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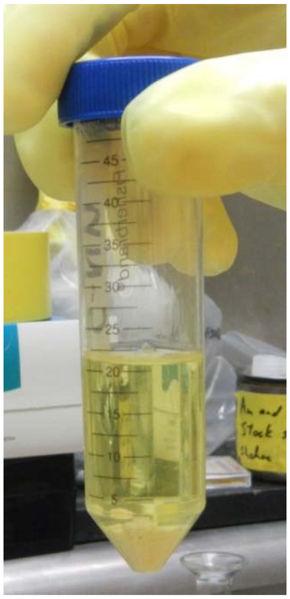
Dissolution of Used Nuclear Fuel using a TBP/n-paraffin Solvent


Dissolution of Surrogate Used Nuclear Fuel in Tributyl Phosphate

The dissolution of unirradiated light water reactor fuel pellets pretreated for tritium removal by an oxidizing gas was demonstrated using a solvent containing tributly phosphate which is used in the PUREX (Plutonium Uranium Reduction Extraction) process. Dissolution of pretreated fuel in tributyl phosphate could potentially combine fuel dissolution with two cycle of solvent extraction required for separating the actinide and lanthanide elements from other fission products. Simplified flowsheets which reduced the equipment footprint and facility size are needed to improve the economic viability of complete recycle of used nuclear fuel. Dissolutions were performed using used fuel surrogates prepared from both uranyl nitrate and uranium trioxide produced from the pretreatment process by adding selected actinide and stable fission product elements. In the laboratory-scale experiments, the U dissolution efficiency ranged from 80-99+% for surrogates prepared from either the nitrate or oxide forms of pretreated fuel. On average, 80% of the Pu and 50% of the Np and Am in the nitrate surrogate dissolved; however, little of the Np, Pu, or Am oxides which were added to the used fuel surrogate containing uranium trioxide dissolved. Approximately 60-90+% of the lanthanide elements (Nd, Eu, and Ce) in the 3+ oxidation state (as both nitrates and oxides) dissolved; however, little of the Ce in the 4+ oxidation state (as cerium oxide) was solubilized, which was consistent with the transuranic oxides. Only small amounts of Sr (0-1.6%) and Mo (0.1-1.7%) and essentially no Cs, Ru, Zr, or Pd in either used fuel surrogate dissolved.

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.

SRNL Legal Signature

Matthew C. Ennis 10/2/2017

Signature **Date**

LDRD-2017-00017
LDRD Report

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

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Thrust Areas:
Environmental Stewardship
Clean Energy
Nuclear Materials Management

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Abstract. *The dissolution of unirradiated used nuclear fuel (UNF) pellets pretreated for tritium removal was demonstrated using a tributly phosphate (TBP) solvent. Dissolution of pretreated fuel in TBP could potentially combine dissolution with two cycle of solvent extraction required for separating the actinides and lanthanides from other fission products. Dissolutions were performed using UNF surrogates prepared from both uranyl nitrate and uranium trioxide produced from the pretreatment process by adding selected actinide and stable fission product elements. In laboratory-scale experiments, the U dissolution efficiency ranged from 80-99+% for both the nitrate and oxide surrogate fuels. On average, 80% of the Pu and 50% of the Np and Am in the nitrate surrogate dissolved; however, little of the transuranic elements dissolved in the oxide form. The majority of the 3+ lanthanide elements dissolved. Only small amounts of Sr (0-1.6%) and Mo (0.1-1.7%) and essentially no Cs, Ru, Zr, or Pd dissolved.*

FY2017 Objectives

- Demonstrate the feasibility of dissolving and purifying the actinide materials in used nuclear fuel (UNF) using a tributyl phosphate (TBP)/n-paraffin solvent following pretreatment with nitrogen dioxide gas (NO_2) to remove tritium
    - Ship uranium trioxide (UO_3) and uranyl nitrate ($UO_2NO(NO_3)_3$) from Oak Ridge National Laboratory (ORNL) which was pretreated for tritium removal to the Savannah River National Laboratory (SRNL) for use in TBP dissolution studies
    - Add Np, Pu, and Am and key fission products (as non-radioactive elements) to simulate UNF
    - Perform dissolutions in a 30 vol % TBP/n-paraffin solvent and characterize the distribution of the actinides and fission products between the TBP and residual solids
    - Perform optimization studies (e.g., dissolution temperature, solid-to-liquid ratio, nitric acid (HNO_3) saturation of TBP, and mixing) to maximize dissolution efficiency

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 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. A conceptual flowsheet for the headend facilities including the hybrid process is shown in Figure 1.

