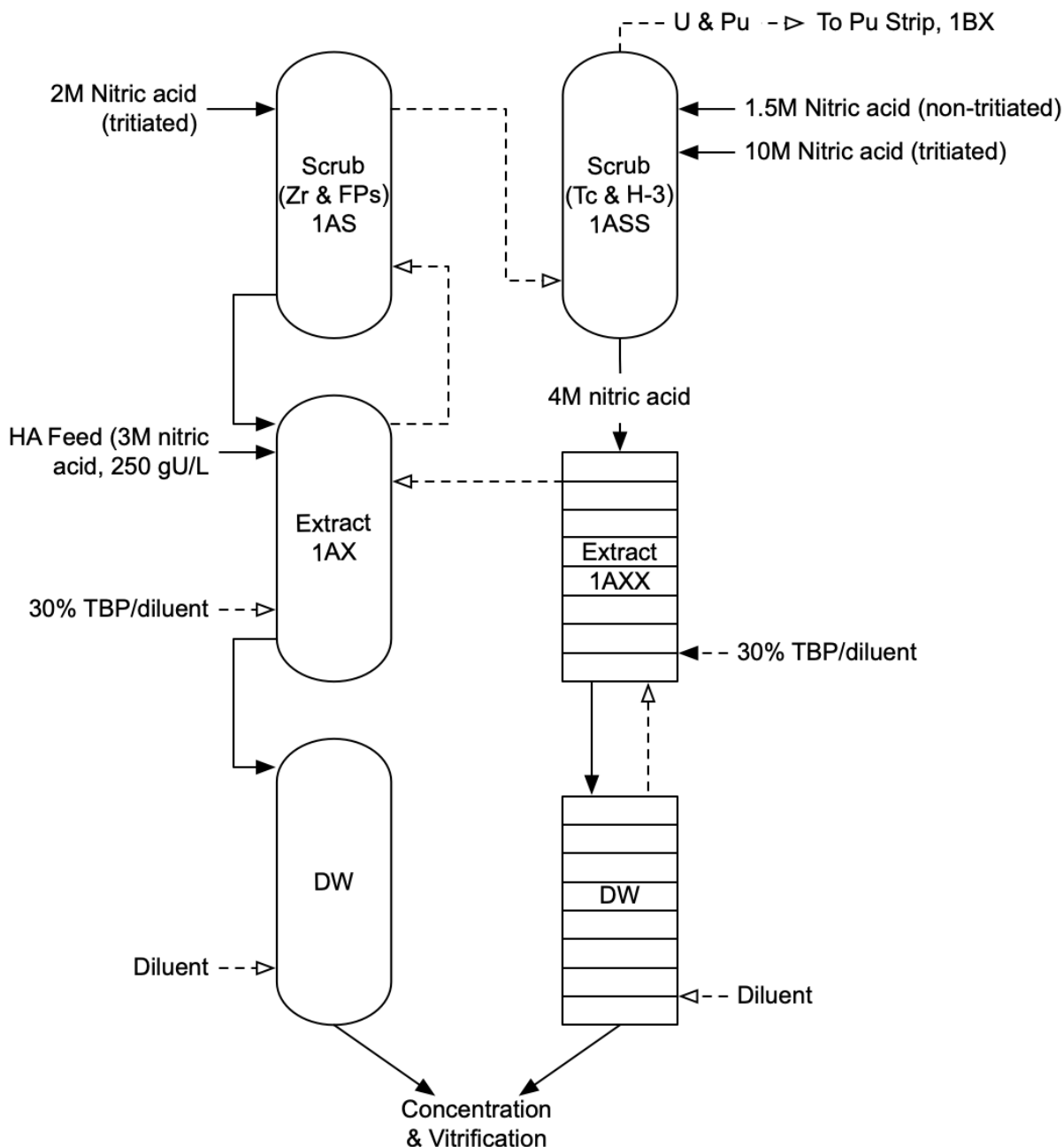


Figure 4-2. UP2-800 and UP-3 Primary Separations Flowsheet

The HA feed of 3M nitric acid and 250 gU/L enters the extraction pulsed column, 1AX, where it is contacted with 30% TBP in the diluent, hydrogenated tetrapropylene. The raffinate is subsequently washed with diluent in the pulsed column DW to remove any dissolved TBP. The solvent is passed to the 1AS scrub column where it is contacted with 2M nitric to separate any zirconium and any other co-extracted fission products (except technetium). The raffinate from the 1AS column is fed to the extraction column.

The solvent then passes to the 1ASS scrub column. Here, the solvent is scrubbed of tritium and technetium. Tritium is an important radionuclide for waste management in a reprocessing facility because it exists as tritiated water and can migrate throughout a reprocessing flowsheet to

contaminate liquid effluent and limit options for its disposal. The solvent has limited solubility for water but tritium can migrate beyond the primary separations portion of the plant. To mitigate tritium's migration, the separations flowsheet is split between high and low areas with their own acid recovery operations. The split occurs at the 1ASS scrub column. Here, the solvent is contacted with fresh (i.e., non-tritiated water) 1.5M nitric acid, into which most of the tritium is stripped. The acid produced by the acid recovery operation in the high tritiated area is recycled for dissolution while any excess appears to be treated and discharged to the sea.

Additionally, technetium is scrubbed with tritiated 10M nitric acid. The raffinate from the 1ASS column is passed to a complementary extraction operation, 1AXX, which uses mixer-settlers. A complementary extraction is used rather than routing the raffinate to the 1AX column because the technetium would otherwise accumulate in the 1AX, 1AS and 1ASS loop. The solvent from 1AXX passes to the 1AX extraction column while the raffinate is scrubbed of TBP, concentrated and vitrified.

The flowsheet for uranium and plutonium separation is provided in Figure 4-3. Key references for this flowsheet are Bernard et al (1991), Fournier et al (1992), Bernard et al (1993), Baron et al (1993), Drain et al (1991), Drain et al (1997), Drain et al (2003) and CEA (2008). The UP2-800 and UP3 flowsheets are essentially identical except one solvent extraction operation is performed in different equipment and another is not performed, as indicated in the figure.

