

CETE R&D at Oak Ridge National Laboratory Supporting Management of Nuclear Waste – 9227

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ABSTRACT

Oak Ridge National Laboratory (ORNL) is conducting a complete, coupled end-to-end (CETE) demonstration of advanced nuclear fuel reprocessing to support the Advanced Fuel Cycle Initiative (AFCI) Research and Development Program. The CETE project under way at ORNL is focused on (1) the demonstration of separations technology that would significantly reduce the quantity of nuclear waste that would require long-term geologic disposal and (2) providing products and waste streams for further treatment and testing to develop suitable forms for recycle or disposal.

Equipment for the CETE research and development (R&D) capability has been installed to provide all primary processing operations, ranging from spent fuel receipt to production of products and waste forms. The head-end treatment and off-gas recovery as well as the various solvent extraction processes separate the spent fuel into a number of discrete product streams, each with unique properties. As part of the CETE project demonstrations at ORNL, each of these product streams is recovered to serve as the feed to other critical process and waste management research, development, and demonstration activities. These include the production of recycle MOX fuel, transmutation fuels, recycle cladding, and new waste forms.

The paper discusses the separation and recovery processes used in the CETE demo and the resulting products from the first campaign.

INTRODUCTION

The first CETE campaign was initiated in June 2007 using approximately 3 kg of used fuel from the Dresden-1 Boiling Water Reactor (BWR). This fuel had a burn-up between 24–28 GWd/metric ton of heavy metal. The fuel was discharged from the reactor in 1975.

The overall recycling process plan used in this CETE campaign is shown in Figure 1. This flow sheet was configured to enable demonstration of the UREX+3 process which produces three products: (1) uranium, (2) uranium-plutonium-neptunium, and (3) americium-curium, as well as several fission product waste “products” for further studies at ORNL and other labs. It will produce the following streams as a result of the treatment of the spent fuel specimens and subsequent testing of the separation processes: (1) tritium product, (2) carbon-14 product, (3) iodine loaded sorbent, (4) Xe/Kr product, (5) hulls or cladding, (6) undissolved solids (UDS), (7) solidified low-enriched-uranium product, (8) solidified technetium, (9) solidified U/Pu/Np, (10) solidified Am/Cm, and (11) solidified residual fission product(s).

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Each of the major separation and recovery processes used in the CETE demonstration and the resulting products are discussed below. It should be noted that the voloxidation process was carried out to remove and trap volatile components in temporary equipment for this campaign. Also, the fuel powder was dissolved in batch operations. Specifically designed equipment for these operations will be available during subsequent campaigns. No attempt was made to recover xenon or krypton in the first campaign.

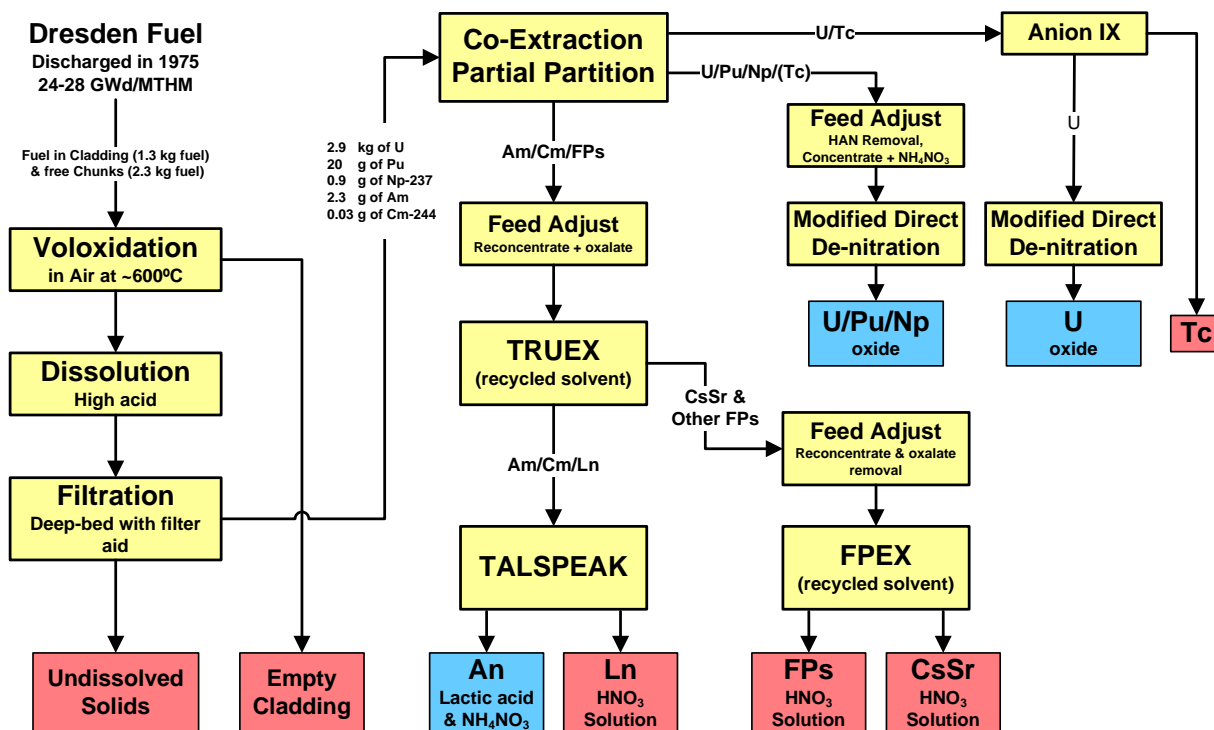


Fig. 1. Overall plan for the UREX+3 process evaluation – Dresden Fuel Campaign.

