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Dissolution of Used Nuclear Fuel using a TBP/n-paraffin Solvent

The complete recycle of used nuclear fuel (UNF) is desirable to recover the energy value from the remaining U and the higher actinides produced during fuel irradiation; however, the construction of a large-scale reprocessing facility is prohibitively expensive. A simplified flowsheet with a reduced equipment footprint is needed to improve the economic viability. To address this issue, we evaluated a hybrid process which combines the dissolution of UNF pretreated (oxidized) for tritium removal in a tributyl phosphate (TBP) solvent with the solvent extraction cycles required for recovery of the actinide and lanthanide elements. To demonstrate the feasibility of the hybrid process, we prepared actinide solid solutions containing selected fission product elements as surrogates for pretreated, irradiated light water reactor fuel. The distribution of the actinide and fission product elements was measured between the solvent and residual solids to determine dissolution efficiencies. Dissolution of the solid solutions in the TBP solvent was effective for the recovery of both the



Dissolution of surrogate used nuclear fuel in a tributyl phosphate solvent

actinide and lanthanide elements. An increase in the TBP concentration and temperature improved the dissolution efficiencies for these elements. Two-stage dissolutions were successfully used to recover nearly all the actinides and most of the lanthanides from the solid solutions. Our data indicate that most of the fission products generated during fuel irradiation except for the lanthanides and Tc (based on data for Re) would remain in the undissolved solids. The Am/Cm, lanthanides, and other fission product are easily scrubbed from the solvent by contact with nitric acid generating a pure U/Np/Pu stream.

Awards and Recognition

Not Applicable

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

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Date

Dissolution of Used Nuclear Fuel using a TBP/n-paraffin Solvent

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Thrust Area:

Environmental Stewardship

Clean Energy

Nuclear Materials Management

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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 the higher actinides; however, construction of a large-scale facility is prohibitively expensive. To address this issue, we evaluated a hybrid process combining the dissolution of UNF pretreated (oxidized) for tritium removal in tributyl phosphate (TBP) with solvent extraction cycles required for recovery of actinide and lanthanide elements. We prepared actinide solid solutions containing selected fission product elements as surrogates for pretreated, irradiated reactor fuel. The distribution of the actinide and fission product elements was measured between the solvent and residual solids to determine dissolution efficiencies. Dissolution of solid solutions in the TBP solvent was effective for the recovery of both the actinide and lanthanide elements. Our data indicate that most of the fission products generated during fuel irradiation except for the lanthanides and Re(Tc) would remain in the undissolved solids.

FY2018 Objectives

- Overall FY17/18 Objective – Demonstrate the feasibility of dissolving and purifying the actinide materials in UNF using a TBP/n-paraffin solvent following pretreatment with nitrogen dioxide gas (NO₂) to remove tritium
 - FY18 Objective – Evaluate the dissolution of irradiated Dresden reactor fuel in a 30 vol % TBP/n-paraffin solvent and characterize the distribution between the solvent and residual solids; pretreated irradiated Dresden fuel was not available from ORNL due to the termination of the tritium removal project by the DOE-NE Fuel Cycle Program
 - Revised FY18 Objective – prepare actinide solid solutions as materials which are representative of pretreated UNF and evaluate their dissolution efficiency in a TBP/n-paraffin solvent

Introduction

When UNF is removed from a reactor, approximately 95% of the initial U is still present in the fuel. 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 prohibitively expensive. Simplified flowsheets which reduced the equipment footprint and facility size are needed to improve the economic viability of complete recycle. To address this issue, we have performed a 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. A conceptual flowsheet for the headend facilities including the hybrid process is shown in Figure 1.

