PNNL-31863

Flowsheet Evaluation of Dissolving Used Nuclear Fuel in PUREX Solvent

September 2021

Stuart T Arm

Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

This study explores the potential benefit of a process simplification to the flowsheet for recovering actinides from used nuclear fuel, and establishes the experimental work needed to develop the simplified flowsheet. The simplification is based on replacing acid dissolution of used nuclear fuel with dissolution in the tri-butyl phosphate solvent used in the industrially mature Plutonium Uranium Reduction Extraction flowsheet. Though characterized by considerable uncertainty, simplified flowsheets appear feasible and potentially offer significant reductions in process complexity, nitrate inventory, secondary liquid effluent generation and plant footprint. Initial development of the technology should focus on key fission product and actinide dissolution as a function of process conditions and understanding the fundamental chemistry of tri-butyl phosphate solvent chemistry. Development of ancillary technologies for minor actinide separations and fuel pretreatment for tritium management is also recommended.

Summary

In the United States, the current approach to managing used nuclear fuel (UNF) is once-through, with UNF stored at the reactor sites while a geological repository is established for its disposal. The United States Department of Energy Office of Nuclear Energy is leading development of technologies for processing UNF to recover actinides for recycle into reactors, improve repository utilization and help inform future decisions regarding the nuclear fuel cycle. Advanced separation chemistry processes have been and are being developed with several goals, including preventing the separation of pure plutonium, process simplification, minor actinide management, and waste minimization. This study was initiated to explore the potential benefit to the UNF actinide recovery flowsheet of a process simplification and establish the experimental work needed to develop the simplified flowsheet. The simplification is based on replacing acid dissolution of UNF with dissolution in the tri-butyl phosphate (TBP) solvent used in the industrially mature Plutonium Uranium Reduction Extraction (PUREX) flowsheet.

Three conceptual flowsheets were developed for the purposes of this study. A baseline flowsheet was established with standard voloxidation pretreatment of UNF, dissolution of the voloxidized UNF in hot nitric acid and subsequent actinide separations using advanced PUREX, Transuranium Extraction (TRUEX) and Trivalent Actinide-Lanthanide Separations by Phosphorus Reagent Extraction from Aqueous 'K'omplexes (TALSPEAK) solvent extraction processes. Two alternative flowsheets replacing acid dissolution with dissolution in TBP solvent were established incorporating standard and advanced voloxidation pretreatment. The flowsheets were based on the limited experimental results available in the published literature and the expert technical judgment of the author.

Flowsheets that replace acid dissolution of UNF with TBP solvent dissolution appear feasible. Important differences between acid and TBP solvent dissolution flowsheets include:

- Dissolution in TBP solvent of the minor actinides and lanthanide fission products. In contrast, these constituents are inextractable in a conventional PUREX solvent extraction flowsheet with acid dissolution of UNF.
- TBP solvent dissolution can be practically undertaken at near-ambient temperatures whereas acid dissolution is conducted at a near-boiling temperature.

There is little difference in the nitrate inventory between acid and TBP solvent dissolution flowsheets. This is principally because the nitrate inventory is dominated by the concentrated nitric acid needed to separated technetium from uranium. The major advantage potentially offered by TBP solvent dissolution arises from its near-ambient process temperature. However, a TBP solvent dissolution flowsheet potentially offers significant benefits over a conventional flowsheet incorporating acid dissolution when minor actinide management is desired. Dissolution of minor actinides means the TRUEX solvent extraction system is not needed with benefit to reducing secondary liquid effluent generation and nitrate inventories to levels a little more than what are expected from a PUREX-only flowsheet. Application of TBP solvent dissolution to development of a single cycle flowsheet is largely dependent on whether technetium can be made insoluble so that its separation from uranium in a purification cycle is not required. Doing so would also introduce benefit in significantly reducing the nitrate inventory.

There is considerable uncertainty in the TBP solvent dissolution flowsheets, which is reflected in the low Technology Readiness Level. Major areas needing further elaboration in a Technology

Maturation Plan and using simulated UNF to advance the technology's readiness for demonstration with actual UNF include:

- Dissolution characteristics of key fission products including noble metals, technetium, ruthenium, zirconium and iodine.
- Establishing the envelope of potential process conditions (temperature and nitric acid concentration in the TBP phase) and dissolution characteristics of actinides and key fission products.
- Understanding the fundamental chemistry of TBP dissolution (i.e., extraction without a separate acid phase) especially for minor actinides and lanthanide fission products.

Removal of the need for the TRUEX system does mean some modification of the TALSPEAK flowsheet that necessitates further development with respect to a dilute nitric acid feed; alkali and alkali earth metal fission products in the feed; and higher concentrations of minor actinides and lanthanide fission products.

Significant dissolution of iodine in the TBP solvent when employing standard voloxidation will require an improved understanding of its behavior in the separations processes including the PUREX scrub and the modified Reverse TALSPEAK processes to establish a management strategy for the radionuclide.

Standard and advanced voloxidation are UNF pretreatment technologies that are important in managing tritium in actinide recovery flowsheets. Though not the subject of this evaluation, these technologies should be evaluated for their readiness levels to underpin development and subsequent implementation of technology maturation plans.

Acknowledgments

This work was sponsored by the U.S. Department of Energy Office of Nuclear Energy through the Nuclear Fuel Cycle and Supply Chain office. The author thanks Stephen Kung (Federal Program Manager) and Ken Marsden (National Technical Director) for their support of this work. The author also thanks Gregg Lumetta of Pacific Northwest National Laboratory and Stephanie Bruffey and Allison Greaney of Oak Ridge National Laboratory for their helpful suggestions during the course of this study. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

ALSEP	Actinide-Lanthanide Separation
BoC	Basis of Comparison
FP	Fission Product
HEDTA	N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid
LFP	Lanthanide Fission Product
NMFP	Noble Metal Fission Product
NOx	Nitrogen OXide
PUREX	Plutonium Uranium Reduction Extraction
TALSPEAK	Trivalent Actinide-Lanthanide Separations by Phosphorus Reagent Extraction from Aqueous ‘K’omplexes
TBP	Tri-Butyl Phosphate
THORP	Thermal Oxide Reprocessing Plant
TRU	Transuranium element
TRUEX	Transuranium Extraction
UNF	Used Nuclear Fuel

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1.0 Introduction

1.1 Background

Aqueous separation technologies have been successfully used to recover and recycle uranium and plutonium from irradiated commercial used nuclear (UNF) most notably in Europe. Uranium and plutonium recycle results in increased power production from mined uranium resources and contributes to the national energy security of the country recycling their UNF. Additionally, appropriately processing the UNF reduces the volume of high-level waste requiring geologic disposal and there are potential benefits in reducing the radiotoxicity of the disposed material. Processing the UNF to also separate the minor actinides for transmutation results in further improving the utilization of a geologic repository by reducing the heat load.

As applied industrially, UNF is mechanically chopped into small pieces (~3 cm long) and dissolved in hot nitric acid. The resulting dissolver product is processed via solvent extraction to separate actinides for fabrication into nuclear reactor fuel. The remaining metals and fission products are vitrified into borosilicate glass for disposal as a high-level waste. The Plutonium Uranium Reduction Extraction (PUREX) process is the most common, and current state of the art solvent extraction technology employed to recover and purify uranium and plutonium from UNF.

In the United States, the current approach to managing used nuclear fuel is once-through, with used fuel stored at the reactor sites while a geological repository is established for its disposal. The United States Department of Energy Office of Nuclear Energy is leading development of technologies for processing UNF to help inform future decisions regarding the nuclear fuel cycle. Advanced separation chemistry processes have been and are being developed with several goals, including preventing the separation of pure plutonium (improved proliferation resistance), process simplification (reduced cost), minor actinide management (repository benefit), and waste minimization (e.g., fuel cladding waste decontamination and conversion to low level waste or potential reuse). These technologies include PUREX based flowsheets as well as processes based on alternative extractants.