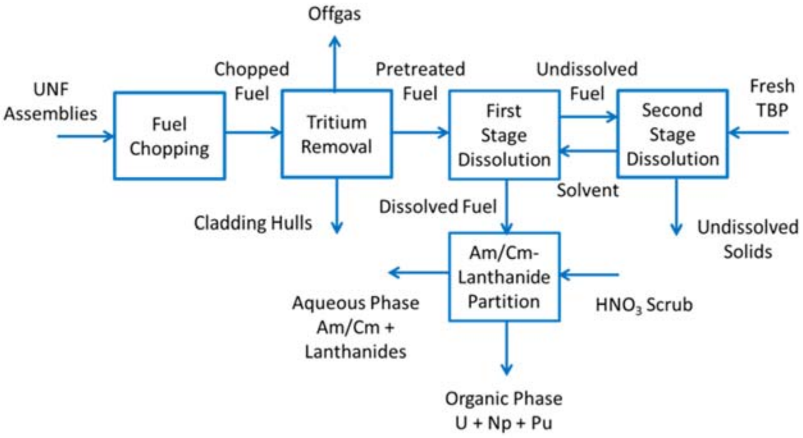

Figure 1. Conceptual Headend Process for the Recycle of UNF

A dry pretreatment process based on the oxidation of UNF is under development at 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 simulated UNF from unirradiated, depleted uranium dioxide (UO_2) fuel pellets (which were oxidized for tritium removal at ORNL) by adding selected actinide and stable fission product elements. 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 both the UO_3 and $UO_2NO(NO_3)_2$ 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 products, and the U compounds with the addition of transuranic elements (e.g., Np, Pu, and Am).

Approach

Fourteen fission and activation products were selected to prepare the surrogate UNF's. These elements included: transuranics (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. Trace quantities (< 0.02 g) of the transuranic elements were used in the actinide only dissolution experiments. 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 5 or 10 M HNO_3. 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 (22-25 °C) and 50 °C using dissolution times of a 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 (Figure 2). 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 undissolved solids (UDS) from a number of 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 potassium fluoride (KF). The small amount of UDS from the U and actinide only experiments dissolved reasonably well; however UDS from the dissolutions containing the non-radioactive fission product elelments did not completely dissolve. Residual solids were characterized by x-ray diffraction analysis.

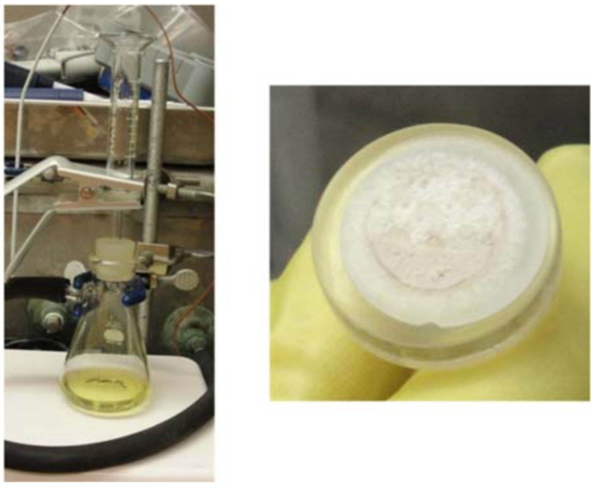

Figure 2. Filtration of Surrogate UNF Dissolved in TBP/n-paraffin solvent

Results/Discussion

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, 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. A small amount of hydrogen peroxide (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 [4]. 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 U measurements (Table 1). 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.

Table 1. Dissolution Efficiency and Material Balance Closure for U 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

Similar U dissolution efficiencies were measured in experiments performed with UNF surrogates containing non-radioactive fission product elements compared to the U only experiments. The efficiency varied from approximately 88-99+% (Table 2). The same effect of temperature on the 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 cerium oxide (CeO_2) was solubilized. The dissolution of the 3+ lanthanides indicates that these elements will likely exhibit the same behavior in the hybrid dissolution process as the Am and Cm present in UNF's. A small amount of Sr dissolved (0.1-1.6%) in several experiment. 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 concentration of I_2 in the solvent was not measured due to the complexity of the analysis; however, we recognized that I_2 was extracted 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 also volatilizes I_2 as well as tritium. The material balance closures for most of the elements used in these experiments were generally very good (Table 3). Little of the Ru (added as ruthenium oxide (RuO_2) in both the nitrate and oxide surrogates) or zirconium oxide (ZrO_2) were solubilized using either the TBP solvent or during dissolution of the UDS in 8 M HNO_3 containing 0.05 M KF. X-ray diffraction analysis of the residue from the UDS dissolutions showed the presence of Ru and Zr as well as 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.