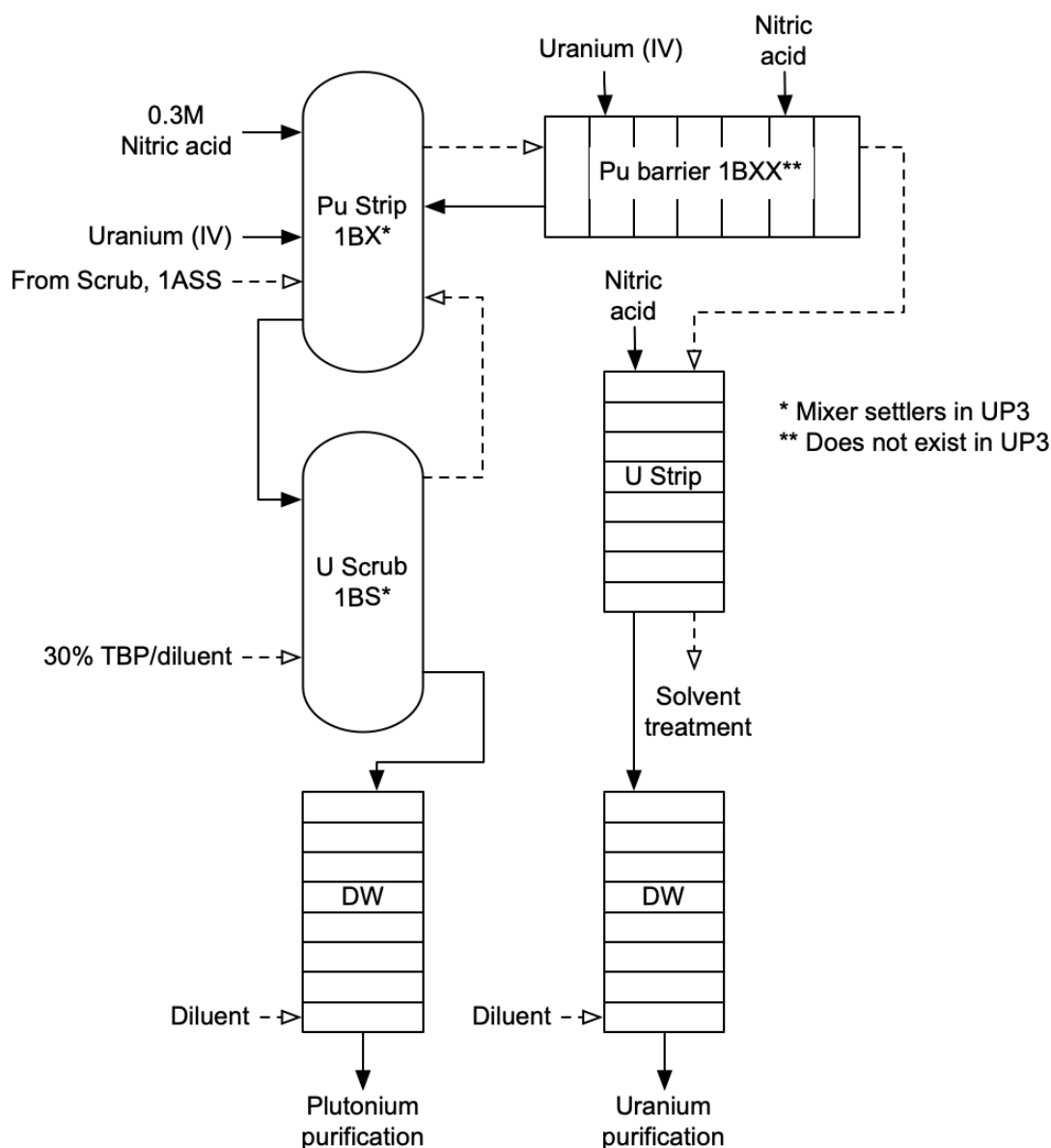


Figure 4-3. UP2-800 and UP3 Uranium and Plutonium Separation Flowsheet

Uranium and plutonium separation occurs in the 1BX pulsed column. Here, uranous nitrate [uranium(IV)] reduces plutonium to the inextractable +3 valence so that it is stripped. A stabilizer, hydrazine, is added to react with any nitrous acid that would otherwise re-oxidize the plutonium and uranium. The technetium content is reduced by a factor of 30 in the 1ASS and the extent to which excess hydrazine must be added is not clear. The aqueous plutonium product is routed to the 1BS column where it is scrubbed with solvent to primarily separate residual uranium. The solvent is passed to the 1BX column and the aqueous raffinate is contacted with diluent to strip any TBP before it is routed for plutonium purification. Meanwhile, the uranium-bearing solvent from 1BX is scrubbed of plutonium in the 'plutonium barrier' operation. Here, additional uranous nitrate reduces plutonium to the +3 valence state so it is stripped from the solvent. The uranium product passes to uranium stripping while the raffinate is routed to the 1BX column. There is little information published on the uranium stripping operation but appears to be a well-established process.

4.1.3 RRP Primary Separations

As described by Kawakatsu (1994), the primary separations flowsheet is identical to that employed in UP2-800.

4.1.4 Comparison of Primary Separations Flowsheets

There are several similarities between the THORP and UP2-800/UP3/RRP flowsheets:

- Both use 30% TBP in an organic diluent to extract uranium and plutonium and leave most fission products in the raffinate, which is subsequently volume-reduced and vitrified.
- Both use uranium(IV) as the reductant to reduce the plutonium valency to +3 and thereby make it separable from uranium. Using uranium(IV) is beneficial because it is recovered with the uranium in the UNF whereas, historically, other reductants add to the fission product waste.
- The flowsheets for separating the uranium from the plutonium are essentially identical although different in the solvent extraction equipment used.

The major difference between the flowsheets concerns technetium management and where it is separated. Technetium is problematic because it catalyzes the destruction of hydrazine, which is used to minimize the generation of nitrous acid that would otherwise oxidize plutonium(III) and uranium(IV). Furthermore, the dominant form of technetium in nitric acid is pertechnetate (TcO_4^-) that replaces a nitrate group in the uranyl-TBP complex. Technetium's extractability is also enhanced by its complexation with zirconium and subsequent extraction. Technetium management, therefore, has a profound effect on the flowsheets implemented in the reprocessing plants under consideration.

- In THORP, zirconium is scrubbed but all the technetium, as pertechnetate, is allowed to enter the 1BX column. Here, it is reduced to inextractable technetium(IV) by the uranium(IV) and so leaves with the plutonium product to be separated in the plutonium purification process. The additional hydrazine required to account for that destroyed was considered safe but operationally undesirable according to Denniss and Phillips (1990b). Therefore, Denniss and Phillips (1990b) considered several options to limit the contact time between the technetium and hydrazine in the 1BX column, which led to an extensive development program on the column itself as well as the chemistry. By these measures, the required additional hydrazine was reduced to acceptable quantities.
- In contrast, in UP2-800/UP3 and in RRP, technetium is scrubbed with concentrated nitric acid in a second scrub column (1ASS) before the solvent product enters the 1BX column. Therefore, the catalytic destruction of hydrazine by technetium appears to have been largely avoided. To avoid the technetium accumulating in a recycle loop, the raffinate from 1ASS cannot be simply returned to the HA column for separation of any uranium and plutonium. Instead, the 1ASS raffinate is processed through a complementary extraction process, 1AXX. The solvent containing the extracted uranium and plutonium is returned to the primary extraction column, 1AX. The raffinate from the 1AXX column is concentrated and vitrified with that from the 1AX column.