This study was initiated to explore the potential benefit to the UNF actinide recovery flowsheet of a process simplification and establish the experimental work needed to develop the simplified flowsheet. The simplification is based on dissolving the UNF in the PUREX solvent and so avoid the hot nitric acid dissolution step.

1.2 Scope

This study was limited to considering the simplification in the context of the PUREX-based flowsheet for actinide recovery. As such, alternative solvents are not considered (some are considered by Kulyako et al. (2007)), nor are alternative separations flowsheets (e.g., supercritical carbon dioxide conceptually considered by Kulyako et al. (2007)). The limited experimental work of Kulyako et al. (2003) considered simulated UNF containing uranium, plutonium, neptunium, americium and europium as solid solutions. The authors' later work in 2007 included only uranium and plutonium. Key to the initiation of this study is more recent work by Rudisill et al. (2019) who experimentally investigated PUREX solvent dissolution again with simulated UNF but containing major and minor actinides as well as a variety of fission products. Rudisill et al. (2019) essentially confirmed and expanded upon the earlier work of Kulyako et al. (2003, 2007) and DelCul (2015).

The study described in this report is an evaluation of the flowsheet benefits to dissolving UNF in PUREX solvent. In this context ‘flowsheet’ refers to inventories of key constituents, secondary process wastes and process complexity. While there are consequential benefits to plant size and layout, they were not explored in this study given the very initial stage of development. Likely plant benefits are, however, noted at summary levels where appropriate.

2.0 Potential Flowsheets for Evaluation

This section describes the conceptual flowsheets and their uncertainties that are used to evaluate the benefits of UNF dissolution in PUREX solvent. While historic and current actinide recovery plants all dissolve chopped UNF in nitric acid, the baseline flowsheet considered here incorporates voloxidation pretreatment to facilitate the control of tritium. Tritium is not controlled in historic and current plants so that it is released to the environment. That practice is not considered legally or socially viable for a future plant in the United States and so dissolution of chopped UNF was not considered baseline for the purpose of this study.

2.1 Basis of Comparison

2.1.1 Flowsheet Description

A flowsheet incorporating established aqueous dissolution of UNF was developed based on the full recycle case study prepared by Law et al. (2014) and Vienna (2015) and serves as the basis of comparison. This Basis of Comparison (BoC) flowsheet is illustrated in Figure 2-1.

Disassembly and chopping of the UNF assemblies exposes the fuel to standard voloxidation to drive tritium into the off-gas, which is filtered of fuel fines before the tritium is separated. Various options are available for tritium separation from the voloxidation off-gas as described by Vienna (2015). The fuel powder generated by voloxidation is dissolved in hot concentrated nitric acid. Off-gas from acid dissolution is treated first through a condenser before iodine is separated. The off-gas is further treated to separate nitrogen oxides and oxygen before separation of noble gases. Insoluble fission products, typically noble metal fission products (NMFPs), are separated from the dissolved fuel and stabilized with the fuel hulls into a metal waste form for disposal.

The clarified dissolved UNF solution is adjusted for nitric acid concentration and processed using the organic extractant tri-butyl phosphate (TBP) to separate the major actinides (uranium, plutonium and neptunium) and technetium. The separated major actinides are further purified for fabrication into fuel. Technetium is separated from the major actinides in the organic solvent using concentrated nitric acid. The UNF solution can be further processed to separate minor actinides (americium and curium) to improve geologic repository utilization. Minor actinide separation can be accomplished either using the Actinide-Lanthanide Separation (ALSEP) process or a combination of Transuranium Extraction (TRUEX) and Trivalent Actinide-Lanthanide Separations by Phosphorus Reagent Extraction from Aqueous ‘K’omplexes (TALSPEAK) processes. An overview of the minor actinide separation processes is provided by the Nuclear Energy Agency (2018).

The fission products and minor actinides if not separated are calcined and vitrified into a glass waste form for disposal into a geologic repository. Any residual iodine is separated from the calciner off-gas and the nitrogen oxides abated.

While the majority of the iodine is released into the dissolver off-gas (between 95% and 99% was estimated by Jubin et al. (2013)) the fractions reporting to other process streams must also be considered for environmental protection purposes. According to Jubin et al. (2013), much of the dissolved iodine is extracted into the solvent and is distributed between vessel off-gas and stabilized secondary waste arising from solvent and aqueous effluent treatment. Much of the iodine in the vessel off-gas is expected to be more recalcitrant organo-iodine species. In summary, iodine separation from the dissolver off-gas alone is insufficient and it must also be removed from the larger volume of vessel off-gas.

