Dissolution of Used Nuclear Fuel Using a Tributyl Phosphate/n-Paraffin Solvent

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Key Words
Nuclear fuel reprocessing
Fuel dissolution
Tributyl phosphate

Running Title
Dissolution of Used Nuclear Fuel

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ABSTRACT

The complete recycle of used nuclear fuel (UNF) is desirable to recover the energy value from the remaining U and higher actinides; however, construction of a large-scale facility is extremely expensive. To address this issue, a hybrid process was evaluated in which UNF pretreated for tritium removal is dissolved in a tributyl phosphate (TBP) solvent. The distribution of the actinides and selected fission products was measured between the solvent and residual solids. Dissolution of these elements in the surrogate fuels was very effective. Most fission products from fuel irradiation except for the lanthanide elements would remain in the undissolved solids.

INTRODUCTION

When UNF is removed from a reactor, approximately 95% of the initial U is still present in the fuel.[1] The fuel also contains higher actinides (e.g., Np, Pu, Am, and Cm) which can be recovered, fabricated into fuels or targets, and used to generate additional energy. However, construction of a large-scale reprocessing facility with the capability to completely recycle UNF is extremely expensive. Simplified flowsheets which reduce the equipment footprint and facility size are needed to improve the economic viability of complete recycle. To address this issue, we have performed an initial demonstration of a hybrid process which combines the dissolution of pretreated UNF in a TBP-containing solvent with two cycles of solvent extraction required for the recovery of the actinide and lanthanide elements. The hybrid process would be used to dissolve the actinide (U, Np, Pu, Am, and Cm) and lanthanide fission product elements directly into TBP. The minor actinide (Am and Cm) and lanthanide fission products could then be scrubbed from the solvent using dilute nitric acid. Additional solvent extraction processes would be used to recover and purify the desired products. A conceptual flowsheet for the headend facilities including the hybrid process is shown in Figure 1.

A dry pretreatment process based on the oxidation of UNF was demonstrated at Oak Ridge National Laboratory (ORNL) for the removal of tritium (and I_2) in the headend portion of a fuel reprocessing facility (Figure 2). In this process, contact with a NO_2/O_2 mixture converts the fuel into a fine UO_3 powder, and with further reaction time and temperature adjustment, the UO_3 can be converted to $UO_2NO(NO_3)_2$.[2] In the nitrate form, U can be dissolved (extracted) directly into TBP. The direct dissolution of the UO_3 product into TBP can also be achieved by using TBP pre-equilibrated with nitric acid.[3] Although, the direct dissolution of both UO_3 and $UO_2(NO_3)_2$ into TBP has been demonstrated,[4] the extent of dissolution of other components of UNF into a TBP solvent has not been investigated. Uranium(VI), Pu(IV), Np(IV), and Np(VI) are extracted into TBP as their electro-neutral nitrate salts.[5-6]. The nitrates of Am(III), Cm(III), and the 3+ lanthanides are not normally extracted into TBP; however, under high nitrate salting conditions, these species will extract (dissolve).[2] The speciation of the actinide and fission product elements which dissolve in a TBP solvent was not evaluated as a part of this work; however, future work should be performed in this area to allow for potential optimization of a dissolution process.

To demonstrate the feasibility of the hybrid process, we prepared simulated UNF from unirradiated, depleted UO_2 fuel pellets (which were oxidized for tritium removal at ORNL) by adding selected actinide and stable fission product elements. In addition, we prepared actinide solid solutions containing stable fission product elements as representative surrogates for light water reactor (LWR) fuel pretreated for tritium removal. The surrogate UNF's and solid solutions were subsequently used in dissolution experiments to evaluate the distribution of the actinides and fission product elements between the solid and liquid phases. The feasibility of dissolving both the UO_3 and $UO_2NO(NO_3)_2$ compounds in TBP was investigated in three series of experiments performed with only the U compounds, the U compounds with the addition of selected stable fission product elements, and the U compounds with the addition of transuranic elements (e.g., Np, Pu, and Am). The feasibility of dissolving the actinide solids solutions was investigated using 30 and 50 vol % TBP, at ambient temperature (24-28 ˚C) and 50 ˚C, and using a two-stage dissolution process in which the initial volume of TBP was decanted from the undissolved solids (UDS) and fresh TBP added for a second stage of dissolution.