HEAD-END PRODUCT RECOVERY

Voloxidation

A basic voloxidation process was designed to prepare the existing Dresden fuel for dissolution for a series of tests. The inventory of ~4.2 kg of Dresden fuel consisted of segmented cladding pieces ~5 cm-long containing fuel material and loose fuel fragments. It was discovered that ~60% of the fuel had fallen out of the cladding either during the initial shearing, the long storage, or current handling. This fuel was separated by sieving through a 1-mm screen to remove fines that might contain rust or other debris to yield about 2.3 kg of fuel fragments and particles, and about 1.3 kg of fuel still in the cladding. Of the clad fuel, 12 segments (comprising about 0.58 kg of fuel and 0.16 kg cladding) were set aside for future small-scale voloxidation experiments.

Two simple voloxidation vessels were prepared to process the fuel: (1) a quartz vessel for use in an existing vertical tube furnace for processing clad fuel and (2) a stainless steel vessel for processing the loose fuel fragments in an existing box furnace.

A total of ~2.0 kg of clad fuel was processed in the quartz vessel (1.3 kg of fuel and 0.7 kg of cladding), representing several process runs of about 200 g of fuel per run. The processing temperature was 600°C, and air flow rate to the system ranged from 2.4×10^{-6} to 6.3×10^{-6} m³/s (0.3 to 0.8 cfh). The processing rate was generally limited by the air feed rate, and processing times ranged from 6 h to 12 h. The expected weight gain for the conversion of UO₂ to U₃O₈ is 4.0% (without correcting for fission product or other actinide changes). The average weight gain from the heat treatment for the clad fuel was 3.4%, which represents a conversion of ~86% of the UO₂ to U₃O₈. The fuel was effectively released from the cladding. The second voloxidizer vessel was fabricated of

stainless steel to fit a larger box furnace in the Radiochemical Engineering Development Center (REDC) hot cells. The top of the vessel was equipped with a clamp-flange to allow for the addition of fuel pellets and removal of the voloxidized product. Two 0.635 cm (1/4-in.) gas lines provided air feed and off-gas exhaust. One of the lines extended into the vessel to prevent air bypass and force the air to flow over the solids. This system was used for the voloxidation of the Dresden fuel fragments and particles which were separated from the fuel cladding.

A simplified treatment system was designed to capture the tritium (as water), carbon-14 (as carbon dioxide), iodine (as elemental iodine), and other volatilized fission products from the voloxidizer off-gas. It consisted of four columns in series, as shown in Figure 2. The first two columns were packed with molecular sieve type-3A to capture tritiated water released during voloxidation of the fuel. It was anticipated that the all the tritiated water would be captured on the first column, and capture of any tritium on the secondary column would provide clues to the width of the sorption front. Carbon dioxide (containing C-14) and iodine (I-129) would be captured on the third Ascarite® (sodium hydroxide-coated silica) column. Capture of CO₂ and I₂ occurs by chemical reaction which forms sodium carbonate and sodium iodide, respectively. As a backup to this trap, a sodalime column [a mixture of calcium hydroxide (70 to 80%), water (10 to 20%), sodium hydroxide (1 to 4%), and potassium hydroxide (0 to 4%)] was used to trap I₂, CO₂ (C-14), and many of the other possible trace level emissions (e.g., Tc₂O₇, SeO₂). It was anticipated that metal-based semivolatiles (e.g., cesium-containing species) would plate on the metal exhaust lines of the voloxidizer or condense as finely divided particulates as the gas stream cooled. If the latter occurred, the particulates would collect in the packed columns on the packing material. The four columns were connected in series with flexible tubing.

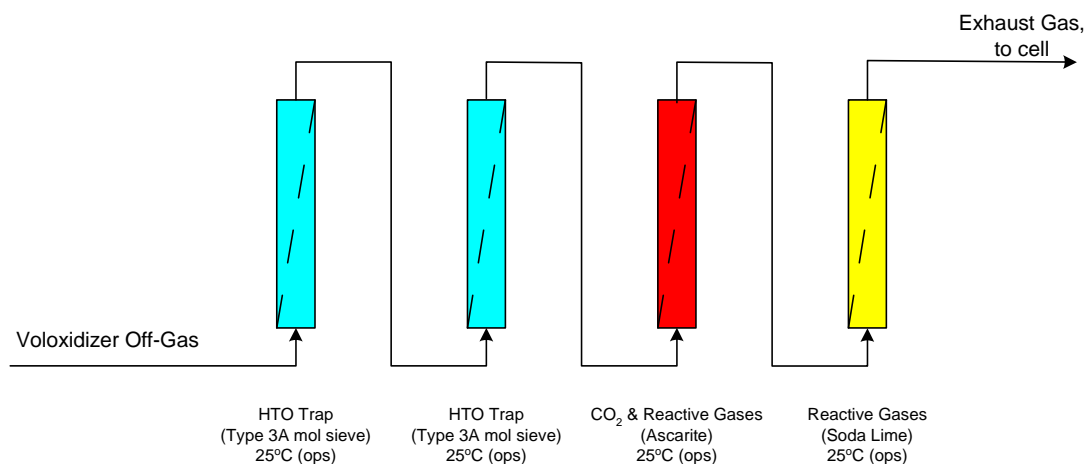


Fig. 2. Simplified off-gas trapping system for tests with Dresden fuel.