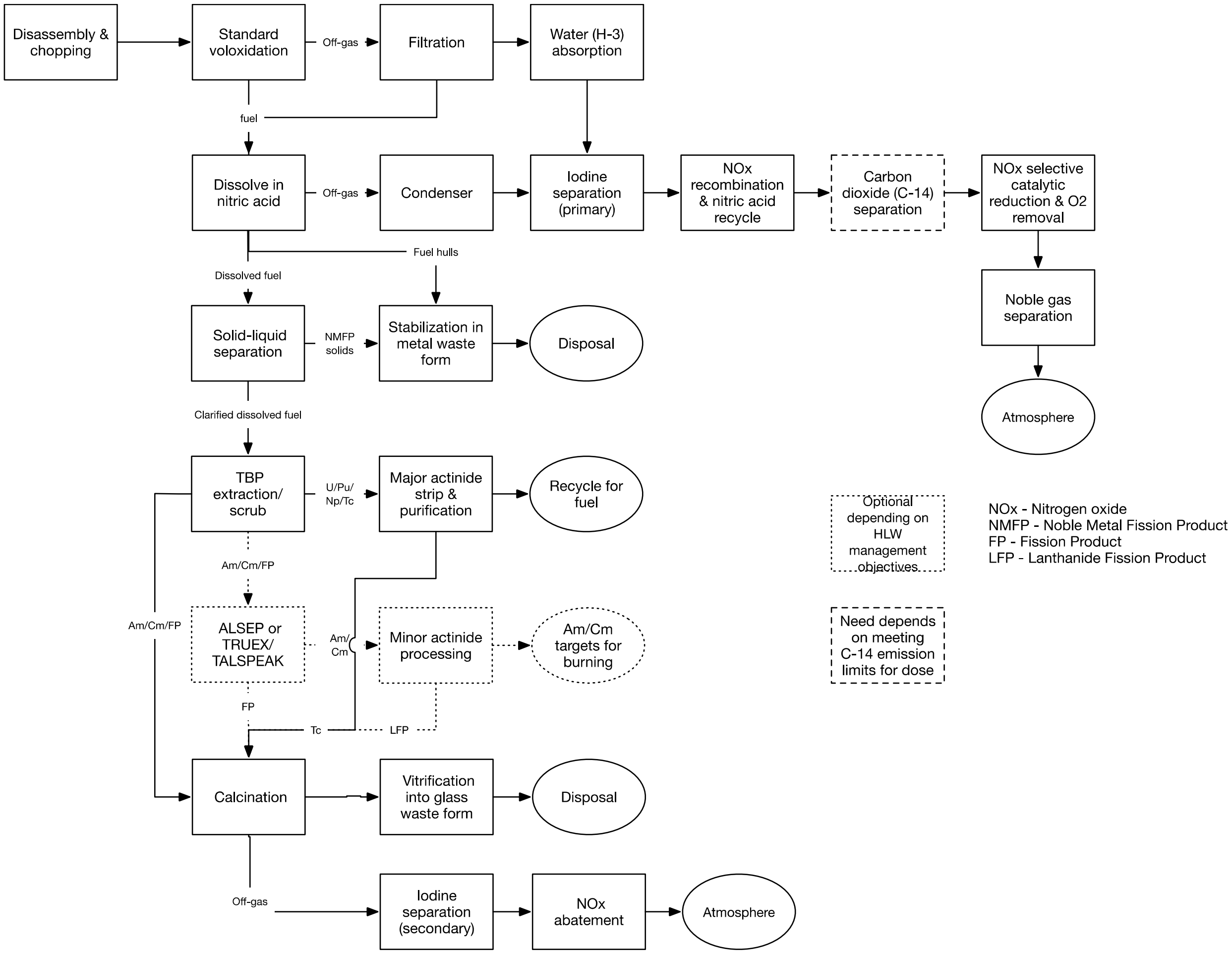

Figure 2-1. Basis of Comparison Flowsheet for UNF Actinide Recovery

2.1.2 Opportunities for Flowsheet Optimization

The opportunities for optimizing the BoC flowsheet have been described at length elsewhere, by Law et al. (2014), for example. However, in the context of this study, certain specific areas of optimization are noteworthy.

- In contrast to the flowsheet described by Law et al. (2014), the BoC flowsheet incorporates standard voloxidation such that the iodine evolves into the dissolver off-gas. The various aqueous scrubbing and solid sorbent approaches to iodine separation have been amply reviewed elsewhere; reviews by Riley et al. (2016) and Huve et al. (2018) are recent examples. Whereas the BoC and most other flowsheets focus on using only a solid sorbent, Jubin et al. (2018) have recommended a flowsheet integrating an aqueous scrubber with a polishing sorbent bed. Such a system has the advantage of improving process operability and reducing the volume of solid waste. In summary, there is significant room for optimizing the flowsheet for iodine separation.

- A number of solid sorbents for iodine separation have been investigated (as most recently described by Riley et al. (2016) and Huve et al. (2018)) but commercially available silver mordenite has arguably become the media most accepted in the United States. Greaney et al. (2020) have shown the chemical stability of silver mordenite is eroded by exposure to nitrogen dioxide, which it is when UNF is dissolved in nitric acid. Bruffey (2019) has demonstrated the stability of other developmental media, silver aerogel for example, when exposed to nitrogen dioxide and Jubin (1979) identifies silver alumina silicate as stable in the presence of nitrogen dioxide and has some commercial pedigree. In summary, and as also noted by Law et al. (2014), an efficient and stable iodine sorbent requires development toward a point where commercial production could be undertaken.

- The iodine separation and nitrogen dioxide recombination (by nitric acid scrubbing) steps could be reversed to potentially negate the need for an iodine sorbent tolerant of nitrogen dioxide. The disadvantage of doing so would mean some contamination of the recombined nitric acid with iodine but this order of operations has been successfully implemented on the Thermal Oxide Reprocessing Plant (THORP) as described by Phillips (1993). Notably on THORP, nitric oxide is converted to nitrogen dioxide after the nitric acid scrubber and is separated with the iodine by caustic scrubbing. Greaney et al. (2020) has shown silver mordenite to be unaffected by the presence of nitric oxide in contrast to nitrogen dioxide. In summary, there is room for optimizing the processing of the off-gas for iodine and the nitric oxide and nitrogen dioxide chemistry.

2.2 Flowsheet for Standard Voloxidation and UNF Dissolution in PUREX Solvent

2.2.1 Flowsheet Description

The first flowsheet developed to consider PUREX solvent dissolution of UNF simply replaced the acid dissolution step of the BoC with TBP dissolution. The Standard Voloxidation – Organic Dissolution flowsheet is largely based on the experimental work of Rudisill et al. (2019) and is depicted in Figure 2-2.

The off-gas from the TBP dissolution step is largely speculative since it has not been quantitatively studied. Limited earlier work by DelCul (2015) that indicated more than 90% of the iodine is dissolved appears to confirm the assumption of Rudisill et al. (2019) that most dissolves based on the observed change in color of the solvent. Therefore, the flowsheet assumes most of the iodine is routed with the solvent. This is likely also because the dissolutions were performed at 25 °C and 50 °C and nothing was done to encourage the iodine into the off-gas. Nonetheless, some iodine is likely to arise in the off-gas and most likely in organic forms given the nature of the solvent. Noble gases would seem likely to be lost to the off-gas and require separation. The UNF hulls will likely require some washing of organic material before they are processed into the metal waste form to avoid volatile and semi-volatile organic compound management in the off-gas.

The volume of TBP solvent used to dissolve the UNF powder is assumed to give the same actinide concentration as that of the product from the BoC PUREX extraction. Based on the work of Rudisill et al. (2019), the UNF product from organic dissolution will consist of dissolved actinides (both major and minor), lanthanide fission products (LFPs), iodine and technetium. Remaining fission products are assumed to remain in solid form as oxides, which are separated from the solvent. That the minor actinides and LFPs are dissolved by the TBP is considered by Rudisill et al. (2019) to be consistent with expected extraction behavior with high nitrate salting behavior as indicated by Thompson (1973). Nonetheless, certainly TBP solvent dissolution of UNF challenges current paradigms associated with TBP chemistry of minor actinides and needs to be better understood. The solvent is scrubbed with dilute nitric acid to remove all but the major actinides, neptunium and technetium from the organic phase. The solvent can be further processed by a number of processes to strip and purify the major actinides. Importantly for this evaluation, the technetium is scrubbed using nitric acid of high concentration consistent with the full recycle case study prepared by Law, et al. (2014). The minor actinides can be separated from the LFPs using a process such as Advanced TALSPEAK (i.e., there is no requirement for a two-step process incorporating TRUEX or the mixed extractant system used in ALSEP).

The lanthanide fission products, minor actinides, if not separated, and technetium, all dissolved in nitric acid, are calcined before vitrification with the insoluble fission products arising from the TBP solvent dissolution step. The latter most likely will require washing to reduce their organic content before vitrification to mitigate the organic challenge to the melter off-gas treatment system and can be slurried using water. As before, the nitrogen oxides are abated although this is the only location in the flowsheet where it is required. Assuming the iodine is scrubbed from the TBP solvent and is routed with the lanthanide fission products then it must be separated from the calciner off-gas. Throughout the flowsheet, the iodine, likely organo-iodine because of the organic solvent dissolution, burden on the vessel off-gas is greater than in the BoC flowsheet.