There is an explicit tritium management approach in the UP2-800/UP3 and RRP flowsheets. In THORP, most of the tritium will be routed with the HA raffinate due to the limited solubility of water in the solvent but there is no further attempt to control its downstream migration. The HA raffinate is concentrated by evaporation and the tritiated nitric acid solution is recycled. The effectiveness of this simple approach can be partially measured from data presented by Burrows et al (2006) that indicates THORP tritium discharges to the sea from 1994 to 2004 represented <0.01% of the Sellafield site limit. In UP2-800/UP3 and RRP, any tritium extracted into the solvent as water is further scrubbed with non-tritiated nitric acid in the second scrub column. The extent to which tritium is blocked from contaminating aqueous streams downstream of the 1ASS column is unknown but would be valuable to ascertain. The management of tritium in RRP could be especially important because radioactive discharges to sea appear to be very limited given the limitations on iodine-129 discharge to the sea from the plant.

4.2 Uranium Purification Flowsheets

4.2.1 THORP Uranium Purification

The THORP Uranium Purification (UP) flowsheet is shown in Figure 4-4. Key references for the flowsheet include Denniss and Phillips (1990a), Garraway (1984), Phillips (1991), Phillips (1992) and Phillips (1993).

The primary objective of the UP flowsheet is to separate the uranium from the neptunium and any residual plutonium. Pretreatment of the uranium feed facilitates oxidation of neptunium from the +4 valence to the inextractable +5 valence. Therefore, in the UP1 mixer-settlers, uranium is extracted into 20% TBP/OK while the neptunium remains in the aqueous phase. Additional separation is accomplished in the UP2 mixer-settlers. Additionally, hydroxylamine nitrate (HAN) is added to UP1 and UP2. HAN reduces any residual plutonium(IV) to inextractable plutonium(III) but does not reduce neptunium(V) to neptunium(IV). Therefore, the aqueous products from UP1 and UP2 contain the residual plutonium and neptunium and are concentrated with the raffinate from the HA column for vitrification. The organic product from UP2 contains the uranium and enters the UP3 mixer-settlers where it is stripped into 0.01M nitric acid. The UP cycles operated at a range of temperatures as indicated in Figure 4-4. A steam stripper removes any TBP/OK and the uranium solution is concentrated by evaporation ready for product finishing.

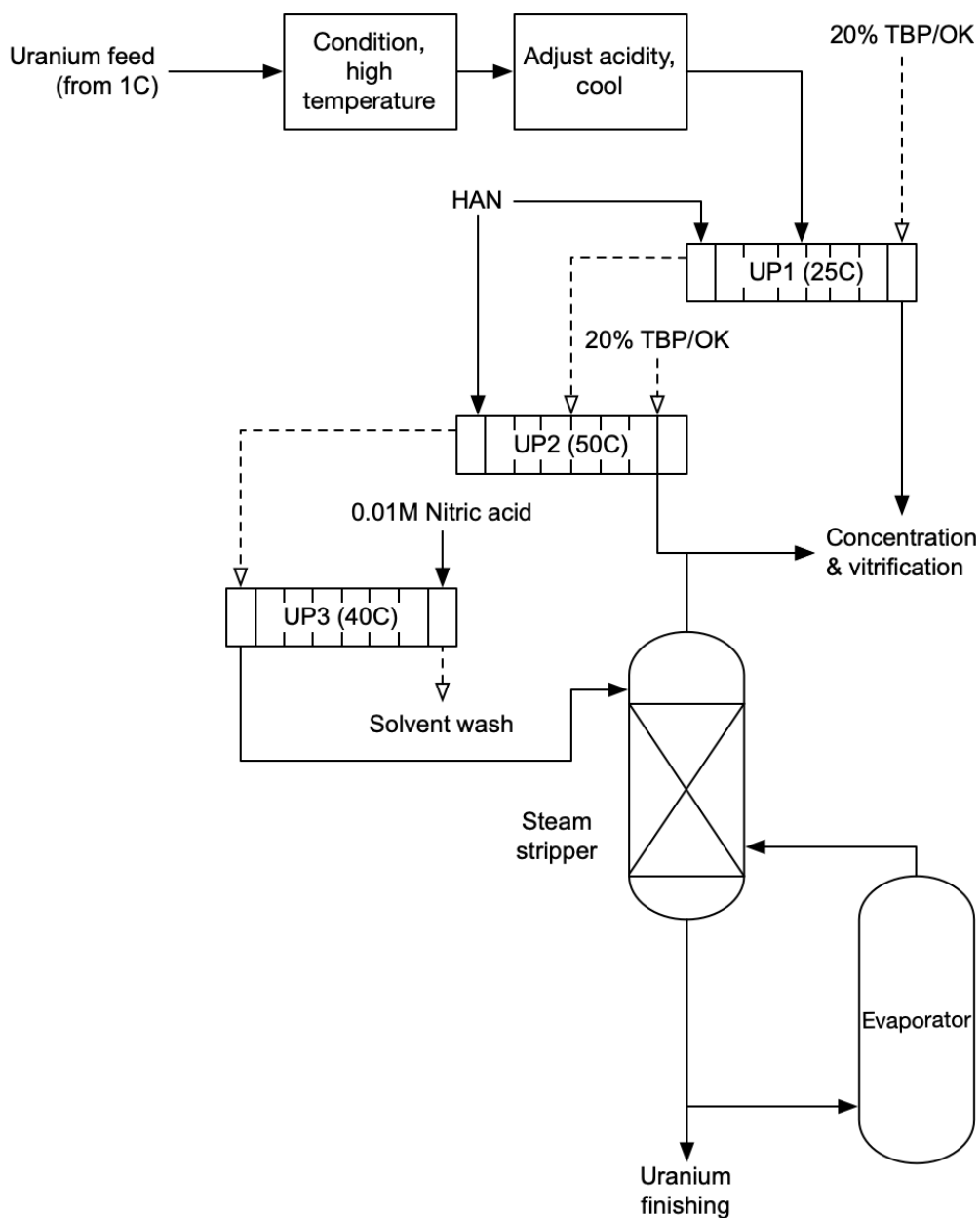


Figure 4-4. THORP Uranium Purification Flowsheet

4.2.2 UP2-800/UP3 Uranium Purification

There is little published on the details of the UP2-800/UP3 flowsheets for uranium purification with Baron et al (1993) and CEA (2008) providing relevant information. The main challenge for uranium purification is the separation of most of the neptunium arising from the UNF. From the published narrative the flowsheet in Figure 4-5 was constructed but could be a simplification of actuality.