To minimize the loading of the off-gas traps with water and CO₂ from the supplied air, a pre-column containing Drierite (anhydrous calcium sulfate) and Molecular Sieve 5A (mean zeolite composition of 0.7 CaO, 0.3 Na₂O, Al₂O₃, 2 SiO₂ n H₂O) was connected between the air supply and the voloxidizer unit. Off-gas traps were used during the voloxidation of fuel during the runs in the stainless steel box voloxidizer. The traps were removed from the hot cell following the processing and were transferred to the analytical laboratories for analysis. The trapping material was removed from the columns and placed in secondary containers for measurement of changes in sorbent mass. Gamma scans were used as a coarse measurement of radioactive materials capture. The main technique for analysis was liquid scintillation counting, preceded by leaching of the solid trapping material and distillation to obtain a clean analyte.

The data shown in Table I indicate a mass increase (except for trap #4, where some material may have been lost during transfer) of the traps. The increase was mostly attributed to moisture and carbon dioxide in the air fed to the voloxidizer. Most of the tritium (2.1 mCi) was captured on the first trap as expected. The quantity of tritium was much lower than expected based on the age and burn-up of the fuel (expected about 100 mCi/kg or 200 mCi for

these tests). However, this fuel was chopped many years ago and the tritium may have slowly diffused out of the chopped fuel during storage.

Table I. Summary of Analysis of Off-Gas Traps

Trap #	Initial Sorbent Mass (g)	Mass Increase (g)	Total Collected (Bq)		
			H-3	C-14	I-129
1	19.91	0.9704	7.8E+7	<2.8E+3	1.6E+3
2	19.61	0.2412	<1.7E+4	<9.9E+3	4.0E+1
3	26.74	0.6712	-	<1.3E+3	<3.6E+1
4	18.87	-0.9987	1.4E+2	<8.9E+3	<8.3E+0

It was expected that a small amount of iodine would trap on the molecular sieve (first two columns) and the bulk would be captured on the Ascarite® (columns 3 and/or 4). However, most of the iodine-129 (0.042 μ Ci) was trapped on the molecular sieve, likely due to the low mass of iodine. The carbon-14 dioxide was expected to trap almost exclusively on the Ascarite®. Difficulties with the analysis of carbon-14 did not provide conclusive results. An improved method and apparatus are being evaluated for analysis of 14 C-containing samples for future experiments.

Fuel Dissolution in Nitric Acid

The existing dissolver tank was originally designed for dissolving fuel from sheared cladding pieces. It is constructed of stainless steel with a capacity of 14 L and an external water jacket that can either cool or heat the tank. A removable basket made of stainless steel screen is also available to hold fuel pieces but was not used during the powder dissolutions. Two simple batch dissolutions were made to prepare the necessary feed to allow the solvent extraction tests to proceed.

The fuel powder from the voloxidation treatments were combined and then divided into equal parts for two separate dissolutions in nitric acid. The steps for the first dissolution included adding a portion of the HNO_3 to the dissolver tank, then adding the fuel powder (1.8 kg), followed by metering in additional HNO_3 , heating for 8 h, cooling, and finally filtering to the feed accountability tank. The dissolution steps for the second batch dissolution included adding fuel powder (1.8 kg) to an empty dissolver, metering in the HNO_3 , followed by heating for 8 h, cooling, and finally filtering to the feed accountability tank. Both techniques worked well, and the actinides measured in the aqueous solution were close to the expected values. The first technique allowed some fission gases and NO_x fumes to escape into the hot cell before the dissolver lid was re-installed, and the second had some minor problems with instrument probes plugging until enough liquid was in the tank to dissolve or adequately suspend the powder. A new powder feeder which will be used in subsequent CETE runs has been designed and tested that will allow for controlled additions of voloxidized powder to the dissolver tank to maintain a controlled dissolution rate and allow for the capture of any volatile fission products in the off-gas stream.

The dissolver off-gas was routed through a temporary off-gas trap system in an attempt to capture ^{129}I . During the first dissolution run, the system used activated charcoal in the two beds. The rapid dissolution of the fuel that occurred during the direct addition to the hot nitric acid and the subsequent release of NO_x into off-gas train adversely affected the trapping ability of the charcoal. For the second dissolution, the charcoal was replaced with silver-exchanged mordenite (AgZ). Follow each dissolution batch, the beds were taken from the hot cell, and the contents removed for analysis. The results are shown in Table II.

Table II. Summary of Analysis of Dissolver Off-Gas Traps

Sample	Total I-129 (Bq)	Total I-129 (g)
Dissolution Batch 1 – Trap 1	1.4×10^5	0.0215
Dissolution Batch 1 – Trap 2	4.7×10^5	0.0723
Dissolution Batch 2 – Trap 1	8.2×10^5	0.126

Based on ORIGEN calculations, the quantity of ^{129}I contained in each of the 1.8-kg batches should have been ~0.203 g. This amounts to 46% to 62% of the expected iodine recovered from the off-gas system. During the first dissolution, some fraction was lost to the cell prior to the dissolver being closed, which may account for the recovery from this being lower than from dissolution batch 2.

Undissolved Solids (UDS) Recovery

Both dissolver solutions were pumped through a deep-bed filter (DBF) to remove UDS. The DBF is filled with diatomaceous earth in layers of coarse (Johns-Manville Celite 535), fine (Johns-Manville Hyflow Super Cel), and coarse (Johns-Manville Celite 535) that are placed over a 40-micron sintered metal frit. The DBF has been a very reliable technique for preparing well-clarified solvent extraction feeds from irradiated materials. While insoluble fines will quickly blind and plug bare metal or single-surface filters, the layers of filter-aid in the DBF allow the particles to be dispersed and trapped before they can reach the surface of the filter.