Table 2. Dissolution Efficiencies for U + nonRad 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 + nonRad 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

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 oxide and nitrate UNF surrogates by adding individual compounds is not completely representative of real fuel. The presence of Pu and the minor actinides (Np, Am, and Cm) as solid solutions with U will almost certainly affect the dissolution rate and efficiency. Performing experiments with actual irradiated fuel pretreated for tritium removal is necessary to be certain of the actual behavior of the actinides (and fission products) during dissolution in a TBP-containing solvent. The material balance closures for the actinide only dissolution were generally good, with closures exceeding 75% for a majority of the experiments.

Table 4. Dissolution Efficiency for Actinide Only Dissolutions

Exp	Temp	Dissolution Efficiency (%)			
	(°C)	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

FY2017 Accomplishments

- Dissolution of unirradiated UO_2 fuel pellets pretreated for tritium removal in a TBP/dodecane solvent was demonstrated in laboratory-scale experiments
    - Dissolution efficiency for the U only surrogate (oxide and nitrate forms) varied from 80-99+%
    - Highest U recovery efficiency was obtained at lower temperatures (22-25 °C versus 50 °C)
- Majority of U and lanthanides in UNF surrogates containing U and non-radioactive fission product elements dissolved
    - U dissolution efficiency varied from 88-99+%
    - 60-90% of the Nd(III), Eu(III), and Ce(III) dissolved (as both nitrates and oxides); little Ce(IV) (as CeO_2) was solubilized
    - Generally less than 1% of the Sr and Mo dissolved
    - Essentially no Cs, Ru, Zr, or Pd dissolved
    - I_2 extracted into the TBP solvent, but was not quantified
- Dissolution of actinide only surrogates (containing U, Np, Pu, and Am) 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 half of the Np and Am nitrates was observed
    - Little of the Np, Pu, and Am oxides dissolved which was consistent with the behavior of the Ce(IV) oxide

Future Directions

- Demonstrate the dissolution of irradiated UNF pretreated for tritium removal in a 30 vol % TBP solvent
    - Pretreat irradiated fuel sample to prepare UO_3 and/or $UO_2NO(NO_3)_3$ for dissolution tests; this work was previously performed for the DOE-NE Fuel Cycle Technologies Material Recovery and Waste Forms Development Campaign at ORNL
    - Ship small quantities (2-5 g) of pretreated fuel to SRNL to demonstrate dissolution process in SRNL Intermediate Level Cell
    - Demonstrate baseline dissolution process with irradiated fuel
    - Perform additional experiments to address difference in observed behavior of irradiated and unirradiated fuel

- Limited demonstration of dissolution process with irradiated fuel was funded by the SRNL 2018 LDRD program

FY 2017 Publications/Presentations

1. T. S. Rudisill, T. C. Shehee, D. H. Jones, and G. D. DelCul, *Dissolution of Used Nuclear Fuel using a TBP/n-Paraffin Solvent*, SRNL-MS-2017-00067, 41st Annual Actinide Separations Conference, Argonne National Laboratory, Argonne, IL, May 23, 2017.

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2. F. A. Dorda, V. V. Lazarchuk, V. A. Matyukha, M. V. Sirotkina, and V. V. Tinin, *Kinetics of UO_3 dissolution in nitric acid saturated 30% TBP in a hydrocarbon diluent*, Radiokhimiya, Vol. 52, No. 5, p. 397-398 (2010).
3. Hiroshi Tomijima, Totsuka-ku, Yokohama, Kazushige Tsukui, Direct Dissolution of Water-insoluble Uranium Compounds by Contact with Neutral Organic Solvents Pretreated with Nitric Acid, Patent 3,288,568 (November 29, 1966).
4. M. L. Hyder , W. C. Perkins, M. C. Thompson, G. A. Burney, E. R. Russell, H. P. Holcomb, and L. F. Landon, *Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant*, DP-1500, E. I. du Pont de Nemours and Co. (1979).

Acronyms

UNF	used nuclear fuel
TBP	tributyl phosphate
NO_2	nitrogen dioxide
UO_3	uranium trioxide
$UO_2NO(NO_3)_3$	uranyl nitrate
ORNL	Oak Ridge National Laboratory
SRNL	Savannah River National Laboratory
HNO_3	nitric acid
UO_2	uranium dioxide
ICPES	inductively-coupled plasma emission spectroscopy
ICPES	inductively-coupled plasma mass spectroscopy
H_2O_2	hydrogen peroxide
CeO_2	cerium oxide
RuO_2	ruthenium oxide
ZrO_2	zirconium oxide

Intellectual Property

Not applicable

Total Number of Post-Doctoral Researchers

Not applicable