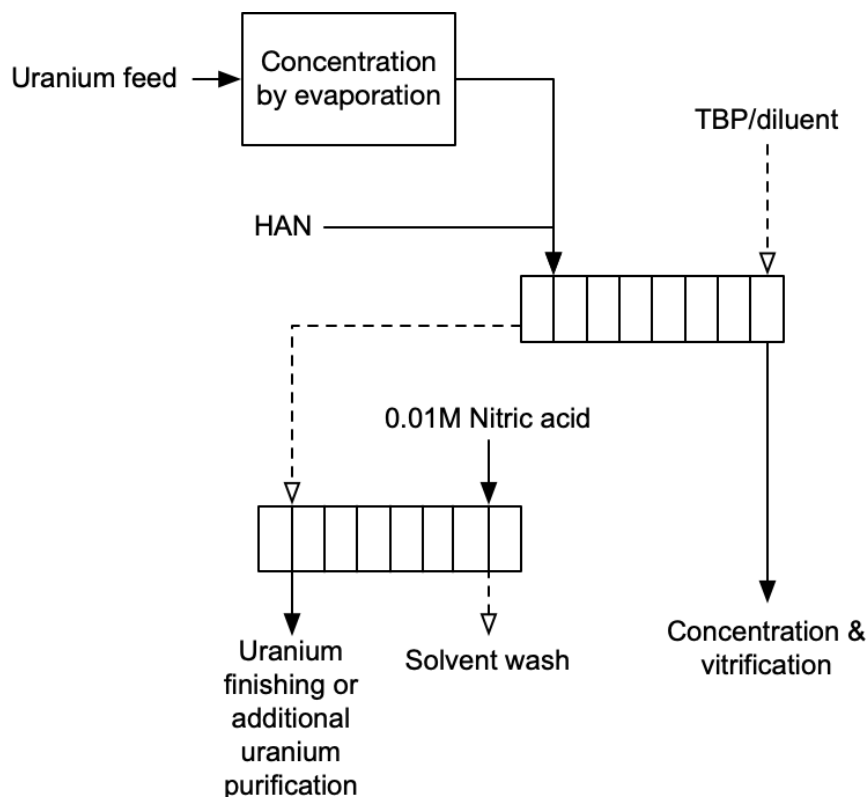


Figure 4-5. UP2-800/UP3 Uranium Purification

The uranium product from the preceding strip operation in Figure 4-3 is relatively dilute and so is concentrated to optimize the succeeding solvent extraction operations. The effect of evaporation is also to oxidize the neptunium to the +5 and +6 valence states. Neptunium(VI) is reduced with HAN in the succeeding solvent extraction operation such that the uranium is extracted using TBP in a diluent while neptunium remains in the aqueous phase. The aqueous raffinate containing the neptunium is concentrated and vitrified. Meanwhile the uranium in the loaded solvent is stripped with dilute nitric acid and the solvent treated and recycled. The destination of the uranium aqueous product from UP2-800 is unclear. It could be routed for uranium finishing or transferred to a third uranium purification cycle in UP3. The third uranium purification is intended to provide the final transuranic actinide decontamination and uses uranous nitrate to reduce residual neptunium and plutonium to their lowest inextractable valence states. In the case of neptunium, the effectiveness of this approach may be equipment dependent since uranium(IV) will reduce neptunium all the way to the extractable +4 state if the residence time is sufficiently long.

4.2.3 RRP Uranium Purification Flowsheet

The RRP uranium purification flowsheet is identical to that employed in UP2-800. Kawakatsu (1994) indicates two purification cycles are available but that data from then current plant (presumably UP2-800 and UP3, as also indicated by Emin (2005)) shows only a single cycle is needed. Therefore, the RRP purification flowsheet may only be operated with a single cycle.

4.2.4 Comparison of Uranium Purification Flowsheets

Identifying differences between the uranium purification flowsheets is challenging not least because the THORP flowsheet appears to have been reported in more detail than those employed in UP2-800/UP3 and RRP. The THORP flowsheet appears to employ two cycles of extraction/scrub in contrast to the single cycle in UP2-800/UP3 and RRP. This difference could be due to the additional scrubbing undertaken in the UP2-800/UP3/RRP primary separations.

4.3 Plutonium Purification Flowsheets

4.3.1 THORP Plutonium Purification

Very little detail of the THORP Plutonium Purification (PP) flowsheet has been published known to this report's author. Key references for the flowsheet depicted in Figure 4-6 include Denniss and Phillips (1990a), Phillips (1991), Phillips (1992) and Phillips (1993). However, all these references depict essentially the same flowsheet shown with little detail. NEA (2018) shows the operating temperature and identifies the reducing agent.

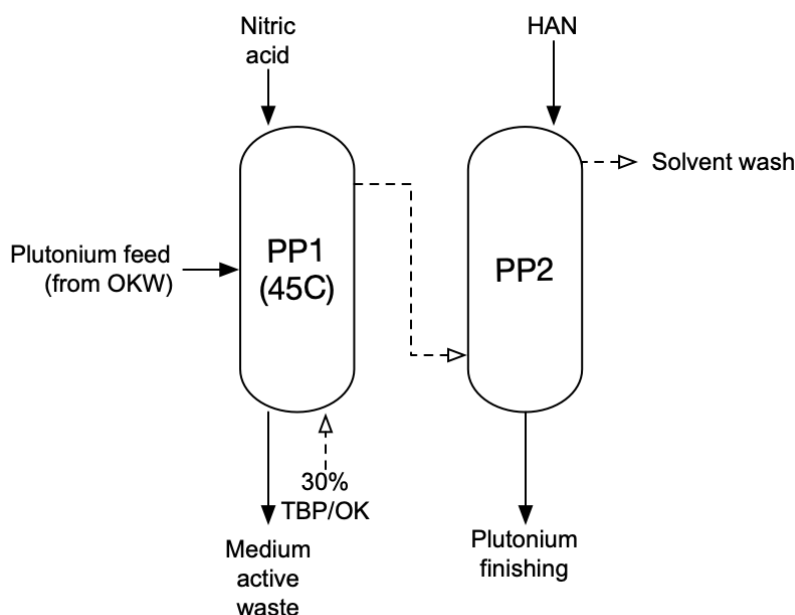


Figure 4-6. THORP Plutonium Purification Flowsheet

All solvent extraction steps in the PP flowsheet are undertaken with pulsed columns but no detail as to which phase is continuous is published. Essentially, the plutonium feed from the OKW column enters the PP1 column operating at 45°C where plutonium is extracted into 30% TBP/OK while technetium largely remains in the aqueous phase because there is no uranium or zirconium with which to form extractable complexes. The scrub must be sufficiently effective to separate any technetium co-extracted with the plutonium. The technetium-bearing aqueous product is considered 'medium active waste' in the references and is vitrified with the HA raffinate. The plutonium-bearing solvent passes to the PP2 column where HAN reduces the plutonium to the inextractable +3 valence such that it transfers to the aqueous phase for finishing.