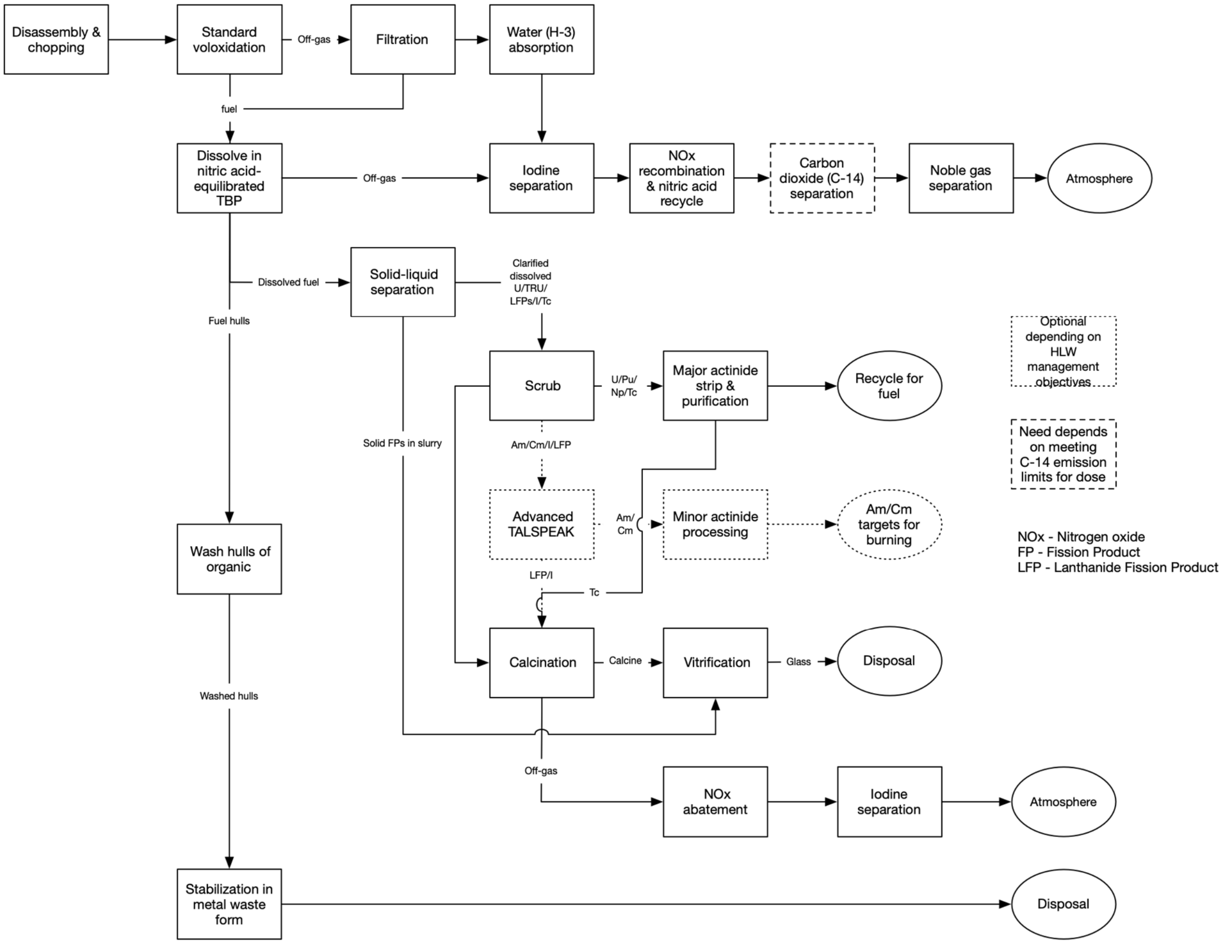

Figure 2-2. Standard Voloxidation and PUREX Solvent Dissolution Flowsheet for UNF Actinide Recovery

2.2.2 Flowsheet Uncertainties

There is a great deal of uncertainty associated with this flowsheet because very little experimental work (largely limited to Rudisill et al. (2019)) has been completed to consider dissolving UNF in TBP. That work has been limited to simulated UNF containing a fraction of the number of fission products. Flowsheet uncertainties are grouped by technical area in the following sections.

2.2.2.1 Iodine Management

Although Rudisill et al. (2019) did include iodine in their simulated UNF, no chemical analysis of the TBP solvent was completed. Instead, Rudisill et al. (2019) surmised the iodine was qualitatively dissolved by the TBP by the solvent’s change in color. However, there were no noble metals (such as silver and palladium) included in the simulated UNF that, as summarized by Jubin et al. (2013), are known to form colloids with iodine that would intuitively seem unlikely to dissolve in TBP. On the other hand, nearly half of the iodine dissolved in nitric acid as colloids is estimated by Jubin et al. (2013) to be extracted by TBP in a conventional flowsheet. That observation appears to support the qualitative conclusion of Rudisill et al. (2019). In any case, there is considerable uncertainty in the behavior of iodine in this flowsheet.

Further, the probable higher inventory of iodine migrating into the separations portion of the flowsheet is likely to place a higher burden on the vessel off-gas system. In this regard, an abatement system is likely needing to process a high inventory of organo-iodine especially given the dissolution in organic solvent. Organo-iodine is known to complicate iodine abatement using silver mordenite. Bruffey and Jubin (2015), for example, showed the separation of methyl iodide was slower than iodine on silver mordenite. The volume of vessel off-gas requiring treatment being also significantly higher than from the dissolver also means iodine concentrations are lower and the abatement technically more challenging.

2.2.2.2 Dissolution

The nature of the solids remaining following TBP dissolution is unknown. The flowsheet assumes these solids remain as oxides but they could equally be converted to nitrate forms or a mixture. The consequence of this uncertainty is reflected in uncertainty in how they are processed. As oxides, the solids are slurried into the melter for vitrification but as nitrates they could be dissolved in nitric acid or water and then would require calcination. As such, noble metal fission products are routed to the calciner for subsequent vitrification. Noble metals have historically been problematic to vitrify because they adversely affect the fluid properties of the melt. However, Labe et al. (2014) have shown they can be incorporated at acceptable concentrations into the high-level waste feed given modifications to the Hot Crucible Melter to improve mixing of the melt. Incorporation is further improved in the Cold Crucible Melter.

The trivalent minor actinides and lanthanide fission products are considered inextractable by TBP in a conventional PUREX flowsheet. That Rudisill et al. (2019) found significant dissolution of them in TBP solvent is indicative of the ways in which TBP solvent dissolution of UNF challenges current paradigms. All reviewed studies of the chemistry of the minor actinides in the context of TBP are considered with respect to extraction from nitric acid. In nitric acid, the minor actinides are most stable as trivalent species and their extraction by TBP can be encouraged by inextractable metal nitrates such as aluminum or sodium as shown by Thompson (1973). Alternatively, Mincher et al. (2008) has shown americium can be oxidized to higher valence states and effectively extracted by TBP. That current paradigms of ‘inextractable’ constituent chemistry in TBP are fundamentally challenged is further exemplified by the observations by Rudisill et al. (2019) of not insignificant dissolution of cesium and strontium. These uncertainties are manifested as uncertainties in the chemistry and configuration of the initial scrub and subsequent major actinide processing.

2.2.2.3 Separations

A key step in the flowsheet is scrubbing with nitric acid of the TBP solvent to separate the minor actinides and as many fission products as possible. The assumption is that the resulting solvent product is equivalent to that from the first cycle of BoC flowsheet containing essentially the major actinides and technetium. In the case study of Law et al. (2014), the scrub flowsheet is driven by zirconium and ruthenium fission products, which require low and moderately high nitric acid concentrations, respectively. If neither fission product is present then a low concentration should be sufficient to separate the minor actinides and lanthanide fission products, which are considered inextractable by TBP in a conventional PUREX process. This uncertainty leads to uncertainty in the nitrate content of the feed to the calcination process. However, the technetium scrub of uranium purification dominates the calcination nitrate feed to the extent that a moderately high acid concentration scrub would contribute no more than ~5% of the total nitrate feed. In summary, this uncertainty leads to uncertainty in the scrub configuration with little consequence for nitrate management.

To reiterate the point made in section 2.2.2.2, uncertainties in the chemistry of single, double and trivalent metals are manifested as uncertainties in the chemistry and configuration of the initial scrub and subsequent major actinide purification cycles.