EXPERIMENTAL

Surrogate UNF

Fourteen fission and activation products were selected to prepare the surrogate UNF's. These elements included: transuranic actinides (Np, Pu, and Am), lanthanides (Ce, Nd, and Eu), Cs and Sr, transition metals (Mo, Zr, and Re as a surrogate for Tc), noble metals (Ru and Pd), and I_2. Generally, nitrates were added to the $UO_2NO(NO_3)_2$ and oxides were added to the UO_3. Exceptions included the addition of I_2 as cesium iodide, Mo, Ru, and Re(Tc) as oxides to both fuel surrogates, and Pd as elemental Pd. The U mass in all experiments was nominally 1 g. The non-radioactive fission products were added to the surrogates at approximately 10% of the U mass. Although this concentration is much higher than would be present in UNF's, the higher concentrations were necessary to ensure the concentrations in the TBP and residual solids were above analytical detection limits. Trace quantities (< 0.02 g) of the transuranic elements were used in the dissolution experiments that only contained the actinides. Transuranic actinide nitrates were prepared by controlled evaporation of the nitrate solutions. The surrogate UNF's were dissolved in 50 mL centrifuge tubes using 30 vol % TBP. For the oxide dissolutions, the TBP was equilibrated three times using a 1:1 organic to aqueous ratio with either 5 M HNO_3 (for experiments with only U) or 10 M HNO_3 (for experiments with U and non-radioactive fission products). The solution volume was 20 mL for actinide-only dissolution and 40 mL for the surrogates containing U with the addition of the non-radioactive fission products. Dissolutions were performed at ambient temperature (22-25 °C) and 50 °C using dissolution times of at least 2 h.

An Eppendorf Thermomixer R heating/cooling block was primarily used for temperature control and agitation. A limited number of dissolution experiments were performed using a VWR tube rotator and in a beaker with a stir bar for improved mixing. The U-loaded solvent in all experiments was initially filtered to remove solids. Multiple 2 mL aliquots of dodecane were used to wash the solids. Samples of the organic solvent were prepared for analysis by inductively-coupled plasma emission or mass spectroscopy (ICPES or ICPMS) by Parr bomb digestion of the TBP/dodecane. The UDS from a number of the dissolution experiments were dissolved to evaluate material balance closure. The UDS were dissolved using either 8 M HNO_3 or 8 M HNO_3 containing 0.05 M KF. The small amount of UDS from the U and actinide only experiments dissolved reasonably well; however, the UDS from the dissolutions containing the non-radioactive fission product elements did not completely dissolve. Residual solids from the HNO_3 dissolution were characterized by x-ray diffraction analysis.

Solid Solutions

We were not able to obtain irradiated LWR fuel which was pretreated for tritium removal for use in TBP dissolution experiments; therefore, we elected to prepare actinide solid solutions containing selected non-radioactive fission products as a pretreated fuel surrogate for use in dissolution experiments. Based on the work with the UNF surrogates, the solid solutions were prepared from a $UO_2(NO_3)_2$ solution containing transuranic actinides (Np, Pu, and Am), Cs and Sr, lanthanides (Ce, Nd, and Er), and Re (whose chemical behavior should mimic the behavior of Tc). Other major fission product elements (e.g., Mo, Zr, Ru, and Pd) which did not extensively dissolve in the UNF surrogate dissolution experiments were eliminated from the experimental design. The nominal masses of U and non-radioactive fission product elements used in the experiments were 1.25 and 0.2 g, respectively. Concentrations of non-radioactive fission products above values found in irradiated LWR fuel were again used to ensure the concentrations in the TBP and residual solids were above the analytical detection limits. Only trace quantities (< 0.02 g) of the transuranic actinides were used in the experiments. The solid solutions were prepared by initially combining the nitrate solutions of the elements of interest. The actinides and non-radioactive fission products were then precipitated by adding NH_4OH to the nitrate solution. Co-precipitation is a common method to synthesize solid solution phases.[7] The hydroxide precipitates were filtered and transferred to an alumina crucible and dried in a muffle furnace at 110 ˚C for 30 min. The dry powder was subsequently calcined at 600 ˚C for 2 h to prepare the solid solution. Prior to use in a dissolution experiment, the solid solutions were ground to a fine, free-flowing powder using a mortar and pestle to simulate the morphology of UNF powder following pretreatment by the tritium removal process.[2]