4.3.2 UP2-800/UP3 Plutonium Purification

As for THORP, there is little published information on the plutonium purification flowsheets for UP2-800 and UP3. There are some flowsheet details, partly in narrative form, published by CEA (2008) and Bernard et al (1993) while Drain et al (2003) provide some solvent extraction technology information. From the published narrative the flowsheet in Figure 4-7 was constructed but could be a simplification of actuality.

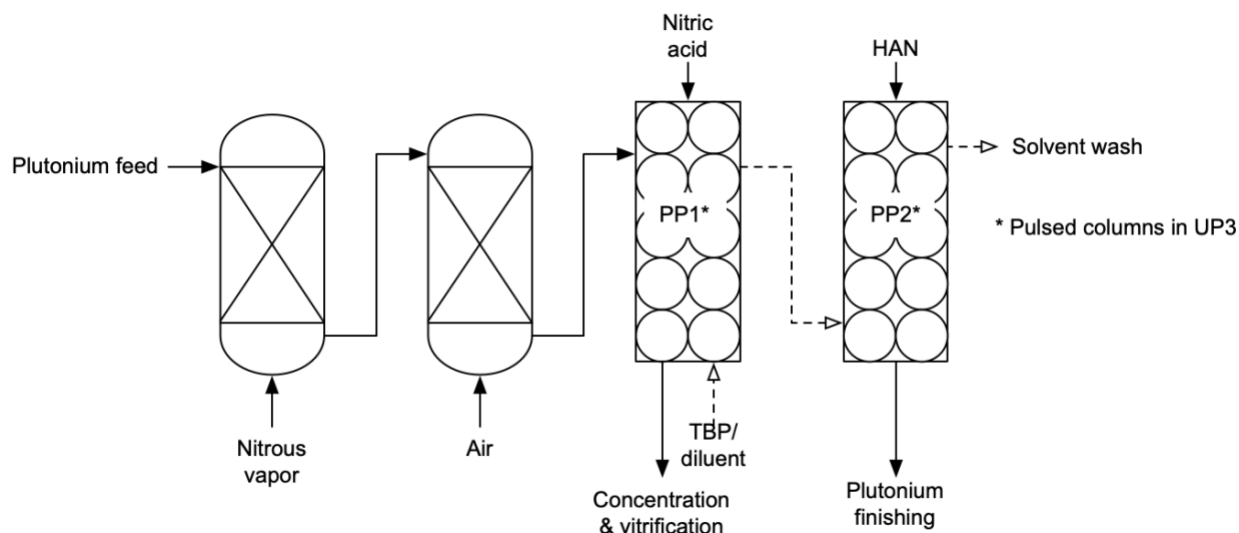


Figure 4-7. Plutonium Purification in UP2-800 and UP3

As a preliminary step, the plutonium product is contacted in a packed column with what are described as nitrous vapors to oxidize the plutonium to an extractable state. Subsequently, air is used in another packed column to remove excess nitrous acid. The PP1 bank of centrifugal contactors then extract the plutonium into a mixture of TBP and a diluent. The nitric acid raffinate is concentrated and vitrified. HAN is then used to reduce the plutonium to the inextractable +3 valence so it is stripped in PP2. The plutonium product is then ready for finishing.

4.3.3 RRP Plutonium Purification Flowsheet

The RRP plutonium purification flowsheet is identical to that employed in UP3. Kawakatsu (1994) indicates two purification cycles are available but that data from then current plant (presumably UP2-800 and UP3, as also indicated by Emin (2005)) shows only a single cycle is needed. Therefore, the RRP purification flowsheet may only be operated with a single cycle.

4.3.4 Comparison of Plutonium Purification Flowsheets

More so than the uranium purification flowsheet, there is little detail published on the plutonium purification flowsheet in any plant. They are likely essentially identical.

4.4 Implications for the Separations Flowsheet of a US Material Recovery Plant

Likely the most important implication for a US plant concerns plutonium recovery assuming it is desired. Notwithstanding the uranium-plutonium product finished in RRP, non-proliferation

policies would likely also mean pure plutonium should not be separated anywhere within a US plant. In this regard, the COEX™ flowsheet developed in France is applicable and could be considered nearest to an industrialized state-of-the-art. Drain et al (2008) and NEA (2008) describe the COEX™ separations flowsheet, which is very similar to that employed in UP2-800 and UP3. The major difference arises from adjusting the chemistry in the Uranium Scrub (1BS) of Figure 4-3 for it to become a scrub for only neptunium, which is directed to the UP cycle. Thereby, some uranium is routed with the plutonium into the subsequent uranium-plutonium purification cycle. Any scrubbing of uranium is avoided in the purification cycle. Details of the chemistry adjustments in developing the COEX™ flowsheet from that implemented in UP2-800 and UP3 have not been published. Alternatively, Lumetta et al (2018) showed that a significant portion of the uranium can be routed with the plutonium simply by adjusting the organic feed to the 1BS column.

Another consideration for a US plant is tritium management. Tritium is difficult to manage because it is essentially manifested as water and so, without some form of management, is historically permitted for discharge to the sea as wastewater. Discharging tritium to the sea will likely prove unacceptable if not impractical if a plant is located away from the ocean or large river. There are four technical management strategies for tritium that can be implemented in any one of the industrialized flowsheets:

- Voloxidation is a technology that has drawn significant attention mainly at US national laboratories for several decades although it has not yet been implemented in a plant. As described by DeCul et al (2012), standard voloxidation would involve heating the chopped fuel elements prior to dissolution (i.e., in the head-end) at between 500 and 600°C in air or oxygen. The effect of such conditions is to transform the uranium dioxide pellets to triuranium octoxide (U_3O_8) powder and to drive off tritium as water into the off-gas where it can be collected and immobilized into a suitable waste form. Most of the tritium is thereby separated from the UNF before any aqueous processing.
- Significant control over the migration of tritium (as tritiated water) is naturally accomplished by the solvent in the HA column. The solvent feed to the HA column will be pre-equilibrated with nitric acid from the solvent wash. Furthermore, the water solubility in the solvent will be reduced upon extraction of uranium and plutonium. Therefore, likely only limited migration of tritiated water into the solvent will occur. The UP2-800/UP3 flowsheet also includes a tritium scrub as depicted in Figure 4-2 and described in the same section. Tritium will preferentially remain in the HA raffinate, which is concentrated by evaporation and the water/nitric acid recycled into the headend. Thereby, most of the tritium is limited to the head-end and HA cycle separations with the water recycled as nitric acid. However, there likely is some purge of tritiated water given addition of the non-tritiated tritium scrub. Disposal of the purge is not published but could either be immobilized and dispositioned or discharged to the sea. How much tritium makes it through to the 1BS system in any flowsheet and how it is managed has not been published. However, the tritium scrub appears to be effective at least to satisfy regulators in France and Japan although its applicability to the US by itself is unknown.
- There are two options for tritiated liquid effluent:
 - Any liquid effluent containing tritium at concentrations above the regulatory standard could be immobilized and dispositioned as LLW. There is no limit on tritium for LLW. Instead, the regulations anticipate practical considerations for transportation, handling and disposal will limit the concentration.