There is no TRUEX system included in this flowsheet because the minor actinides were already separated from the non-lanthanide fission products by TBP dissolution. The minor actinides and lanthanide fission products are scrubbed from the TBP solvent with dilute (~0.5M) nitric acid. Ideally, this dilute nitric acid stream should be fed directly to the TALSPEAK system. However, the TALSPEAK system of Law et al. (2014) is fed with a solution of citric acid and the complexant N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) consistent with the demonstrated approach for advanced TALSPEAK. The purpose of the HEDTA is to complex the minor actinides in the aqueous phase while the fission products are extracted by the TALSPEAK solvent (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester in dodecane). The extracted fission products are subsequently stripped with 6M nitric acid. To accommodate the dilute nitric acid product from the truncated PUREX system, a Reverse TALSPEAK flowsheet could be employed consistent with the concept described by Nilsson and Nash (2007). Here, the minor actinides and lanthanide fission products are coextracted and then subsequently stripped in separate steps; minor actinides by a solution of HEDTA in citric acid and the fission products by nitric acid.

Rudisill et al. (2019) report relatively high dissolution (compared to conventional TBP liquid-liquid extraction) of alkali and alkaline earth metal simulated fission products (cesium and strontium, respectively). These fission products would be expected to be scrubbed into the dilute nitric acid stream with the minor actinides and lanthanide fission products to feed the Reverse TALSPEAK system. They would not be expected to extract into the TALSPEAK solvent but would remain dissolved in the nitric acid feed. However, other fission products such as zirconium were not simulated by Rudisill et al. (2019) and are likely to exhibit complex behavior in the TALSPEAK system.

2.3 Flowsheet for Advanced Voloxidation and UNF Dissolution in TBP Solvent

2.3.1 Flowsheet Description

The Advanced Voloxidation – PUREX Solvent Dissolution flowsheet is depicted in Figure 2-3.

Whereas standard voloxidation uses air at up to ~550 °C to oxidize the UNF, advanced voloxidation, as described by DelCul et al. (2010) and Law et al. (2014), uses nitrogen dioxide, which facilitates a lower reaction temperature up to 375 °C. Nitric oxide is the primary off-gas constituent while advanced voloxidation also enables iodine to be driven into its off-gas. The advanced voloxidation off-gas treatment flowsheet is based on that presented by Vienna (2015) and includes a means to recycle nitrogen dioxide. Iodine and tritium separation from advanced voloxidation has since been experimentally demonstrated by Jubin et al. (2019) who found the tritium was absorbed by the silver mordenite and silver alumina used to separate the iodine. Advanced voloxidation can be configured to generate uranium trioxide or a uranyl nitrate nitroso complex; the latter by further contacting the former with nitrogen dioxide gas at near ambient conditions. This flowsheet assumes the fuel is completely nitrated although this is by no means certain.

Dissolution of the nitrated UNF powder then proceeds. There is no experimental precedence for dissolving nitrated UNF in TBP solvent but the results of Rudisill et al. (2019) are assumed on the basis that the metals are first nitrated and then complexed by the TBP. Pre-equilibration of the TBP solvent with nitric acid is presumably not required since the metals are already nitrated. As before, the actinides, lanthanide fission products and technetium are dissolved, which are processed in the same way as before. Separated from the TBP solvent are the solid nitrate forms of the remaining UNF constituents. These are all, including the noble metal fission products, assumed dissolved in water or dilute nitric acid and fed to the calciner with the technetium and lanthanide fission products. As before, the former most likely will require washing to reduce their organic content before calcination to mitigate the organic challenge to the off-gas treatment system and can be slurried using water. As before, the nitrogen oxides are abated in the calciner off-gas. Assuming any residual iodine is scrubbed from the solvent then it must be separated from the calciner off-gas. Throughout the flowsheet, the residual iodine, likely organo-iodine because of the organic solvent dissolution, in the vessel off-gas must be abated.

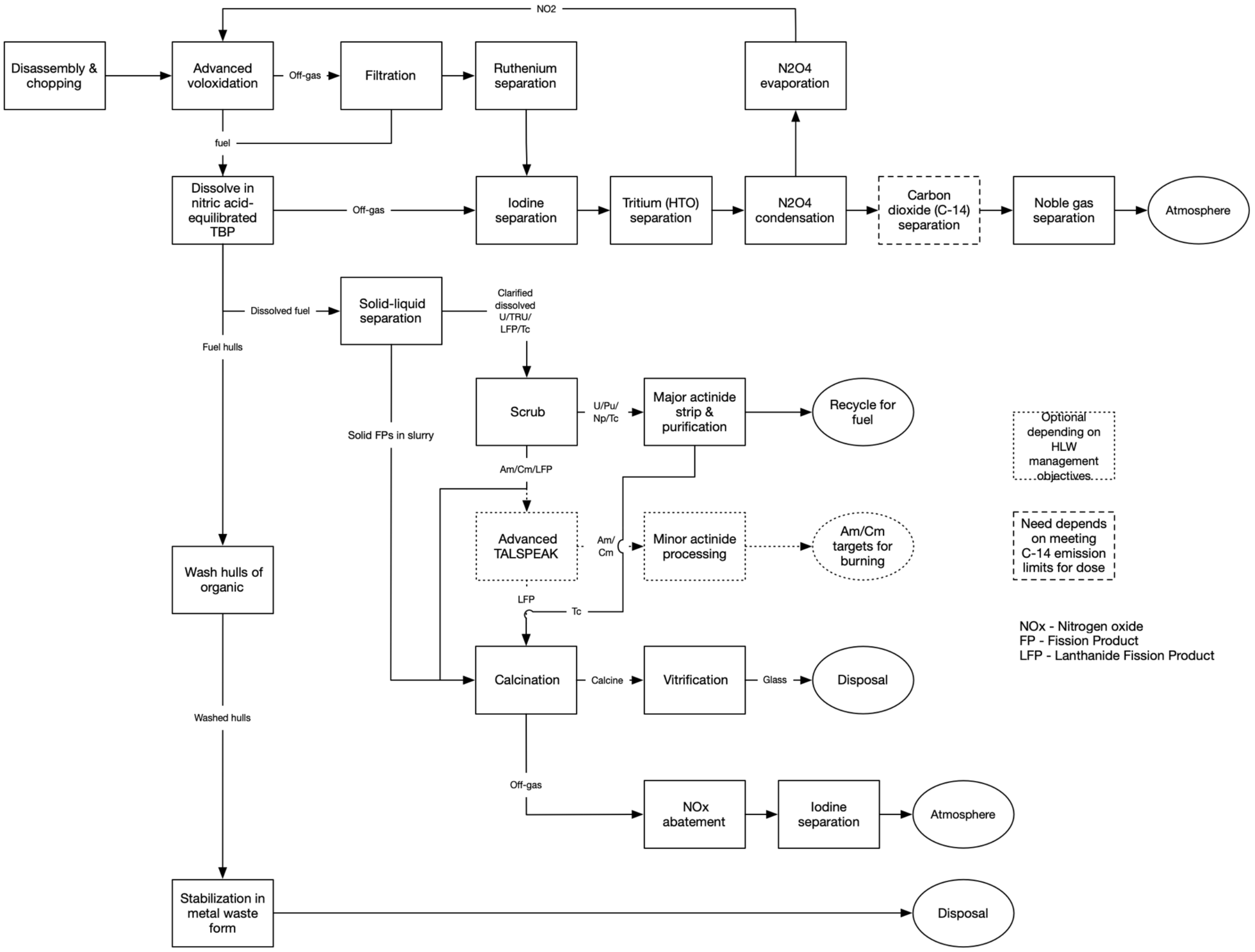

Figure 2-3. Advanced Voloxidation and PUREX Solvent Dissolution Flowsheet for UNF Actinide Recovery

2.3.2 Flowsheet Uncertainties

As before, there is a great deal of uncertainty associated with this flowsheet because very little experimental work (largely limited to Rudisill et al. (2019)) has been completed to consider dissolving UNF in PUREX solvent. Furthermore, there is no known experimental work completed dissolving pre-nitrated UNF in PUREX solvent. Flowsheet uncertainties are grouped by technical area in the following sections.