The solid solution dissolution experiments were performed in a 100-mL beaker using a hot plate/stirrer to provide heating (when necessary) and mixing with a magnetic stir bar. A 50-mL aliquot of solvent was used in all experiments. Experiments were performed using 30 and 50 vol % TBP in dodecane and at the ambient glovebox temperature and 50 ˚C. The TBP was equilibrated three times using a 1:1 organic to aqueous ratio with 10 M HNO_3. An external thermocouple controlled by the hot plate/stirrer was used to maintain the dissolving temperature at 50 ˚C. The ambient temperature in the glovebox ranged between 24 and 28 ˚C. The dissolution time was maintained consistently at 4 h. Once the dissolution was complete, the residual solids were separated from the solvent by filtration. A small aliquot of dodecane (typically 8 mL) was used to wash residual solvent from the solids. The solids were then dissolved using a 50-mL aliquot of 8 M HNO_3 containing 0.05 M KF at 60 to 80 ˚C. Two-stage dissolution experiments were performed using 30 and 50 vol % TBP. Following the first-stage dissolution, a majority of the solvent was decanted from the beaker and an additional 50-mL aliquot of fresh TBP was added to perform the second stage of the dissolution. The organic (TBP solvent) and aqueous (HNO_3/KF) solutions generated during the dissolution experiments were sampled and analyzed for the elements of interest by ICPMS. Samples of the organic solvent were prepared for analysis by Parr bomb digestion of the TBP/dodecane. Recovery efficiencies for each element were calculated from the ICPMS analyses and the measured volumes of the aqueous and organic solutions recovered following completion of the experiments.

RESULTS AND DISCUSSION

Surrogate UNF

The initial dissolution experiments were performed using only the U compounds as received from the ORNL tritium removal process. Both U compounds began dissolving immediately upon contact with the TBP solvent. Following the dissolution cycle, a small amount of UDS was present in the centrifuge tubes. Fine white solids remained from the nitrate dissolutions and course brown solids remained from the oxide dissolutions. We also observed a small volume aqueous phase (most likely generated from water present in the TBP) which appeared to form a barrier (to dissolution) between the UDS and TBP. For this reason, several dissolutions were performed using a rotary mixer and a beaker with a stir bar to increase the mixing intensity; however, results from these experiments did not show increased dissolution efficiency. Small improvements in efficiency may not have been observable based on the precision of the data.

The dissolution efficiency for the U only experiments varied from 80-99+% (Table 1). The efficiency was based on the total U measured in the solvent and UDS. The efficiencies measured in this work were consistent with dissolution efficiencies measured by Tomijima et al. [4] disclosed in a patent for the dissolution of water-insoluble U compounds in neutral organic solvents treated with nitric acid. Experiments performed using the two U compounds ($UO_2NO(NO_3)_2$ and UO_3) were designated UN and UO, respectively. There does not appear to be an advantage of dissolving one compound over the other based on the measured dissolution efficiencies. A small amount of H_2O_2 was added in several experiments to ensure the U was present as U(VI) (to increase dissolution efficiency); however, the H_2O_2 resulted in the precipitation of uranium peroxide (UO_4). The highest U recovery efficiencies were obtained at nominally 25 °C compared to experiments performed at 50 °C. This observation is consistent with U distribution coefficients between TBP and HNO_3 decreasing with increasing temperature.[6] The material balance closures for all experiments except for ones in which H_2O_2 was added were greater than 100% due to uncertainties in the initial U measurements (Table 1). The closures of the U material balances for experiments performed with the addition of H_2O_2 were biased low due to losses of UO_4 during handling of the solid residues. A limited number of two stage dissolution experiments in which most of the organic phase was removed from the centrifuge tubes and replaced with fresh solvent for a second dissolution cycle showed slight improvement in U dissolution efficiency.

Similar U dissolution efficiencies were measured in experiments performed with UNF surrogates containing non-radioactive fission product elements when compared to the U only experiments. The efficiency varied from approximately 88-99+% (Table 2). The same effect of temperature on the U dissolution efficiency was observed with the highest efficiencies measured at lower temperatures. The amount of the lanthanide elements dissolved in the TBP solvent varied with oxidation state. Approximately 60-90+% of the Nd, Eu, and Ce in the 3+ oxidation state (as both nitrates and oxides) dissolved; however, little of the Ce(IV) as CeO_2 was solubilized. The dissolution of the 3+ lanthanides likely indicates that Am and Cm present in UNF’s will exhibit similar behavior in the hybrid dissolution process. A small amount of Sr dissolved (0.1-1.6%) in several experiments. Little Cs dissolved in any of the experiments. The amount of Mo dissolved varied from 0.1-1.7%. Essentially no Ru, Zr, and Pd dissolved. The retention of many impurities in the UDS is consistent with work performed by Tomijima et al. in which a large part of the impurities in powdered UO_2 remained undissolved during extraction experiments.[4] The concentration of I_2 in the solvent was not measured due to the complexity of the analysis; however, we recognized that I^- was reduced and I_2 was extracted into the TBP due to the purple color of the solvent. It is unlikely that very much I_2 will be present in UNF pretreated for tritium removal since the pretreatment process will also volatilize and capture I_2 as well as tritium.