Two samples containing UDS were obtained from the system. The first, MSA-229, was recovered from the DBF; the second, MSA-230, was recovered from the dissolver heel. MSA-229, which contained undissolved solids and diatomaceous earth filter material, was washed with deionized water repeatedly and centrifuged. This allowed the separation of the undissolved fuel solids that stayed in the solution (black) from the earth filter (grey/white). The wet weight of the recovered solids was 0.6248 g. MSA-230, which only contained undissolved solids, was washed with deionized water repeatedly and transferred to a clean vial. The wet weight of the recovered solids was 1.1164 g.

Microwave Digestion

Samples of the UDS were dried at 105°C in an oven over night and cooled in a desiccator to room temperature. Samples were then weighed into each digestion vessel, and 10 mL of concentrated nitric acid and 0.5 mL of concentrated hydrofluoric acid were added. No reaction or off-gassing was observed upon acid addition. This initial digestion run did not yield a complete digestion. Hydrochloric acid was added to each vessel, and the digestion was performed again.

Digested samples were quantitatively transferred into 50-mL centrifuge flasks, diluted to volume, and centrifuged at 2500 rpm for 15 minutes to separate the remaining undissolved solids from liquids. Following separation of the liquid from the solids, the MSA-229 solids read 2.8 mR/h on contact, and the liquid read 7 mR/h on contact. The MSA-230 solids read 15 mR/h on contact, and the liquid read 110 mR/h on contact. The remaining solids were washed and centrifuged in preparation for alkaline fusion and Scanning Electron Microscopy (SEM) analysis.

Caustic Digestion

After microwave dissolution of the undissolved solids samples, some solids remained (~30%). These remaining solids were then subjected to a caustic leach. The remaining solids were centrifuged and the liquid decanted. Next 4 mL of 4 M KOH and 2 mL NaOCl were added to each sample, which was then heated to ~90°C for 8 h. Discoloration of liquid indicated partial digestion. The process was repeated and further reaction was noted, but solids remained.

The digests were centrifuged, and the liquids removed and analyzed. The remaining solids were used in the sodium tetraborate fusion dissolution step.

Fusion Digestion

A combination flux was prepared (80% $\text{Na}_2\text{B}_4\text{O}_7$ /20% NaNO_3). The solids remaining from the caustic digestion step were washed with deionized water onto the flux material in a zirconium crucible and taken to dryness. The samples and flux were placed in a muffle furnace preheated to 500°C. The temperature was then ramped to 800°C and maintained for 10 min. The samples were allowed to cool, and then 10% HNO_3 was added with mild heat and agitation. All of the samples appeared to be digested, with a small amount of black solids developing post-digestion. This dusting of solids was also present in the blank, indicating that it is a by-product of the method, probably attributed to the use of zirconium crucibles.

Alpha and gamma results for the microwave dissolution, the caustic digestion, and the fusion digestion, as well as the totals, are presented in Table III. The data is presented in terms of the amount recovered in the dissolution media for each preparation phase. The residual alpha after the acid digestion was less than 0.4% of the total present in the

Table III. Radiochemical Analysis of Undissolved Solids from Dresden Fuel

	MSA 229				MSA-230			
	Acid Prep	Caustic Prep	Fusion Prep	Total	Acid Prep	Caustic Prep	Fusion Prep	Total
	Bq dissolved /gm initial	Bq dissolved /gm initial	Bq dissolved /gm initial	Bq/gm initial	Bq dissolved /gm initial	Bq dissolved /gm initial	Bq dissolved /gm initial	Bq/gm initial
Alpha								
Gross Alpha	9.6E+07	8.4E+04	1.8E+05	9.6E+07	4.1E+08	6.9E+05	6.5E+05	4.1E+08
Pu-239/ Pu-240	20.50%	9.00%	19.80%	20.90%	15.8	27.70%	10.50%	15.60%
Am-243	0.60%			0.60%	0.50%			0.50%
Cm-245/Cu-246	1.00%			1.00%				
Am-241/ Pu-238	55.70%	88.00%	73.60%	55.60%	38.40%	72.30%	37.70%	38.40%
Cm-244	22.20%	3.00%	6.60%	21.90%	45.30%		51.80%	45.50%
Gamma								
Co-60					2.3E+05		5.0E+03	2.4E+05
Sb-125	2.3E+06	8.6E+04	1.8E+05	2.60+06	2.9E+06	8.4E+04	1.2E+05	3.1E+06
Cs-137	4.3E+07	5.5E+05	1.5E+06	4.5E+07	2.0E+08	1.7E+06	2.7E+06	2.0E+08
Eu-154					3.9E+05		1.0E+04	4.0E+05
Eu-155	5.5E+05	8.4E+03	2.7E+04	5.9E+05	7.0E+05	9.5E+03	2.2E+04	7.3E+05
Am-241	3.9E+06		8.7E+04	4.0E+06	4.6E+06		9.4E+04	4.7E+06
Am-243						5.5E+02		

sample. The gamma emitters were harder to get into solution, and ranged from 88 to ~98%. Caustic digestion increased the recovery by 1 to 3%, leaving ~1% to 9% in the undissolved residue.