2.3.2.1 Iodine Management

The uncertainties associated with iodine behavior in this flowsheet are less consequential than those described for the standard voloxidation flowsheet because advanced voloxidation facilitates near complete removal of this fission product from the fuel. Instead, uncertainties are associated with the low technical maturity of the advanced voloxidation off-gas treatment system. In particular, the stability of the iodine absorbent present in the high nitric oxide environment needs confirmation. As already highlighted, Greaney et al. (2020) has shown silver mordenite to be unaffected by the presence of nitric oxide in contrast to nitrogen dioxide and Jubin (1979) has even suggested that nitric oxide may improve silver mordenite stability. Associated with this uncertainty is the stability of nitric oxide in the presence of oxygen and any propensity to form nitrogen dioxide. Residual or unreacted nitrogen dioxide from the advanced voloxidation process step also needs to be considered for management.

As for the prior flowsheets, an abatement flowsheet integrating an aqueous scrubber with a polishing solid sorbent as recommended by Jubin et al. (2018) could be advantageous in improving process operability and reducing the volume of solid waste.

2.3.2.2 Dissolution

The nature of the solids remaining following advanced voloxidation is unknown. The flowsheet assumes the UNF is completely nitrated given the high temperature and its intimate contact between the nitrogen dioxide gas in the advanced voloxidation process. In contrast, nitration in the standard voloxidation and TBP dissolution flowsheet occurs at lower temperature and nitrate concentration during TBP dissolution and so the solids are assumed to remain as nitrates. However, these assumptions are purely speculative and the UNF could equally form a nitrate-oxide mixture especially if the advanced voloxidation process conditions are optimized to solely focus on maximally releasing the iodine and tritium so that the extent of nitration becomes incidental.

The consequence of this uncertainty is reflected in uncertainty in how the solids are processed. If all UNF constituents are nitrated, then the solids remaining after dissolution could be dissolved in nitric acid or water and then calcined. Complete nitration of the UNF may lead to faster dissolution of fission products with impacts to the separations flowsheet. As before, the route of the noble metal fission products is determined or can be controlled by whether they are oxide or nitrate. On the other hand, if the UNF is only partially nitrated during advanced voloxidation then the solids remaining after dissolution being unchanged from their feed state would seem intuitively reasonable. That being the case could enable some manipulation of the flowsheet to route the noble metal fission products as desired.

2.3.2.3 Separations

Notwithstanding the consequences of uncertainties in the form of the UNF exiting the advanced voloxidation process, uncertainties in the separations processes are the same as described for the standard voloxidation and TBP dissolution flowsheet. However, separations uncertainties are compounded by those associated with the forms of the UNF, whether the constituents are nitrated, remain oxidized or mixed.

3.0 Flowsheet Comparison

3.1 Nitrate Management

One of the preconceived advantages of dissolving UNF directly in TBP solvent is a reduction in the volume of nitric acid required for the flowsheet. There is then a consequent overall benefit to its management as a recycled contaminated reagent and in abatement of nitrogen oxide gases arising from calcination of the HLW. The total nitrate inventory of each flowsheet can be considered representative of the nitric acid management and nitrogen oxide gas emission challenges. The flowsheet of Law et al. (2014) provides a means to compare the nitrate inventory of each flowsheet because nitrate concentrations are provided for each feed with volume flows normalized to a solvent system feed of unity. Therefore, the total nitrate inventories for each flowsheet were established for comparative purposes by simply summing the products of concentration and relative volume flow. Volume flows for each solvent extraction system were scaled for a BoC PUREX UNF feed of unity. Table 3-1 provides a comparison of the relative nitrate inventories for each flowsheet and variants considering PUREX-only or PUREX and minor actinide separation.

Table 3-1. Comparison of Nitrate Inventories for Each Flowsheet Alternative

Flowsheet	Nitrate Inventory* PUREX only	Nitrate Inventory* PUREX and Minor Actinide separation
Basis of Comparison	47.1	106
Standard voloxidation and organic dissolution	42.5	50.6
Advanced voloxidation and organic dissolution	40.0	48.1

* Moles per unit volume of Basis of Comparison PUREX feed

Overall, organic dissolution moderately reduces the overall nitrate inventory for PUREX-only flowsheets with advanced voloxidation leading to a ~15% reduction. The reduction is limited mainly due to the large contribution to nitrate inventory from the PUREX technetium scrub, which contributes over half of the total. Alternative approaches to separating technetium from uranium have been demonstrated with ion exchange being the most notable. For example, Pereira et al. (2007) used an anion exchange resin, Reillex^{TM} HPQ resin but this media is challenging to elute. Previous work reviewed by Duncan et al. (2011) for application to alkaline Hanford tank wastes indicated concentrated (8M) nitric acid was insufficient to elute the media but elution with a solution of stannous chloride, ethylenediamine and sodium hydroxide proved successful. As well as the complex elution reagent, process complexity also increases by adding a unit operation different from liquid-liquid extraction.

A small reduction in nitrate inventory is achievable by using advanced in place of standard voloxidation because the TBP solvent does not need to be equilibrated with nitric acid in the former case. However, an overall reduction of ~50% is achievable when minor actinide separation is employed to make it essentially comparable to the basis of comparison PUREX-only flowsheet. This is because the TALSPEAK system is sized based on the PUREX dilute nitric acid scrub volume rather than that of the PUREX extraction raffinate (i.e., PUREX UNF feed combined with the scrub feeds). That then introduces an uncertainty because the minor actinides and fission products are introduced into the TALSPEAK system more concentrated by a factor of ~20 compared to the Basis of Comparison.

Although the nitrate associated with the UNF post advanced voloxidation is included in this analysis, not included are considerations associated with production of nitrogen dioxide from nitric acid. However, the production process would be expected to be operated independent of the separations nitric acid management systems and so the challenges are different and purely industrial. One industrial method for manufacturing nitrogen dioxide involves heating ammonia with air over a rhodium/platinum catalyst to form nitric oxide, which is then converted to nitrogen dioxide with oxygen. Perhaps more conveniently for this application, nitrogen dioxide can be generated by the thermal decomposition of nitric acid.

3.2 Dissolution Process Technology

Historically and currently, UNF is dissolved in hot concentrated nitric acid. This has typically been a batch operation using relatively large vessels to obtain the required residence time. Such large vessels do not offer a critically safe geometry and a neutron poison such as gadolinium may be added. However, gadolinium is a lanthanide element and will increase the size of the TRUEX and TALSPEAK systems. Alternatively, a semi-continuous operation can be implemented using a rotary dissolver as described by Emin et al. (2005) but such processes introduce additional mechanical complexity. Furthermore, the consideration of voloxidation treatment prior to dissolution means additional shielded floor space is required. A means to reduce the dissolution time and provide less demanding process conditions is, therefore, desirable for several reasons.