The material balance closures for most of the elements used in this series of experiments were generally very good (Table 3). Each experiment was performed in duplicate. The average material balance closures have uncertainties less than 10% for elements which completely dissolved in the TBP solvent and/or 8 M nitric acid solutions containing 0.5 M fluoride. Confidence intervals associated with these material balance closures would include complete recovery of the elements. The material balance closure of elements which remained in the UDS and only partially dissolved in the acid solutions are biased low. Little of the Ru (added as RuO_2 in both the nitrate and oxide surrogates) or ZrO_2 were solubilized using either the TBP solvent or during dissolution of the UDS. X-ray diffraction analysis of the residue from the UDS dissolutions showed the presence of Ru and Zr as well as Pd (Figure 3). The RhO_2 observed is isostructural with PdO_2; therefore, the peaks shown in the diffraction pattern should be assigned to Pd. Two stage dissolution experiments were also performed with surrogates containing the non-radioactive fission product elements; however, little difference in the recovery efficiencies were observed compared to the one stage dissolutions.

In experiments performed with UNF surrogates containing just the actinide elements (U, Np, Pu, and Am), near complete dissolution of the U was achieved for both the nitrate and oxide compounds (Table 4). On average, approximately 80% of the Pu nitrate and half the Np and Am nitrates dissolved in the TBP solvent. However, little of the Np(IV), Pu(IV), or Am(IV) oxides dissolved which was consistent with the behavior observed for the Ce(IV) oxide. The preparation of actinide oxide and nitrate UNF surrogates for pretreated LWR fuel by mixing individual compounds is not completely representative of the solid solutions which occur in actual fuel. The TBP dissolution behavior of the actinide solid solutions prepared in this study was different as is shown in the following section. The material balance closures for the actinide only dissolutions were generally good, with closures exceeding 75% for most of the experiments; although, confidence intervals associated with the uncertainties in the average closures of the duplicate experiments cannot account for complete closure. The low bias in the material balance closures is likely due to the incomplete dissolution of the actinide compounds in the UDS and losses associated with the handling of trace quantities of the transuranic actinides.

Solid Solutions

In experiments performed with actinide solid solutions, the dissolution of the U oxide began almost immediately upon combining the solid solution and the TBP solvent as evident from the yellow color of the solvent. The residual solids remaining from the dissolution were sticky and tended to coat the wall of the beaker. Rather than rinse the beaker clean with dodecane, the recovered solids were returned to the beaker where the acid dissolution was performed. Complete dissolution of the solids was obtained in all experiments. The dissolution efficiencies for experiments performed using 30 and 50 vol % TBP are compared in Table 5. Comparable data from previous dissolutions using the UNF surrogates (UO_3 plus non-radioactive fission products and UO_3 plus transuranic elements) are also provided in the table.

Inspection of the data show that the dissolution efficiencies for the actinides from the solid solutions are much improved compared to the dissolution efficiencies from the surrogate UNF's (i.e., mixtures of oxides) measured in the previous series of experiments. Increased dissolution efficiencies were also observed for Ce(IV) and Re. The high dissolution efficiencies of the actinides (U(VI), Np(IV), Pu(IV), and Am(III/IV)) and lanthanides (Ln(III/IV)) from the solid solution are consistent with the expected extraction behavior in TBP with high nitrate salting [6,8-9]. We expect the dissolution behavior of the actinides, lanthanides, and Re from the solid solutions to be more consistent with the dissolution behavior of solid solutions formed in reactor fuels during irradiation than the dissolution behavior observed from mixtures of oxides prepared in the previous series of experiments. The data in Table 5 for the solid solutions also shows that the dissolution efficiencies for the actinides, lanthanides, and Re are improved when the TBP concentration was increased from 30 to 50 vol %.

The elemental dissolution efficiencies for solid solution experiments performed at 24 and 50 ˚C using 30 vol % TBP are shown in Table 6. Near complete dissolution of U was obtained in both experiments, so the effect of temperature on the dissolution efficiency was not apparent. The high solubility of the U from the solid solution obscured any noticeable effect. However, the dissolution efficiencies for the transuranic actinides and lanthanides improved in the experiment performed at 50 ˚C. A temperature effect was not discernable in experiments performed using the UNF surrogates in which the fission product elements (Table 2) or transuranic actinides (Table 4) were mixed with the UO_3 from the tritium pretreatment process. The improvement of the dissolution efficiencies of these elements in the solid solution dissolutions (Table 6) suggest there may be a kinetic effect that influences the extent of dissolution. A similar observation was made during work performed by Tomijima et al. where the rate of dissolution significantly increased when the dissolutions were performed at 50 ˚C compared to ambient temperature especially for refractory UO_2.[4]