- Alternatively, there are several technologies available and industrialized for removing tritium from nuclear power plant wastewater, although none have been demonstrated with liquid effluent arising from a reprocessing plant. Key reference material useful for assessing the technologies include those by Zhao et al (2025) and DOE (2022).

Tritium management in a reprocessing plant is intrinsically associated with the plant's water balance. Tritium management should be considered in that context alongside the technical solutions described above to mitigate any liquid effluent containing tritium at concentrations above regulatory standards prior to environmental release.

5.0 Comparison of Product Finishing Flowsheets

5.1 Product Finishing in THORP

There is little published information on the product finishing processes in THORP. Burrows et al (2006) mention the uranium is converted from the dissolved nitrate form to oxide powder by thermal denitration but provides no detail. Conversion of plutonium nitrate to oxide is described by Baxter (1989) from which the flowsheet in Figure 5-1 was derived.

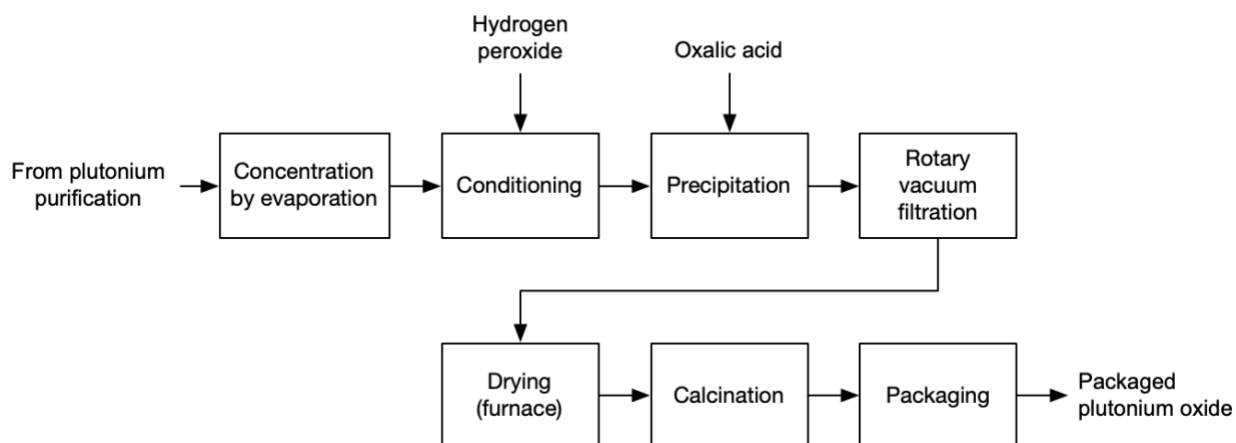


Figure 5-1. Plutonium Finishing at THORP

The well-known oxalate route for plutonium finishing in THORP was adopted. The plutonium aqueous product is first concentrated by evaporation and then conditioned with hydrogen peroxide to ensure the plutonium is in the +4 valence state appropriate for subsequent operations. Plutonium oxalate is precipitated by the addition of oxalic acid and the solids separated by a rotating table vacuum filter. The oxalate cake is dried and converted to oxide in a furnace, which is followed by a calciner in which the surface properties of the plutonium dioxide are adjusted for storage.

5.2 Product Finishing in UP2-800 and UP3

As for THORP, there is little information published on the product finishing processes in UP2-800 and UP3. The current process for uranium finishing involves the precipitation of the metal in peroxide form using hydrogen peroxide. Presumably the uranium peroxide is heat treated to produce the oxide powder. Uranium finishing appears not be undertaken in UP2-800 or UP3 but at other sites in France according to CEA (2008). This perhaps explains why the conversion process currently employed is less compact and yields greater liquid effluent compared to denitration, as explained by CEA (2008).

CEA (2008) describes the oxalate route for finishing plutonium, which is completed in UP2-800 and UP3 according to Emin et al (2005). The flowsheet is depicted in Figure 5-2. As in THORP, plutonium oxalate is precipitated in a vortex reactor and then filtered in a rotary drum. The plutonium oxalate cake is then calcined to produce the oxide powder.

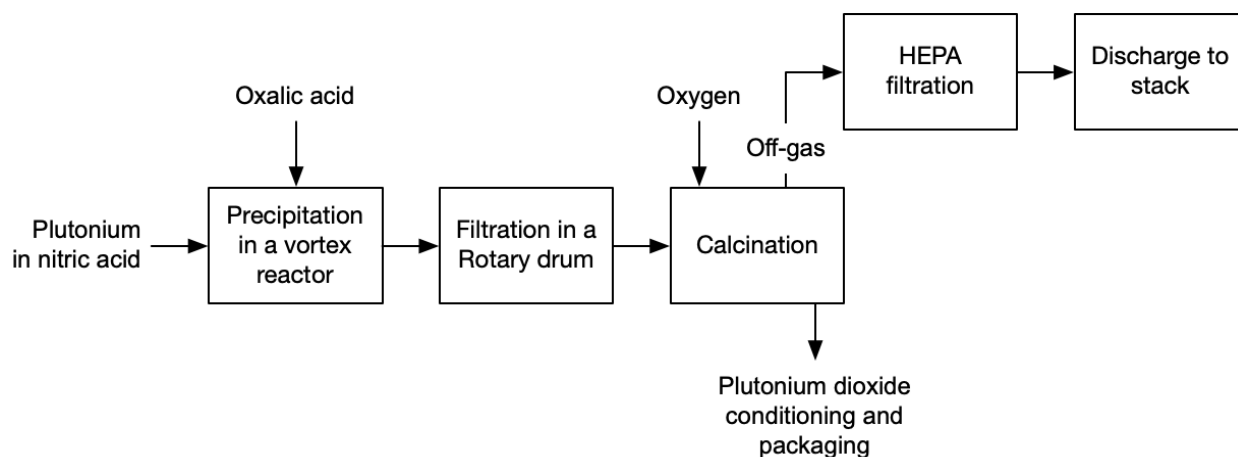


Figure 5-2. Plutonium Finishing Flowsheet in UP2-800 and UP3

5.3 Product Finishing in RRP

Kawakatsu (1994) summarizes the uranium and plutonium finishing processes. The purified uranium product is concentrated in an evaporator and then denitrated in a heated fluidized bed reactor. The uranium trioxide powder is packaged and stored.