Relevant to this study, Johnson and Stone (1980) found no significant difference in the acid-dissolution rates of non-voloxidized UNF and that treated by standard voloxidation with both requiring 2-3 hours to completely dissolve. This could be considered a surprising result given the voloxidized UNF existed as a powder rather than pellets for the non-voloxidized material. However, the result is likely due to ramping the temperature increase and nitric acid addition in both cases to avoid excessive emission of off-gas for the voloxidized UNF. Bensmain et al. (2016) found triuranium octoxide (the product of standard voloxidation) dissolved somewhat faster than uranium dioxide powder followed by uranium trioxide powder. Of relevance to organic solvent dissolution, Kulyako et al. (2007) dissolved a pellet of uranium dioxide in TBP solvent at 40 °C in approximately one hour. Kulyako et al. (2007) also evaluated the effect of temperature and nitric acid concentration on the rate of dissolution of uranium dioxide powder in TBP solvent. They found the powder could be completely dissolved in approximately 30 minutes in TBP solvent containing 0.47M nitric acid at ambient temperature but the time could be shortened to a few minutes by increasing the temperature up 80°C and the nitric acid concentration up to 4.37M. Dorda et al. (2010) showed the dissolution of uranium trioxide powder was complete in approximately ten minutes at 32 °C in TBP solvent pre-equilibrated with 5M nitric acid to provide an organic-phase acid concentration of 0.91M. DelCul et al. (2015) also observed uranium dioxide dissolved ‘in a few minutes’. Rudisill et al. (2019) evaluated the dissolution of uranyl nitrate as might be expected from advanced voloxidation of UNF and observed essentially complete dissolution within the two-hour duration of the tests. They did not investigate the extent of dissolution as a function of time.

While there are uncertainties in how voloxidized actual (i.e., irradiated) UNF will dissolve, the foregoing results overall indicate the dissolution time could be substantially reduced while also reducing the temperature to a value close to ambient. The magnitude of this reduction could mean a continuous dissolution process may be practical without extensive additional mechanical processes.

3.3 Separations Process Technology

The capital cost and complexity associated with the separations plant are associated with the number of vessels, their volumes and the number of separation stages. As before, an initial evaluation of the benefit of organic solvent dissolution can be completed using the information provided by Law et al. (2014) and is summarized in Table 3-2.

Table 3-2. Comparison of Liquid Volumes and Numbers of Separation Stages of Each Flowsheet Alternative

Flowsheet	Volume*		Numbers of Separation Stages	
	PUREX only	PUREX and Minor Actinide separation	PUREX only	PUREX and Minor Actinide separation
Basis of Comparison	36.9	48.9	92	171
Standard voloxidation and organic dissolution	35.8	37.5	68	100
Advanced voloxidation and organic dissolution	35.8	37.5	68	100

* Volume of radioactive streams per unit volume of BoC PUREX feed

The PUREX-only volume comparison largely reflects the smaller volume occupied by the scrubbed minor actinides, lanthanide fission products and insoluble fission products for organic dissolution. The latter are assumed either dissolved or suspended in an aqueous volume a tenth the volume of Basis of Comparison PUREX feed. Likewise, the lower number of stages for organic dissolution PUREX-only reflects the removal of the extraction and high-acid scrub sections of the first cycle. A more dramatic improvement arises when minor actinide separation is considered; volumes and numbers of stages are less than 10% larger than the Basis of Comparison PUREX-only flowsheet. The improvement reflects removal of the TRUEX system and the TALSPEAK volumes being based on the volume of PUREX low-acid scrub.

3.4 Liquid Effluent Management

Solvent extraction systems necessarily involve continuous washing of the organic solvent to remove chemical and radiolytic degradation products, which are typically acidic. These wash systems generate contaminated liquid effluent that must be treated with separated contaminated salts then stabilized. Again, the flowsheet of Law et al. (2014) provides a means to compare the liquid effluent volumes of each flowsheet because wash salt concentrations are provided for each feed with volume flows normalized to a PUREX UNF feed of unity. Table 3-3 provides a comparison of the relative liquid effluent volumes and salt content for each flowsheet and variants considering PUREX-only or PUREX and minor actinide separation.

Table 3-3. Comparison of Liquid Effluent Volumes and Salt Content of Each Flowsheet Alternative

Flowsheet	Volume*		Salt content#	
	PUREX only	PUREX and Minor Actinide separation	PUREX only	PUREX and Minor Actinide separation
Basis of Comparison	4.48	6.26	0.37	0.46
Standard voloxidation and organic dissolution	4.48	4.64	0.37	0.38
Advanced voloxidation and organic dissolution	4.48	4.64	0.37	0.38

* Volume per unit volume of BoC PUREX feed
\# Moles per unit volume of BoC PUREX feed

The results of this analysis reflect the removal of the TRUEX system from the organic solvent dissolution flowsheets and sizing the TALSPEAK system based on the PUREX first cycle low-acid scrub. There is no difference between the organic dissolution flowsheets because the volume of organic solvent is the same in both. Furthermore, there is no difference between any of the PUREX-only flowsheets because the same volume of organic solvent is assumed used whether in the PUREX first cycle extraction or the organic dissolution.

As for the nitrate inventory, liquid effluent volumes and salt content for organic dissolution flowsheets incorporating minor actinide separation are reduced to values a little more (~5%) than those arising from the PUREX-only Basis of Comparison.

3.5 Application to Single Cycle Flowsheet Development

Currently deployed and historic PUREX-based flowsheets have used multiple cycles of extraction, scrub and strip to ensure the separated uranium and plutonium products are sufficiently decontaminated of fission products and undesirable actinides. As described by Law et al. (2020), additional cycles increase the secondary liquid effluent volume and process complexity in many respects all leading to increases in capital and operating costs. Law et al. (2020) have listed the primary constituents leading to deployment of purification cycles as ruthenium, zirconium, technetium and neptunium. More recent flowsheets have reflected the desire to avoid separating plutonium to allay proliferation concerns and this has typically been accomplished by taking advantage of the neptunium chemistry and allowing at least some of it to be separated with plutonium to create a transuranic product that can also contain some uranium. This, then, leaves the fission products to consider in developing a single cycle flowsheet.

The Case Study flowsheet of Law et al. (2014) is arguably a partial single cycle flowsheet. In this flowsheet, a sufficiently pure mixed uranium/transuranic product is assumed generated from the first cycle. However, the uranium-loaded solvent from the first cycle also contains the technetium. Therefore, the flowsheet effects a technetium – uranium separation in a partial cycle that strips uranium from the TBP solvent. Successful implementation of this flowsheet then becomes predicated on sufficiently avoiding other-phase carry-over in the separation stages. In any case, making a direct comment on the application of organic solvent dissolution toward achieving a single cycle flowsheet is difficult for this study because the evaluation is based on the Case Study flowsheet of Law et al. (2014). Rudisill et al. (2019) investigated the behavior of technetium (albeit using rhenium as a surrogate) and observed it dissolved into the organic solvent but they did not investigate the behavior of ruthenium or zirconium in their solid solution experiments. This introduces a significant uncertainty in that technetium and zirconium behavior in PUREX is interrelated. Clearly, preventing technetium dissolution is desirable to avoid the high nitric acid scrub and thereby realize benefit in reducing the nitrate inventory. A means to prevent technetium dissolution may be possible given the fundamentally different chemistry offered by the TBP solvent absent of a separate nitric acid aqueous phase but is not explored here. Understanding the behavior of ruthenium and zirconium will be important to underpinning the single cycle flowsheet presented by Law et al. (2014) modified with TBP solvent dissolution.

4.0 Recommendations for Future Work

4.1 Organic Solvent Dissolution Technology Development

The evaluation described in this report is largely based on flowsheets development from results of limited work conducted by Rudisill et al. (2019) and Kulyako et al. (2007). Their work was performed with simulated UNF powder with constituents limited to the actinides and a few fission products. As such, the technology readiness is arguably at the very early third level consistent with the guidance provided by the U.S. Department of Energy (2015) considering experimental verification occurs at this level. At the third level, analytical and experimental critical function and/or characteristic proof of concept has been demonstrated and it is the upper level of ‘research to prove feasibility’. Levels 4 and 5 move readiness into technology development and comprehensive experimental work at laboratory scale. The data from these levels increasingly underpin process and equipment design and production performance projections. Technology maturation at early readiness levels should also generate sufficient data for an analysis of the engineering trade-offs.