Two-stage dissolutions were effective for the recovery of nearly all the actinide elements and most of the lanthanides from the solid solutions. The elemental dissolution efficiencies for the first and second stages of dissolution and the overall efficiencies are shown in Table 7. Based on our work with the surrogate UNFs and solid solutions, most of the fission products generated during fuel irradiation except for the lanthanides and Re(Tc) would remain in the undissolved solids. The loaded TBP solvent exiting a two-stage process would contain the actinides, a majority of the lanthanides, and small amounts of other extractable fission products such as the Re(Tc). The Am/Cm, lanthanides, and other fission products could be scrubbed from the solvent using dilute HNO_3 (Figure 1). A higher concentration of HNO_3 (nominally 8 M) would be necessary to strip Tc from the TBP solvent [10]. An additional solvent extraction cycle such as the TALSPEAK or Advanced TALSPEAK process would be required to separate the Am/Cm from the lanthanide fission products [11-14]. A solvent extraction cycle could be used to provide additional purification and partition the U, Np, and Pu into the desired product streams.

CONCLUSIONS

The feasibility of dissolving UNF which has been pretreated for tritium removal in a TBP/n-paraffin solvent was demonstrated using surrogate materials prepared from pretreated unirradiated UO_2 pellets and actinide solid solutions. The dissolution efficiencies of the nitrate and oxide forms of U produced by the pretreatment process were consistent with a purification process patented by Tomijima et al. [4] for the dissolution of water-insoluble U compounds in neutral organic solvents treated with nitric acid. In our work, dissolution experiments performed using only the nitrate and oxide forms of pretreated UO_2 resulted in efficiencies which varied from 80-99+%. The highest U recovery efficiency was obtained at the lowest temperature which is consistent with U distribution coefficients between TBP and an aqueous phase decreasing with increasing temperature.

In dissolution experiments in which nonradioactive fission products were mixed with the U compounds from the pretreatment process, the U dissolution efficiency varied from 88-99+%. Approximately 60-90% of the 3+ lanthanides dissolved (as both nitrates and oxides); however, little of the Ce(IV) was solubilized. Generally, less than 1% of the Sr and Mo dissolved and essentially no Cs, Ru, Zr, or Pd dissolved. Likewise, in work performed by Tomijima et al., a large part of the impurities in powdered UO_2 remained undissolved during extraction experiments.[4] In the current work, iodide was reduced to I_2 which extracted into the TBP solvent but was not quantified since the tritium removal process also captures I_2 and it will not be present in pretreated UNF. Dissolution of actinide only UNF surrogates showed significantly different behavior for the transuranic nitrate and oxide compounds. Near complete dissolution of both U compounds was achieved. On average, dissolution of 80% of the Pu nitrate and approximately one-half of the Np and Am nitrates were observed. Little of the Np, Pu, and Am oxides dissolved which was consistent with the behavior of the Ce(IV) oxide.

The dissolution efficiencies of the actinide and lanthanide elements in experiments performed using the solid solutions were generally much improved when compared to the UNF surrogates prepared using UO_3 from the tritium removal process. In all experiments, the final U dissolution efficiency was greater than 99%. The recovery of the transuranic actinides was also much improved. In two-stage dissolution experiments, the dissolution efficiencies for Np, Pu, and Am were 85-99+%. Higher dissolution efficiencies for the lanthanide elements were also measured in experiments with the solid solutions. In the two-stage dissolutions, efficiencies greater than 90% were obtained for Nd and Eu and the dissolution efficiency for Ce(IV) oxide was approximately 70-90%. A majority of the Re(Tc) also dissolved in the TBP solvent with dissolution efficiencies measured from approximately 50 to 90%. In practical terms, these data demonstrate the potential for developing a hybrid process which combines the dissolution of pretreated UNF with two cycles of solvent extraction required for the recovery of the actinide and lanthanide elements. Complete recycle of UNF could be achieved by separating the Am/Cm from the lanthanide fission products using the TALSPEAK or Advanced TALSPEAK process. An additional solvent extraction cycle could be used to purify and partition the U, Np, and Pu into the desired product streams.

When the TBP concentration in the solvent was increased from 30 to 50 vol %, we observed an increase in the dissolution efficiency for all elements of interest. The high solubility of U in the solid solution obscured any noticeable temperature effect in dissolutions performed at ambient temperature and 50 ˚C. However, the dissolution efficiencies for the transuranic actinide and lanthanide elements improved in the experiment performed at 50 ˚C. The improvement of the dissolution efficiencies of these elements in the solid solution dissolved at higher temperature suggest there may be a kinetic effect that influences the extent of dissolution. A similar observation was made in work performed by Tomijima et al.[4] The rate of dissolution significantly increased when the dissolutions were performed at 50 ˚C compared to ambient temperature especially for refractory UO_2. Demonstration of the TBP dissolution process with irradiated UNF pretreated for tritium removal is the logical next step in the evaluation process. An evaluation of the speciation of actinide and fission product elements dissolved by the TBP solvent should also be performed to support process optimization.