Inductively Coupled Plasma (ICP) analysis of the resulting stepwise digestions show that the major constituents of the UDS to be U, Mo, Tc, Ru, Rh, and Pd with Mo, Tc, Ru, Rh, and Pd as the major elements remaining after acid digestion; Mo and Tc were the remaining major constituents following the caustic digestion.

A specimen mount, containing three grains of remaining solids after the microwave dissolution, was recovered and placed on a Tacky Dot™ (carbon adhesive disc) and shipped to for analysis. Total sample mass, as mounted, is estimated at <0.002 g. The material on the mount was examined using a SEM with ancillary energy-dispersive x-ray

spectroscopy (EDS). The results showed that each of the large grains consisted primarily of ruthenium, with trace molybdenum, possibly present as oxides.

TECHNETIUM RECOVERY

The aqueous uranium product solution from the coextraction cycle was treated by ion exchange (IX) to recover Tc-99. Three stainless steel columns containing conditioned Reillex HP resin were prepared for the Tc-99 separation process. Dimensions of each column were 6.02 cm (2.37 in.) ID \times 15.2 cm (6 in.) long, with an internal volume of \sim 434 mL. Reillex HP resin was treated by soaking in concentrated (\sim 15.8 M) nitric acid at 85°C for 6 h followed by washing with demineralized water and air drying prior to column loading. Columns 1 and 2 were each loaded with 145 g of Reillex HP resin obtained from Los Alamos National Laboratory to a height approximately 3.28 cm (1-1/4 in.) below the top flange (resin bed height \sim 80% of column height). Column 3 was loaded with Reillex HP resin obtained from an alternate source and required 172 g of treated resin to fill the column to the 80% height. The discrepancy in density between the two batches of treated Reillex HP resin was not reconciled but is likely attributable to incomplete drying of the second resin batch.

The resin columns were conditioned prior to installation in the hot cell by flowing 800 mL through the three columns in series. The technetium IX feed solution (uranium-technetium product solution) was adjusted to 0.014 H⁺ prior to column treatment. The 53 L of feed solution was pumped through the resin columns (in series) at a rate of \sim 4.1 L/h, followed by 12 L of 0.01 M HNO₃ tank flush solution.

The loaded columns were removed from the hot cell to a glove box for stripping and technetium recovery. Column 1 was first washed with \sim 0.25 L H₂O, then stripped with 2 L of 2 M NH₄OH, and finally rinsed with \sim 0.25 L H₂O. (Note that the \sim 0.25 L H₂O “wash” and “rinse” solutions were principally line flushes, having only a small effect on the solution concentrations in the column.) Columns 2 and 3 were similarly stripped, except only 1 L of 2 M NH₄OH was transferred through the columns.

The analytical data for the preliminary stripping solutions indicates Columns 1 and 2 were not completely stripped of technetium, while Column 3 contained no appreciable technetium loading (i.e., no breakthrough of Column 2). Good correlation between the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and beta spectrometry analyses for ⁹⁹Tc prompted a decision to rely on the relatively simpler beta spectrometry analysis for measurement of ⁹⁹Tc in subsequent strip solutions.

A secondary series of strips was applied to Columns 1 and 2 consisting of 2 L 2 M NH₄OH transferred through each column. The combined data for the preliminary and secondary strip sequences are shown in Table IV.

Table IV. Summary of Technetium IX Primary and Secondary Strip Solution Analyses

Sample code	Solution Description	Volume (L)	Tc-99 (mg)	
			by ICP-MS	by Beta Spec
TC-1W	Column 1 Wash	0.25	0.08	<0.15
TC-1S1	Column 1 Strip #1	1.00	311	284
TC-1S2	Column 1 Strip #2	1.05	132	144
TC-1R	Column 1 Rinse	0.24	9	10
TC-1S3	Column 1 Strip #3 (2 nd)	1.00	N/A	52
TC-1S4	Column 1 Strip #4 (2 nd)	1.00	N/A	15
TC-2W	Column 2 Wash	0.24	0.01	<0.04
TC-2S	Column 2 Strip #1	1.05	20	18
TC-2R	Column 2 Rinse	0.25	15	16
TC-2S2	Column 2 Strip #2 (2 nd)	1.00	N/A	27
TC-2S3	Column 2 Strip #3 (2 nd)	0.73	N/A	7
TC-3W	Column 3 Wash	0.24	0.02	<0.03
TC-3S	Column 3 Strip #1	1.00	0.03	<0.02

TC-3R	Column 3 Rinse	0.25	0.001	<0.004
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The Column 1 and Column 2 “rinse” and “strip” solutions were combined for vacuum evaporation to precipitate the technetium in the expected form of ammonium pertechnetate, NH_4TcO_4 . (Column 1 and Column 2 “wash” solutions and all Column 3 solutions were excluded from further recovery processing due to their negligible technetium content.) The combined product solution volume was 7.3 L containing ~574 mg of Tc-99. The evaporation system consisted of a 2-L three-neck round-bottom glass boiling flask with heating mantle, water-cooled glass condenser, and glass condensate-receiver flask connected to a laboratory diaphragm pump for vacuum generation. A Teflon-coated stirring rod was added for solution agitation to ensure temperature uniformity and promote small-bubble nucleation during boiling. Argon sweep gas was provided to improve the evaporation rate, manually controlled by valve at a typical flow rate of $\sim 1.6 \times 10^{-6} \text{ m}^3/\text{s}$ (0.2 scfh,) but ranging from 7.9×10^{-7} to $7.1 \times 10^{-6} \text{ m}^3/\text{s}$ (0.1 to 0.9 scfh.) Vacuum levels were maintained at ~584 mm Hg throughout the evaporation sequence, and solution temperatures were maintained in the range of 60–68°C. Condensates were collected in 1-L increments and analyzed for ^{99}Tc content by beta spectrometry. The first liter of condensate showed 0.12 mg of ^{99}Tc , likely due to mist entrainment during first initiation of vigorous boiling. Subsequent evaporation batch volumes were reduced and heating rate was reduced to minimize mist entrainment through the condenser. Subsequent condensate collections showed <0.002 mg of ^{99}Tc per liter of condensate.