The plutonium finishing process is unique to RRP and, as described by Oshima (1989), was heavily influenced by an agreement between Japan and the US in 1977 that the former should produce a mixed uranium-plutonium product from its reprocessing plants. The agreement led to the Japanese nuclear establishment developing its own finishing process that was incorporated into RRP. As described by Kawakatsu (1994), the mixed 1:1 uranium-plutonium finishing process is based on a unique microwave heating system that denitrates the mixture. The denitrated mixture is then converted to dioxide powder by calcination and reduction processes.

5.4 Comparison of Product Finishing Flowsheets

Uranium finishing processes are essentially the same across all three plants and uses a well-established technology. The plutonium finishing process in THORP and UP2-800/UP3 employ the same oxalate precipitation technology with potential differences in equipment type although there is some variation in the published detail that precludes discernment of specific differences. The RRP plutonium finishing flowsheet is different in denitrating a mixture of uranium and plutonium to satisfy non-proliferation policies. The mixed product is arguably more amenable to producing Mixed Oxide fuel because it is a solid solution that would not require mixing of powders.

5.5 Implications for the Finishing Flowsheet of a US Material Recovery Plant

As described in section 4.4, US non-proliferation policies will likely require that no pure plutonium be produced in the plant, which has implications for product finishing in a US plant. The philosophy for RRP has been that no pure plutonium would leave the plant. Therefore, even though a pure plutonium solution will be separated in RRP, it is later mixed with uranium prior to finishing a mixed uranium-plutonium product. Therefore, a US plant could employ the RRP technology of microwave denitration. Alternatively, a uranium-plutonium finishing process using

the oxalate technology for plutonium product finishing has been described by Drain et al (2008) for the COEX™ flowsheet and patented by Bertrand et al (2015). Another option is thermal denitration using technology established for uranium product finishing as implemented in the subject reprocessing plants. Successful preliminary testing of such processes has been completed by Hobbs and Parkes (2000), Mailen et al (1982) and Lumetta et al (2017).

6.0 Conclusions

There are several conclusions from this work:

- The flowsheets implemented in the plants are broadly similar. This should not be surprising given the cooperation and information sharing by the British and French plant owners and then the contracted French influence on the Japanese RRP. A key difference between these flowsheets and their precursors is employing uranium(IV) as reductant for plutonium and the absence of any salt in the separations flowsheets. The volume of high active raffinate and subsequent vitrified product is thereby minimized.
- A key difference in the separations flowsheets concerns the management of technetium and its impact on hydrazine stability. The THORP and UP2-800/UP3 flowsheet designers addressed the issue differently with solutions equally as valid with their own advantages and disadvantages. BNFL chose to directly reduce hydrazine decomposition by modifying the contactor to minimize contact time. However, the modification likely did not completely resolve the issue, and additional hydrazine was likely still needed. Areva chose to remove technetium before using hydrazine, but the additional waste stream needed separate processing.
- Volatile radionuclides management depends on local regulations and how they are implemented. Nearly all the iodine-129 in THORP was captured from the off-gas, directed to the liquid effluent and eventually discharged to sea. Nevertheless, some iodine-129 would have been discharged to the air although carbon-14 was captured from the off-gas and immobilized for disposal. On the other hand, essentially all the iodine-129 was captured in UP2-800/UP3 before discharge to the sea but carbon-14 was released to the air. This comparison likely represents a holistic risk-based approach to regulating environmental releases. Conversely, no environmental discharge of iodine-129 is allowed from RRP and the radionuclide is captured on solid media for disposal but there is no separation of carbon-14.
- Tritium management is employed to the extent needed for regulatory compliance. In all flowsheets, tritium migration beyond the HA cycle is significantly limited by the low water solubility of the solvent. In UP2-800/UP3 and RRP, a tritium scrub is also employed that would further reduce environmental discharges.
- Plutonium management has depended on policy and treaty requirements that are evolving. All current flowsheets separate plutonium with the older flowsheets in Europe also producing a pure plutonium product. Japan's RRP was required by treaty to produce a mixed uranium-plutonium product. Policy on plutonium management in reprocessing UNF has now evolved to the point that a plant should not separate pure plutonium.

7.0 Recommendations

Several recommendations arise from the evaluation presented in this report in terms of the subject flowsheets representing the industrialized state of the art:

- The flowsheets evaluated for this report are recommended as baselines against which improvements expected from research initiatives should be qualitatively measured. Only a qualitative measurement can be made because material balances are not available although they could be modeled with some assumptions.
- The tritium management solutions presented in section 4.4 should be evaluated in the context of water and liquid effluent management. The evaluation should aim to understand the advantages and disadvantages of each solution by themselves or in combination.

8.0 References

- Arm, ST and EJ Butcher. 2009. *Treatment and Disposal of Process Wastes Arising from the Recycle of Spent Nuclear Fuel in the USA*. WM'09, March 1-5, Phoenix, AZ.
- Baron, P, B Moullis, M. Germain, JP Gue, P Miquel, FJ Poncelet, JM Dormant, F. Dutertre. 1993. *Extraction Cycles Design for La Hague Plants*. GLOBAL 93, September 12 – 17, Seattle, WA.
- Baxter, W. 1989. *Plutonium Finishing and Product Packaging at THORP*. Atom 397, UK Atomic Energy Authority.
- Bernard, C, P Miquel and M Viala. 1991. *Advanced PUREX Process for the New Reprocessing Plants in France and Japan*. International Conference on Nuclear Fuel Reprocessing and Waste Management (RECOD '91), Sedai, Japan, 14-18 April.
- Bernard, C, JP Moulin, P Ledermann, P Pradel and M Viala. 1993. *Advanced PUREX Process for the New French Reprocessing Plants*. GLOBAL 93, September 12 – 17, Seattle, WA.
- Bertrand, M, S Grandjean, C Bruno, F Auger. 2015. *Method for Preparing an Actinide(s) Oxalate and for Preparing an Actinide(s) Compound*. US Patent US 8,940,817 B2.
- Burrows, C., C. Phillips and A. Milliken. 2006. *The Thermal Oxide Reprocessing Plant at Sellafield – Lessons Learned from 10 Years of Hot Operations and their Applicability to the DOE Environmental Management Program*. WM'06 Conference, February 26 – March 2, Tucson, AZ.
- CEA (Commissariat à l'énergie atomique). 2008. *Treatment and Recycling of Spent Nuclear Fuel*. A Nuclear Energy Division Monograph, Commissariat à l'énergie atomique, CEA Saclay and Groupe Moniteur (Éditions du Moniteur), Paris, France.
- DeCul, GD, BB Spencer, RD Hunt, RT Jubin, ED Collins. 2012. *Advanced Head-End for the Treatment of Used LWR Fuel*. Actinide and Fission Product Partitioning and Transmutation, 11th Information Exchange Meeting, 1-4 November 2010, San Francisco, CA, Organization for Economic Co-Operation and Development, Nuclear Energy Agency.
- Denniss, IS and C Phillips. 1990a. *The Development of a Three-Cycle Chemical Flowsheet to Reprocess Oxide Nuclear Fuel*. Solvent Extraction 1990 (Proceedings of the International Solvent Extraction Conference '90), editor T Sekine, Elsevier.
- Denniss, IS and C Phillips. 1990b. *The Development of a Flowsheet to Separate Uranium and Plutonium Present in Irradiated Oxide Fuel*. Institute of Chemical Engineers Symposium Series Number 119.
- DOE. 2022. *2022 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*. DOE/RL-2022-09. DOE Richland Operations Office, Richland, WA.
- Drain, F, B Boullis, D Hugelman, Y. Ohtou. 1991. *Extraction Process Technology for the New Reprocessing Plants in France and Japan*. International Conference on Nuclear Fuel Reprocessing and Waste Management (RECOD '91), Sedai, Japan, 14-18 April.