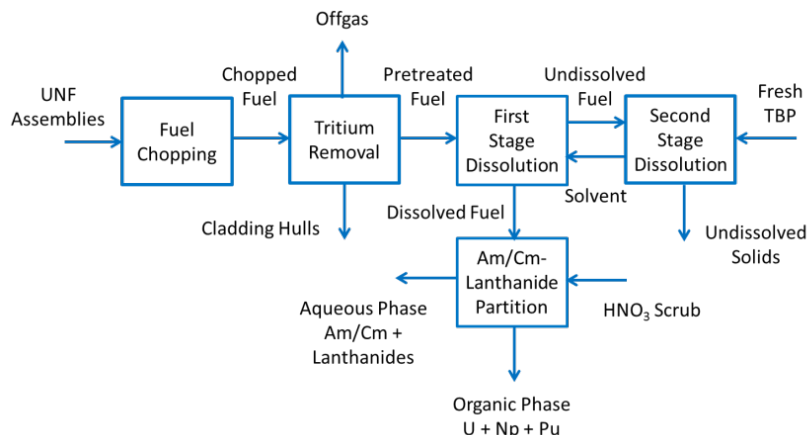


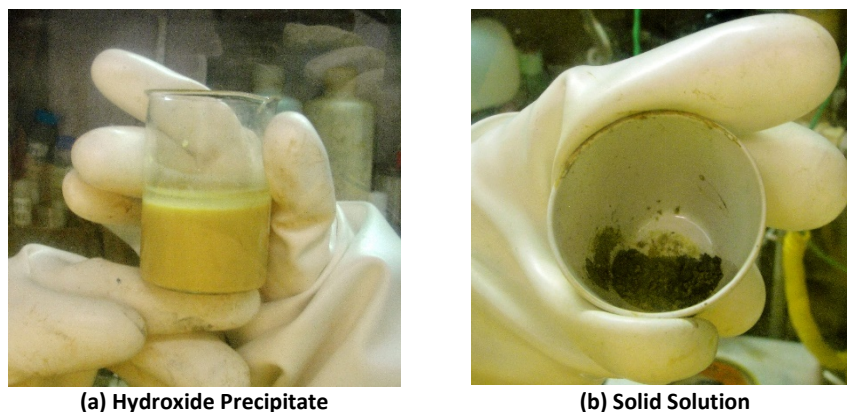
Figure 1. Conceptual Headend Process for the Recycle of UNF

A dry pretreatment process based on the oxidation of UNF was demonstrated at the ORNL for the removal of tritium (and I_2) in the headend portion of a fuel reprocessing facility. 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 $UO_2NO(NO_3)_2$ [1]. 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 [2]. Although, the direct dissolution of both UO_3 and $UO_2NO(NO_3)_2$ into TBP has been demonstrated [3], the extent of dissolution of other components of UNF into a TBP solvent has not been investigated.

To demonstrate the feasibility of the hybrid process, we prepared actinide solid solutions containing nonradioactive fission product elements as representative surrogates for light water reactor fuel pretreated for tritium removal. The surrogate UNF's 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 the solids solutions was investigated using 30 and 50 vol % TBP, at ambient (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 and fresh TBP added for a second stage of dissolution.

Approach

Based on our previous work to demonstrate the dissolution of simulated UNF into a TBP/n-paraffin solvent [4], we chose to prepare solid solutions from a uranyl nitrate solution containing transuranics (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 dissolve in the TBP dissolution experiments performed during the previous work were eliminated from the experimental design. The nominal masses of U and nonradioactive fission product elements used in the experiments were 1.25 and 0.2 g, respectively. Only trace quantities (< 0.02 g) of the transuranic actinides were used in the experiments. The solid solution was prepared by initially combining the nitrate solutions of the elements of interest. The actinides and nonradioactive fission products were then precipitated by adding ammonium hydroxide (NH_4OH) to the nitrate solution (Figure 2a). 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 (Figure 2b). 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 the UNF powder following pretreatment by the tritium removal process.



(a) Hydroxide Precipitate

(b) Solid Solution

Figure 2. Preparation of Actinide Solid Solution Containing Nonradioactive Fission Product Elements

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. 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 (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 inductively-couple plasma mass spectroscopy (ICPMS). 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/Discussion

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. To address the incomplete transfer to the filter, 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 1. Comparable data from previous work are also provided in the table for dissolutions performed using surrogate UNF prepared by adding nonradioactive fission product elements or transuranic actinides to UO_3 produced by treating unirradiated, depleted UO_2 pellets for tritium removal [4]. 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 mixture of oxides measured in the previous work. Increased dissolution efficiencies were also observed for Ce and Re. The dissolution efficiencies of the actinides (U(VI), Np(IV), Pu(IV), and Am(III)) and lanthanides (Ln(III)) from the solid solution are consistent with the expected extraction behavior in TBP with high nitrate salting [5-7]. The dissolution behavior of the actinides, lanthanides, and

Re from the solid solutions prepared in this work are likely 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 work. The present work 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 %.

Table 1. Elemental Efficiencies for Dissolution of Surrogate UNF in a TBP/n-paraffine Solvent

	Solid Solutions		Mixtures of Oxides					
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
NpO	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

The elemental dissolution efficiencies for experiments performed at 24 and 50 °C are shown in Table 2. Near complete dissolution of U was obtained in both experiments. However, the dissolution efficiencies for the transuranic actinides and lanthanides improved in the experiment performed at 50 °C. In the previous work, the highest U recovery efficiencies were obtained at nominally 25 °C compared to experiments performed at 50 °C [4]. This observation is consistent with U distribution coefficients between TBP and HNO₃ decreasing with increasing temperature [6]. A temperature effect was not discernable in the previous work for the transuranic actinides and fission product elements which were mixed with the UO₃ from the tritium pretreatment process. The high solubility of the U from the solid solution in the TBP solvent probably obscured any noticeable temperature effect. The improvement of the dissolution efficiencies of other elements of interest in the present work (Table 2) suggest there may be a kinetic effect that may control the extent of dissolution. The effect of temperature may be more pronounced with actual LWR fuel which has been pretreated for tritium removal.