Evaporation of the supernate (combined strip solution concentrate) continued to a volume of ~420 mL, which upon cooling yielded a grey precipitate in the flask. The precipitate was collected using a 5- μm Millipore® filter. After air drying, this first precipitate was transferred to a glass vial labeled DR-TcX-1 TCP-001. The weight of the first precipitate was measured to be 359 mg. Assuming an ammonium pertechnetate solids basis, the technetium content of the first precipitate would be 196 mg. The first 420-mL filtrate solution was sampled as code TC-FL-001 and analyzed to contain 504 mg of Tc-99.

The evaporator system was changed by substituting a 100-mL three-neck round-bottom boiling flask with heating mantle for the 2-L boiling flask for better management of the reduced filtrate/supernate volumes and anticipated precipitate recoveries. Subsequent evaporation of the 420-mL first filtrate solution proceeded ever more slowly as salt content increased and vapor pressure decreased. Evaporation temperatures were maintained below 68°C to avoid technetium volatilization losses. Solution pH was frequently checked by indicating paper to ensure basic solution maintenance, adding NH_4OH as needed.

No additional grey precipitates were observed during the final evaporation sequences. Rather, a crusty white-to-beige salt ring formed at the top of the concentrated brine in the boiling flask. It was decided to continue evaporating the brine to dryness and recover the salt for analysis and characterization. Final drying temperatures were held to <60°C. The collected salt weighed 74.7 g.

URANIUM/PLUTONIUM/NEPTUNIUM PRODUCT

The uranium/plutonium/neptunium (U/Pu/Np) aqueous product stream from the co-decontamination/partial partition separation of Run 1 fuel was co-converted to mixed oxide using the Modified Direct Denitration (MDD) process. MDD utilizes a rotary kiln to continuously thermally decompose ammonium nitrate/metal nitrates to produce free-flowing powders which have good ceramic properties for fuel fabrication.

The amount of solid MDD product collected was 185.4 g. Condensable vapors from the MDD process and any entrained product were also collected in the condensate/scrubber pot. This solution was sampled, and feed losses were calculated to be 0.4% based upon U and 0.01% based upon Pu analysis. The product bulk and tap densities were measured as 0.76 and 0.94 g/mL, respectively.

A sample of the product was dissolved without heating in order to minimize technetium volatility. A mixture of HF and HNO_3 was used to ensure complete dissolution, and the dissolvent was analyzed by ICP-MS. Previous work has found the MDD-produced mixed oxide to be completely soluble in refluxed nitric acid without the need to add fluoride. No solids were observed in the dissolvent. The results indicate a uranium-to-plutonium mass ratio of 13.7. The ratio of uranium to plutonium being higher in the product in comparison to the feed was attributed to starting the run feeding uranyl nitrate to achieve steady state (to maximize product collection).

Only a single solvent extraction step was performed, and, thus, no significant attempt was made to remove the impurities from the actinides to the level to meet a specification such as ASTM C 788. A small amount of technetium followed the uranium into the U/Pu/Np stream. Analysis was performed to determine whether the technetium was converted to an oxide form with the uranium, plutonium and neptunium or volatilized into the condensate. Results are shown in Table V.

Table V. ICP-MS Technetium Results for Mixed Nitrate and Mixed Oxide MDD Product

Material Sampled	Technetium Concentration	Technetium Concentration: Ratio to Total Uranium, $\mu\text{g/g U}$
Dissolved product	785 $\mu\text{g/g oxide}$	1170
Mixed nitrate initial concentrate	300 $\mu\text{g/ml}$	1822
Mixed nitrate final concentrate—acid reduced and filtered	582 $\mu\text{g/ml}$	1925

URANIUM PRODUCT

The uranyl nitrate product from the coextraction/partial partitioning was converted to uranium trioxide using the MDD following technetium recovery. The glove-box-contained development-scale MDD process converted 2.8 kg of uranium at a rate of ~ 100 g U/h.

During the technetium recovery operations, a portion of the resulting uranyl nitrate effluent was bottled directly and transferred to a glove box (this is referred to as the *clean cut*); the remainder, which was the bulk of the material, was concentrated in a hot cell evaporator. The resulting ~ 7 L of concentrated solution were transferred into 1-L polyethylene bottles (labeled #1 through #8, the last bottle including the tank/line flush) and brought to a glove box. Impurity analyses by ICP-MS of samples taken from one of the bottles and the *clean cut* are given in Table VI. Other than concentration of the dilute flush solution, no other processing was performed out of cell prior to addition of ammonium nitrate and conversion.