ACKNOWLEDGEMENTS

The work was supported by the Laboratory Directed Research and Development program of the Savannah River National Laboratory. The Savannah River National Laboratory is operated by Savannah River Nuclear Solutions for the US Department of Energy's Office of Environmental Management under contract number DE-AC09-08SR22470.

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TABLE 1
Dissolution efficiency for U only dissolutions

Exp	Temp	Dissolved U	Undissolved U	Dissolution Efficiency	Mat Bal Closure
	(°C)	(g)	(g)	(%)	(%)
UN-1	25	1.34	0.001	99.9	123
UN-2	25	1.27	0.001	99.9	117
UO-1	25	1.14	0.163	87.5	116
UO-2	25	1.13	0.216	84.0	118
UN-3	50	1.31	0.267	83.0	144
UN-4	50	1.34	0.273	83.1	148
UO-3	50	1.44	0.135	91.4	142
UO-4	50	1.44	0.134	91.5	140
UN-5(1)	50	0.454	0.291	61.0	68.6
UN-6(1)	50	0.616	0.274	69.2	78.0
UO-5(1)	50	0.705	0.154	82.1	74.3
UO-6(1)	50	0.769	0.174	81.5	82.7

(1) H_2O_2 added to TBP/n-paraffin solvent

TABLE 2

Dissolution efficiencies for U + non-radioactive fission product dissolutions

Element	UN-9 (%)	UN-10 (%)	UO-9 (%)	UO-10 (%)	UN-11 (%)	UN-12 (%)	UO-11 (%)	UO-12 (%)
U	98.2	97.5	98.3	99.5	95.2	91.8	94.1	88.3
Cs	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Ce	56.8	70.5	0.0	0.0	10.8	85.5	2.2	0.2
Nd	65.8	79.4	71.2	65.1	0.7	97.8	66.4	46.0
Eu	84.5	90.3	83.1	82.7	4.8	95.3	83.9	60.4
Sr	0.7	1.0	0.0	0.0	0.2	1.6	0.1	0.0
Re(Tc)	8.8	14.8	11.2	9.2	9.6	9.4	11.1	3.3
Mo	0.1	0.2	1.7	1.2	0.2	0.2	0.5	0.6
Ru	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pd	0.0	0.0	0.0	4.5	0.0	0.0	0.0	0.0
Temp (°C)	22	22	22	22	50	50	50	50

TABLE 3

Material balance closure for U + non-radioactive fission product dissolutions

Element	UN-9 (%)	UN-10 (%)	UO-9 (%)	UO-10 (%)
U	92.6	90.8	100	98.4
Cs	91.5	96.9	85.4	92.6
Sr	86.9	93.6	71.6	67.0
Ce	101	103	91.2	98.1
Nd	103	106	99.1	99.2
Eu	98.7	100	101	102.3
Re(Tc)	87.0	87.0	83.4	88.6
Mo	93.6	93.7	84.8	88.2
Ru	0.1	0.0	0.0	0.0
Zr	85.8	85.5	2.9	2.1
Pd	85.9	84.1	86.5	96.8

TABLE 4
Dissolution efficiency for actinide only dissolutions

Exp	Temp (°C)	Dissolution Efficiency (%) U	Np	Pu	Am
UN-21	25	98	44	83	25
UN-22	25	98	50	64	75
UN-23	50	134	55	87	50
UN-24	50	178	37	86	60
UO-21	25	113	0.3	< 0.4	0.1
UO-22	25	106	0.3	< 0.6	0.1
UO-23	50	150	2.0	12.4	4.0
UO-24	50	118	2.8	3.8	1.9

TABLE 5

Dissolution efficiencies for solid solutions and surrogate UNF's in a TBP/n-paraffin solvent

	Solid Solution		UNF Surrogate					
Exp	Solid-1	Solid-2	UO-9	UO-10	UO-11	UO-12	UO-21	UO-22
TBP (vol %)	30	50	30	30	30	30	30	30
Temp (˚C)	24	24	22	22	50	50	23	25
Element	Dissolution Efficiency (%)							
Sr	0.17	0.12	0.0	0.0	0.1	0.0	-	-
Cs	0.04	0.02	0.0	0.0	0.0	0.0	-	-
Ce	21.5	49.4	0.0	0.0	2.2	0.2	-	-
Nd	55.0	77.5	71.2	65.1	66.4	46.0	-	-
Eu	83.8	93.3	83.1	82.7	83.6	60.4	-	-
Re(Tc)	49.1	61.6	11.2	9.2	11.1	3.3	-	-
U	99.8	99.7	98.3	99.5	94.1	88.3	113	106
Np	99.1	99.6	-	-	-	-	0.3	0.3
Pu	81.8	94.9	-	-	-	-	< 0.4	< 0.6
Am	57.6	81.2	-	-	-	-	0.1	0.1