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 3. Based on the previous [4] and current work, 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 Re(Tc). The Am/Cm, lanthanides, and other fission products could be scrubbed from the solvent using dilute HNO₃. A higher concentration of HNO₃ would be necessary to strip Tc from the TBP solvent [8]. An additional solvent extraction process would be required to separate the Am/Cm from the lanthanide

fission products. A second cycle of solvent extraction could be used to provide additional purification and partition the U, Np, and Pu into the desired product streams.

Table 2. Elemental Dissolution Efficiencies at 24 and 50 °C in 30 vol % TBP

Exp	Solid-1	Solid-2
TBP (vol %)	30	30
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 3. 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

FY2018 Accomplishments

- Dissolution of solid solutions in a TBP/n-paraffin solvent was effective for the recovery of the actinide and lanthanide elements
 - A majority of the Re(Tc) also dissolved in the TBP solvent
 - An increase in the TBP concentration results in an increased dissolution efficiency for the elements of interest

- Near complete dissolution of U was obtained in experiments performed at both 24 and 50 °C
 - Dissolution efficiency of TRU actinides and lanthanide fission products increased with increasing temperature
 - Current work indicates that kinetics may control the extent of dissolution of the solid solutions
- A two-stage dissolution process was successful for recovery of the actinides and lanthanide fission products
 - Lanthanide fission products and Am/Cm are easily stripped from the TBP solvent with dilute HNO₃
 - Additional cycles of solvent extraction can be used to provide additional purification and separate the U, Np, and Pu and Am/Cm

Future Directions

- Demonstrate the dissolution of irradiated UNF pretreated for tritium removal in a TBP/n-paraffin solvent
 - Pretreat irradiated fuel samples to prepare UO₃ and potentially UO₂NO(NO₃)₃ for dissolution tests (work now discontinued by the DOE-NE Fuel Cycle Program)
 - Perform laboratory-scale dissolution experiments to demonstrate the efficacy of the TBP dissolution process
 - Perform experiments to address differences in observed behavior of irradiated and unirradiated fuel and supplement results from experiments performed with UNF surrogates prepared from solid solutions
- Pretreated fuel may be available from the DOE-NE Fuel Cycle Program CoDCon demonstration at Pacific Northwest National Laboratory if the tritium pretreatment process is performed as part of the continuing demonstration

FY 2017 Publications/Presentations

1. T. S. Rudisill, T. C. Shehee, D. H. Jones, G. D. DelCul, *Dissolution of Used Nuclear Fuel using a TBP/n-Paraffin Solvent*, SRNL-MS-2018-00055, 42nd Annual Actinide Separations Conference, Charleston, SC, May 22, 2018.
2. T. S. Rudisill, T. C. Shehee, D. H. Jones, G. D. DelCul, *Dissolution of Used Nuclear Fuel using a TBP/n-Paraffin Solvent*, SRNL-MS-2018-00154, Briefing for the Southern Company, Aiken, SC, August 30, 2018.
3. Presentation of a poster at the 20th Symposium on Separation Science for Energy Applications in Gatlinburg, TN on October 21-24, 2018.
4. Publication of a manuscript in the proceedings from the 20th Symposium on Separation Science for Energy Applications in a special edition of the journal *Separation Science and Technology*.

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2. F. A. Dorda, V. V. Lazarchuk, V. A. Matyukha, M. V. Sirotkina, and V. V. Tinin, *Kinetics of UO₃ dissolution in nitric acid saturated 30% TBP in a hydrocarbon diluent*, Radiokhimiya, Vol. 52, No. 5, p. 397-398 (2010).

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Acronyms

HNO ₃	nitric acid
ICPMS	inductively-coupled plasma mass spectroscopy
KF	potassium fluoride
Ln	lanthanide
NH ₄ OH	ammonium hydroxide
NO ₂	nitrogen dioxide
ORNL	Oak Ridge National Laboratory
SRNL	Savannah River National Laboratory
TBP	tributyl phosphate
UNF	used nuclear fuel
UO ₂	uranium dioxide
UO ₂ NO(NO ₃) ₃	uranyl nitrate
UO ₃	uranium trioxide

Intellectual Property

Not applicable

Total Number of Post-Doctoral Researchers

Not applicable