Table VI. Impurity Analysis for a Sample of the Dresden Uranium Solution

Impurity Element	Bottle #5—Mass Ratio of Impurity to Uranium, $\mu\text{g/gU}$	<i>Clean Cut</i> Mass Ratio of Impurity to Uranium, $\mu\text{g/gU}$
Mg	< 6.7	2.6
Al	< 14.8	15.6
Si	< 6.7	96.3
Ca	< 268.8	< 45.9
Ti	< 6.7	< 1.1
V	< 6.7	< 1.1
Cr	14.9	12.2
Mn	< 6.4	< 1.1
Fe	< 138.6	< 23.6
Co	< 5.5	< 0.9
Ni	52.2	43.6
Cu	< 6.7	< 1.1
Zn	< 26.9	< 22.9
Ta	< 6.7	< 2.3
W	5.0	< 0.1
Pb	< 0.7	< 1.1
Th	11.3	---

The large amount of uranium to be processed provided an opportunity to make oxide under varying operating conditions. Surface area and particle size analyses of the uranium products performed to date indicate that the MDD UO₃ product should make good pellets.

Samples of product oxide were dissolved and the dissolvent analyzed for impurities by ICP-MS. The results are presented in Table VII. Figure 3 shows a representative product from the dilute feed run.

Table VII. Impurity Analyses by ICP-MS for Samples of Dresden Uranium MDD Products

Impurity Element	Oxide from Bottle #2 Solution—Mass Ratio of Impurity to Uranium, $\mu\text{g/gU}$	<i>Clean Cut</i> Oxide—Mass Ratio of Impurity to Uranium, $\mu\text{g/gU}$
Mg	17.2	< 5.9
Al	268	< 12.9
Si	10.7	< 5.9
Ca	253	< 269
Ti	6.0	< 6.7
V	8.3	6.7
Cr	39.9	14.9
Mn	9.1	6.4
Fe	< 86.5	< 139
Co	< 3.4	< 5.5
Ni	66.9	52.2
Cu	31.3	6.7
Zn	< 25.2	< 26.9
Ta	< 4.2	< 6.7
W	0.5	5.0
Pb	6.6	0.7
Th	11.2	11.3

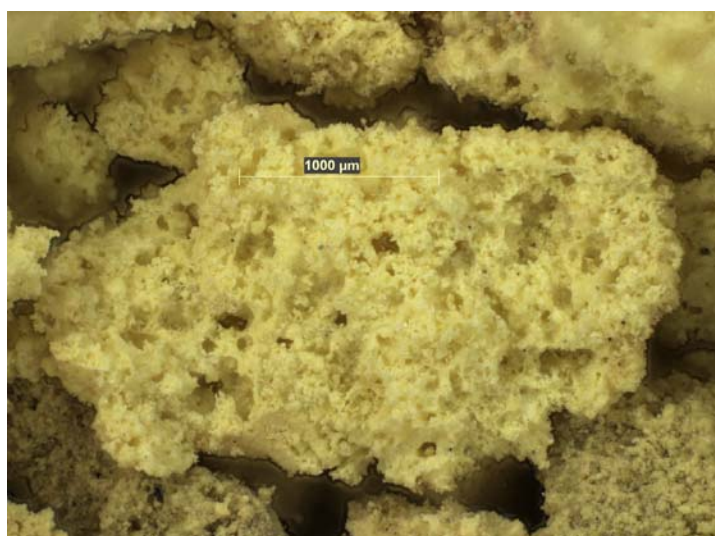


Fig 3. Stereomicroscopic image of MDD-produced UO₃ product.

TRANSURANIUM EXTRACTION (TRUEX) PRODUCT STREAMS

The raffinate stream from the coextraction-scrub flow sheet was collected, adjusted, and processed through a new version of the TRUEX flow sheet. The primary goal for TRUEX is to recover and purify the heavy actinides (americium and curium) from the other fission products.

Table VIII shows the element mass in the feed solution and their normalized distribution in the two effluent streams and the recycled solvent. In addition the table includes the total solution volume and acidity in the feed and each of

Table VIII. Content and Overall Distribution Data for the TRUEX Run with Dresden Fuel

Material	Feed Content	Total Volume Collected and Normalized Distribution Based on Stream Samples Taken during the Run		
		Raffinate	Actinide-Lanthanide Product	Waste Organic (recycled)
Total Volume	19.9 L	65.7 L	34.9 L	11.9 L
Acidity	4.2 N H ⁺	2.6 N H ⁺	3.4 pH	
U	5.2 g	0.51%	98.65%	0.84%
Pu	0.97 g	<0.22%	>99.78%	<0.002%
Np-237	0.219 g	1.28%	98.58%	<0.14%
Am	2.33 g	0.38%	99.62%	0.003%
Cm-244	0.047 g	1.71%	98.27%	0.02%
Total Actinide	8.7 g	0.44%	99.0%	~0.5%
Y	0.86 g	79.25%	20.75%	<0.004%
Zr	4.16 g	90.86%	9.14%	<0.007%
Mo	6.05 g	98.35%	1.65%	<0.005%
Tc	0.27 g	87.60%	6.99%	5.40%
Ru	0.44 g	98.48%	1.46%	0.06%
Pd	0.025 g	29.68%	66.31%	<4.02%
Total	6.79 g			
La	2.56 g	12.14%	87.85%	0.012%
Ce	5.94 g	1.97%	98.02%	0.009%
Pr	2.46 g	0.78%	99.22%	0.004%
Nd	8.38 g	0.76%	99.24%	<0.002%
Sm	1.41 g	0.66%	99.33%	<0.002%
Eu	0.24 g	1.27%	98.71%	<0.014%
Gd	0.30 g	5.19%	94.80%	<0.010%
Total Lanthanide	21.28 g	2.5%	97.4%	~0.005%
Cs	4.43 g	98.96%	1.03%	<0.01%
Ba	4.99 g	98.94%	1.05%	<0.01%
Rb	0.60 g	>98.7%	<1.3%	<0.02%
Sr	1.68	99.14%	0.80%	<0.06%
Total	10.03 g	98.89%	~1.1%	<0.01%
Sr-90	59 Ci			
Cs-137	110 Ci	>99.997%	<0.002%	<3E-05%
Eu-154	0.833 Ci	<3%	>96.6%	<0.01%

the effluent streams. The overall loss of actinides to the raffinate ranged from 1.7 %, 0.38%, and <0.2% for curium, americium, and plutonium, respectively, with an overall actinide loss of 0.4%. The raffinate stream was later processed through the process to recover cesium and strontium.