- Drain, F, P Miquel, JP Moulin, D Alexandre, B Kniebihl, B Boullis and P Baron. 1997. *Uranium/Plutonium Separation in Annular Pulsed Column*. Global '97, Yokohama, Japan.
- Drain, F, R Vinoche, J. Duhamet. 2003. *40 Years of Experience with Liquid-Liquid Extraction Equipment in the Nuclear Industry*. WM'03, February 23 -27, Tucson, AZ.
- Drain, F, JL Emin, R Vinoche and P Baron. 2008. *COEX™ Process: Cross-Breeding Between Innovation and Industrial Experience*. WM'08 Conference, February 24-28, Phoenix, AZ.
- Emin, JL, MF Debreuville, F Drain. 2005. *From a Scientific Feasibility to the Industrial Application: the COGEMA Experience*. WM'05 Conference, February 27 – March 3. Tucson, AZ.
- Fournier, W, D Hugelmann, G Dalverny, C Bernard and P Miquel. 1992. *PUREX Process Improvements for the UP3 Spent Nuclear Fuel Reprocessing Plant at La Hague, France*. Solvent Extraction 1990 (Proceedings of the International Solvent Extraction Conference '90), editor T Sekine, Elsevier.
- Furrer, J and W Weinlander. 1990. *Off-Gas Cleaning in an FRG Reprocessing Plant*. Nuclear Technology 92:1, 66 – 76.
- Garraway, J. 1984. *The Behavior of Technetium in a Nuclear Fuel Reprocessing Plant*. Institute of Chemical Engineers Symposium Series number 88.
- Heinrich, E, R Huffner, F Weirich, W Bumiller and A Wolff. 1985. *Selective Absorption of Noble Gases in Freon-12 at Low Temperatures and Atmospheric Pressure*. Proceedings of the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, Maryland, 12- 16 August, 1984.
- Hobbs, JW, and P Parkes. 2000. *Production of MOX pellets from Plutonia and Mixed Oxide Powders Prepared by Direct Thermal Denitration*. Scientific Research on the Back-end of the Fuel Cycle for the 21st Century. Atalante 2000, Avignon, France, 24-26 October.
- Hudson, PI and AP Jeapes. 1989. *Development of the Thorp Plant*. Atom 393, UK Atomic Energv Authority.
- Hudson, PI and CP Buckley. 1995. *Aerial and Liquid Effluent Treatment in BNFL's Thermal Oxide Reprocessing Plant (THORP)*. Proceedings of the First NUCEF International Symposium, October 16-17. Japan.
- Kawakatsu, T. 1994. *Design and Construction of Rokkasho Reprocessing Plant*. International Conference on Nuclear Fuel Reprocessing and Waste Management (RECOD '94), London, UK, 24-28 April.
- Lumetta, GJ, SA Bryan, AJ Casella, GB Hall, TG Levitskaia, AM Lines and GJ Sevigny. 2017. *CoDCon Project: FY 2017 Status Report*. NTRD-MRWFD-2017-000222. Pacific Northwest National Laboratory, Richland, WA.
- Lumetta, GJ, JR Allred, SA Bryan, GB Hall, FD Heller, TG Levitskaia, AM Lines and SI Sinkov. 2018. *CoDCon Project: FY 2018 Status Report*. NTRD-MRWFD-2018-000224. Pacific Northwest National Laboratory, Richland, WA.

Mailen, JC, DJ Pruett and DR McTaggart. 1982. *Direct Thermal Denitration to Prepare Mixed Oxides for Nuclear Fuel Fabrication*. ORNL/TM-8197. Oak Ridge National Laboratory, Oak Ridge, TN.

Mayson, RTH, and KJ Kunston. 1999. *Challenges in the Application of Burn-up Credit to the Criticality Safety of the THORP Reprocessing Plant*. Proceedings of the 2nd NUCEF international symposium NUCEF'98, Hitachinaka, Japan.

NEA. 2018. *State of the Art Report on the Progress of Nuclear Fuel Cycle Chemistry*. Organization for Economic Co-Operation and Development, Nuclear Energy Agency. NEA 7267.

Oshima, H. 1989. *Development of Microwave Heating Method for Co-Conversion of Plutonium-Uranium Nitrate to MOX Powder*. Journal of Nuclear Science and Technology 26 (1), 161 – 166.

Phillips, C. 1991. *The Separation of Uranium and Plutonium in the Thermal Oxide Reprocessing Plant Using Pulsed Column Contactors*. American Institute of Chemical Engineers International Symposium on Reprocessing and Waste Management, August 18-21, Pittsburgh, USA.

Phillips, C. 1992. *Uranium-Plutonium Partitioning by Pulsed Column in the First Cycle of the Three-Cycle Thermal Oxide Reprocessing Plant*. WM'92, Tucson, AZ.

Phillips, C. 1993. *Development and Design of the Thermal Oxide Reprocessing Plant at Sellafield*. Transactions of the Institute of Chemical Engineers, Vol. 71, Part A, 134 - 142.

Saudray, D., FJ Poncelet, D Hugelmann, S. Mukohara and A. Cho. 1991. *Head End Process Technology for the New Reprocessing Plants in France and Japan*. International Conference on Nuclear Fuel Reprocessing and Waste Management (RECOD '91), Sedai, Japan, 14-18 April.

Schneider, M and Y Marignac. 2008. *Spent Nuclear Fuel Reprocessing in France*. Research Report No. 4, International Panel on Fissile Materials.

von Ammon, R, HG Burkhardt, E Hutter and G Neefe. 1978. *Development of a Cryogenic Krypton Separation System for the Off-Gas of Reprocessing Plants*. Proceedings of the 15th DOE Nuclear Air Cleaning Conference, Boston.

Zhao, Z, Y Sun, Q Chen, T Li, F Liu, T Yan and W Zheng. 2025. *Research Progress in Tritium Processing Technologies: A Review*. Separations **2025** 12, 33.

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