TABLE 6

Elemental dissolution efficiencies at 24 and 50 ˚C in 30 vol % TBP

Exp	Solid-1	Solid-2
Temp (˚C)	24	50
Element	Dissolution Efficiency (%)	
Sr	0.17	0.02
Cs	0.04	0.07
Ce	21.5	69.0
Nd	55.0	88.0
Eu	83.8	96.5
Re	49.1	29.0
U	99.8	99.8
Np	99.1	99.7
Pu	81.8	94.2
Am	57.6	86.2

TABLE 7

Elemental recoveries measured in two-stage dissolutions using 30 and 50 vol % TBP

Exp	Solid-3			Solid-4		
TBP (vol %)	30			50		
Temp (˚C)	27			28		
Element	Dissolution Efficiency (%)					
	Stage 1	Stage 2	Overall	Stage 1	Stage 2	Overall
Sr	0.024	0.024	0.048	0.019	0.016	0.035
Cs	0.068	0.161	0.229	0.080	0.028	0.108
Ce	63.5	24.8	88.3	52.3	16.3	68.6
Nd	76.4	20.6	96.9	72.9	17.3	90.2
Eu	87.4	12.1	99.5	84.1	13.8	97.9
Re(Tc)	70.3	18.7	89.0	55.9	12.4	68.3
U	96.5	3.48	99.9	93.7	6.21	99.9
Np	95.4	4.44	99.8	89.6	10.2	99.8
Pu	78.5	19.3	97.9	81.7	9.83	91.5
Am	19.4	79.6	99.0	63.6	21.8	85.3