Key gaps and uncertainties for organic solvent dissolution have been outlined throughout this report and these and summary level technical approaches to resolve them and move the technology to the fourth readiness level are provided in Table 4-1. One significant engineering trade-off relevant here will be between standard and advanced voloxidation and iodine abatement. In that context, some of the proposed work investigates process performance in dissolving the three potential products of standard and advanced voloxidation to generate the data required for the trade-off study. Establishment of a Technology Maturation Plan expanding on these approaches is recommended to underpin experimental work.

Consistent with the guidance of the Department of Energy (2015), experimental work at the fourth level can be undertaken with simulated UNF. Simulated UNF should be prepared as solids solutions since Rudisill et al. (2019) and Kulyako et al. (2003) found significant difference in the dissolution of those and simple mixtures of constituent powders. Some initial demonstration work with actual UNF is recommended at the fourth level given the chemical and physical complexity of the actual material to confirm the overall results from simulated UNF. Comprehensive experimental work with actual UNF should be undertaken at the fifth readiness level but approaches are not elaborated upon in this report given the gaps and uncertainties that need resolution beforehand with simulated material.

Table 4-1. Summary of Gaps and Uncertainties and Technical Approaches

Gap or Uncertainty	Summary Technical Approach
Quantitative evaluation of the fate of iodine from dissolving triuranium octoxide and uranium trioxide powder and uranyl nitrate crystals in TBP solvent.	Solid solution simulated UNF dissolution with iodine and analyze for iodine in solution. Investigate effect of nitric acid and temperature.
Off-gas characteristics from dissolving triuranium octoxide and uranium trioxide powder and uranyl nitrate crystals in TBP solvent.	Characterize off-gas from dissolution for nitrogen oxides and other radionuclides, especially iodine.
Undissolved solids characteristics from dissolving triuranium octoxide and uranium trioxide powder and uranyl nitrate crystals in TBP solvent.	Characterize undissolved solids from dissolving simulated UNF powder prepared by standard and advanced voloxidation. Employ various microscopic techniques to ascertain whether solids are oxides, nitrates or a mixture, for example.
Envelope of applicable process conditions (particularly temperature, nitric acid concentration) and their effect on constituent dissolutions from dissolving triuranium octoxide and uranium trioxide powder and uranyl nitrate crystals in TBP solvent.	Investigate effect of temperature and nitric acid concentration on overall and constituent TBP solvent dissolution rate using simulated UNF powder prepared by standard and advanced voloxidation.
Dissolution characteristics of technetium	Solid solution simulated UNF dissolution with technetium. Particularly investigate effect of nitric acid concentration.
Dissolution characteristics of the key fission products ruthenium and zirconium	Solid solution simulated UNF dissolution with ruthenium and zirconium.
Dissolution characteristics of the noble metal fission products (e.g., silver and palladium)	Solid solution simulated UNF dissolution with noble metals (e.g., silver and/or palladium). Also investigate combined dissolution of iodine and noble metals.
Fundamental chemistry of TBP dissolution (i.e., extraction without separate acid phase)	Evaluate available literature on the chemistry of TBP extraction of metals for application in understanding dissolution of minor actinides and lanthanide fission products. Design and perform experiments to fill gaps in understanding.

4.2 Ancillary Technology Development

The evaluation described in this report has highlighted the need for developments of other UNF treatment technologies to enable organic solvent dissolution and that are probably needed in any case.

Voloxidation treatment of UNF is a technology that has been progressed over several decades even with actual UNF but never industrially implemented. However, it is clearly a technology important to tritium management, which will be a key consideration for any future UNF recycle plant. Advanced voloxidation is a more recent development that has been demonstrated at laboratory scale with simulated UNF. Its technology readiness is likely little more than what has been ascribed to organic solvent dissolution. A technology readiness assessment and maturation plan consistent with the guidance of the Department of Energy (2015) are needed for this important technology to plan its progression to at least the fifth readiness level and make it ready for a commercial enterprise to mature for industrial application.

A very important potential benefit of organic solvent dissolution is simplified minor actinide separation from UNF. Dissolution of the minor actinides in the organic solvent means that the

TRUEX system is not needed leading to a substantial simplification in the flowsheet and solvent management. Three important areas need to be investigated further with regard to this technology:

- Performance and process conditions for a Reverse TALSPEAK flowsheet with a dilute nitric acid feed.
- Performance of Reverse TALSPEAK including alkali and alkali earth metal fission products in the feed.
- Performance and behavior of the TALSPEAK liquid-liquid system with higher concentrations of minor actinides and lanthanide fission products.

Significant dissolution of iodine in the TBP solvent when employing standard voloxidation will require an improved understanding of its behavior in the separations processes including the PUREX scrub and the modified Reverse TALSPEAK processes to establish a management strategy for the radionuclide.

5.0 Conclusions

This report describes an initial evaluation of flowsheets for dissolving UNF in TBP solvent. The major conclusions of the evaluation include:

- Flowsheets that replace acid dissolution of UNF with TBP solvent dissolution appear feasible. Important differences between acid and TBP solvent dissolution flowsheets include:
    - Dissolution in TBP solvent of the minor actinides and lanthanide fission products. In contrast, these constituents are poorly extracted in a conventional PUREX solvent extraction flowsheet with acid dissolution of UNF.
    - TBP solvent dissolution can be practically undertaken at near-ambient temperatures whereas acid dissolution is conducted at a near-boiling temperature.
- The major advantage potentially offered by TBP solvent dissolution arises from its near-ambient process temperature, which may offer opportunity for continuous dissolution without adding mechanical complexity.
- There is little difference in the nitrate inventory between acid and TBP solvent dissolution flowsheets for recovery of only uranium and plutonium. This is principally because the nitrate inventory is dominated by the concentrated nitric acid needed to separated technetium from uranium.
- A TBP solvent dissolution flowsheet potentially offers significant benefits over a conventional flowsheet incorporating acid dissolution when minor actinide management is desired. Dissolution of minor actinides means the TRUEX solvent extraction system is not needed with benefit to reducing secondary liquid effluent generation and nitrate inventories to levels a little more than what are expected from a PUREX-only flowsheet.
- Application of TBP solvent dissolution to development of a single cycle flowsheet is largely dependent on whether technetium can be made insoluble so that its separation from uranium in a purification cycle is not required. Doing so would also introduce benefit in significantly reducing the nitrate inventory.
- There is considerable uncertainty in the TBP solvent dissolution flowsheets, which is reflected in the low Technology Readiness Level. Major areas needing further development with solid solution simulated UNF to advance the technology's readiness for demonstration with actual UNF include:
    - Dissolution characteristics of key fission products including noble metals, technetium, ruthenium, zirconium and iodine.
    - Establishing the envelope of potential process conditions (temperature and nitric acid concentration) and dissolution characteristics of actinides and key fission products.
    - Understanding the fundamental chemistry of TBP dissolution (i.e., extraction without a separate acid phase) especially for minor actinides and lanthanide fission products.

- Removal of the need for the TRUEX system does mean some modification of the TALSPEAK flowsheet that necessitates further development with respect to a dilute nitric acid feed; alkali and alkali earth metal fission products in the feed; and higher concentrations of minor actinides and lanthanide fission products.

- Significant dissolution of iodine in the TBP solvent when employing standard voloxidation will require an improved understanding of its behavior in the separations processes including the PUREX scrub and the modified Reverse TALSPEAK processes to establish a management strategy for the radionuclide.

- Standard and advanced voloxidation are UNF pretreatment technologies that are important in managing tritium in actinide recovery flowsheets. Though not the subject of this study, these technologies should be evaluated for their readiness levels to underpin development of technology maturation plans.

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Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

www.pnnl.gov