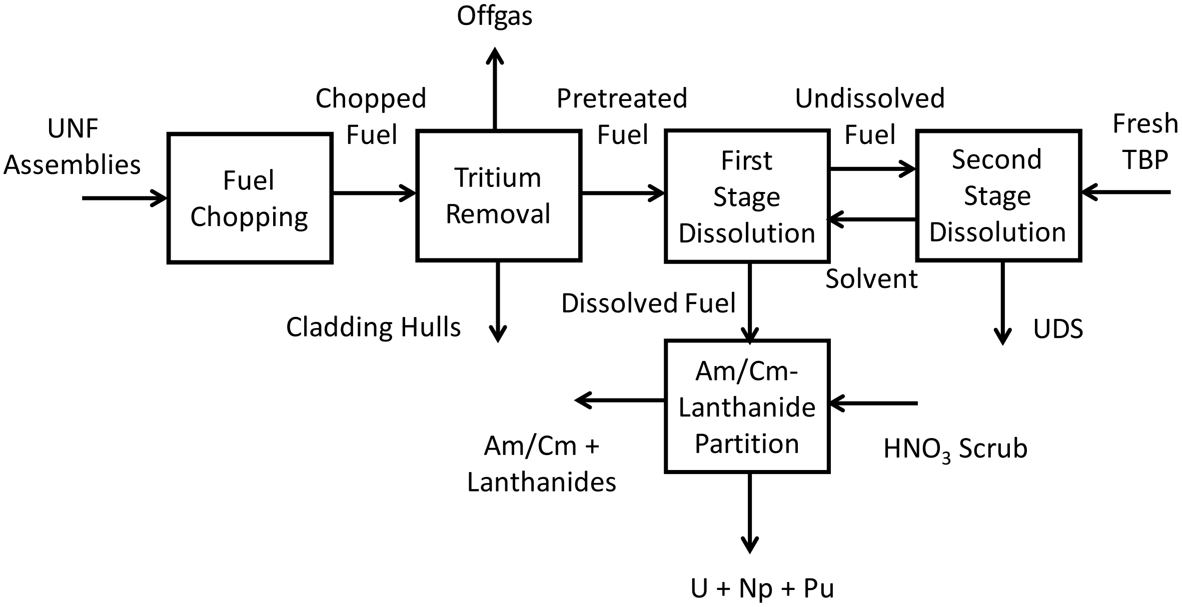

FIG. 1. Conceptual headend processes for the recycle of UNF

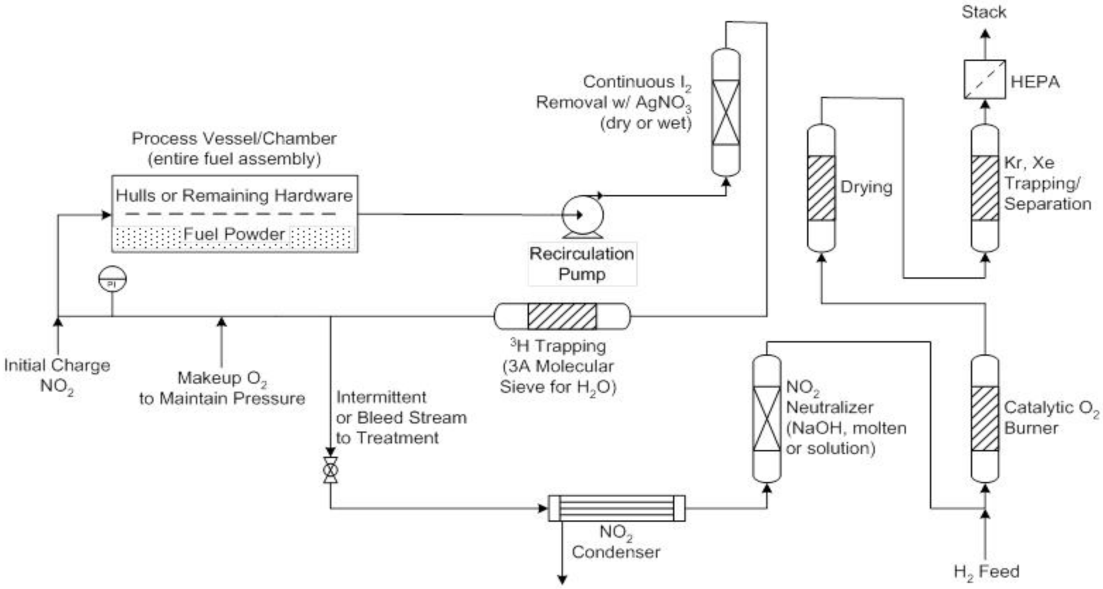

FIG. 2. Closed-loop recirculation system for UNF pretreatment

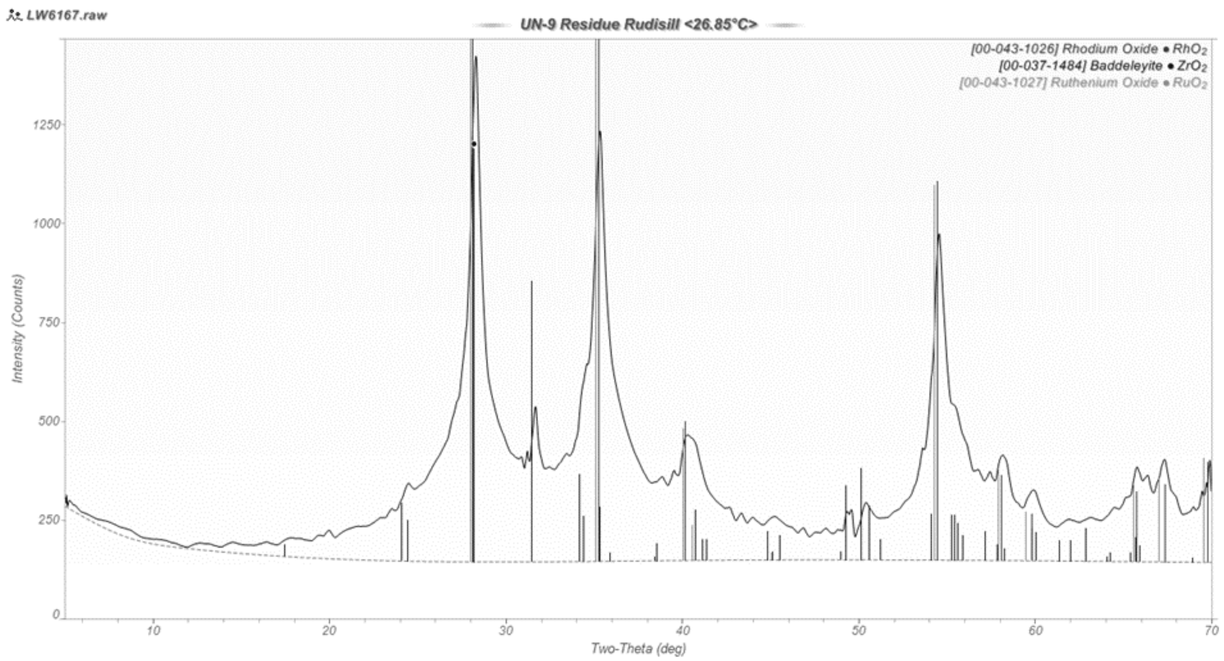

FIG. 3. X-ray diffraction analysis of UDS from experiment UN-9