TRIVALENT ACTINIDE-LANTHANIDE SEPARATIONS BY PHOSPHORUS REAGENT EXTRACTION FROM AQUEOUS “K” COMPLEXES (TALSPEAK) PRODUCT STREAMS

The primary goal for TALSPEAK is to remove the lanthanide and yttrium elements from the actinides. Table IX shows the element masses in the feed solution and their normalized distribution in the three effluent streams as well as the total solution volume and acidity in the feed and each of the effluent streams. As expected, most of the lanthanides did extract into the solvent and were collected in the nitric acid strip while most of the actinides (with the exception of uranium) remained in the aqueous raffinate. The overall actinide/lanthanide separation was not as large as desired with 1% and 2% of the americium and curium, respectively, in the lanthanide product and 0.4% of the lanthanides in the actinide product.

The actinide product and the lanthanide product remain in an aqueous form in tanks awaiting solidification for subsequent use. Some scoping tests to evaluate methods to remove the lactic acid from actinide product are under way.

CESIUM/STRONTIUM PRODUCTS FROM FISSION PRODUCT EXTRACTION (FPEX)

The FPEX flow sheet was used to recover strontium and cesium from solutions generated during the reprocessing of Dresden fuel. An analysis of the adjusted feed solution showed that not only a 30% loss of the ¹³⁷Cs but also a loss of 70% and 80% of the zirconium and molybdenum, respectively. It is assumed that these losses were due to precipitation during the adjustment operations and that the solids either settled or plated out in the tanks or transfer lines. Although routine analyses of process solutions for zirconium and molybdenum are not done, routine gamma scan analyses for ¹³⁷Cs are performed. About 7 to 8% of the lost ¹³⁷Cs was later recovered in solutions from other processing tasks using the same equipment, but a complete recovery has not been made at this time.

Table X shows the element masses in the feed solution and their normalized distribution in the two effluent streams and the recycled solvent. In addition the table includes the total solution volume and acidity in the feed and each of the effluent streams. In general the desired separations were made. The recovery of ¹³⁷Cs was 99.3% with 0.06% lost to the raffinate and 0.6% left in the solvent that was recycled back to the extraction contactor. The Rb-Sr-Cs-Ba product and the residual fission product streams remain in an aqueous form in a tank in the REDC awaiting solidification for subsequent use.

Table IX. Content and Overall Distribution Data for the TALSPEAK Run with Dresden Fuel

Material	Feed Content	Total Volume Collected and Normalized Distribution Based on Stream Samples Taken during the Run		
		Actinide Product (raffinate)	Lanthanide Product (strip)	Waste Organic
Total Volume	26.8 L	81.1 L	35.4 L	39.0 L
Acidity	3.28 pH	3.04 pH	3.5 N H ⁺	
U	4.3 g	1.40%	0.17%	98.42%
P	0.91 g	>97.73%	<1.7%	0.58%
Np-237	0.229 g	99.96%	<0.01%	0.03%
Am	2.47 g	99.00%	0.98%	0.016%
Cm-244	0.039 g	98.09%	1.91%	0.007%
Total Actinide minus U	3.64g	98.4%	~1.3%	0.3%
Y	0.20 g	6.26%	66.95%	26.8%
Zr	2.16 g	99.72%	0.008%	0.275%
Mo	0.15 g	99.83%	0.14%	<0.03%
Tc	0.010 g	98.88%	0.86%	<0.3%
Ru	0.008 g	98.37%	1.59%	<0.04%
Pd	0.024 g	90.98%	5.76%	3.26%
Total	0.189 g			
La	2.43 g	0.41%	99.58%	0.018%
Ce	5.32 g	0.81%	92.77%	6.42%
Pr	2.53 g	0.17%	99.82%	0.017%
Nd	9.26 g	0.33%	99.66%	0.015%
Sm	1.54 g	0.96%	99.03%	0.011%
Eu	0.25 g	1.21%	98.78%	~0.010%
Gd	0.34 g	1.08%	98.45%	0.47%
Total Lanthanide	21.68 g	0.45%	98.04%	1.51%
Cs	0.061 g	98.4%	1.1%	<0.4%
Ba	0.30 g	81.9%	18%	<0.2%
Rb	<0.03 g	98.6%	0.9%	<0.5%
Sr	0.087 g	89.9%	9.7%	<0.4%
Total	0.48 g			
Sr-90	0.26 Ci			
Cs-137	0.084 Ci	>99.3%	<0.6%	~0.08%
Eu-154	0.840 Ci	<1.2%	>98.7%	~0.03%

Table X. Content and Overall Distribution Data for the FPEX Run with Dresden Fuel

Material	Feed Content	Total Volume Collected and Normalized Distribution Based on Stream Samples Taken during the Run		
		Raffinate	Rb-Sr-Cs-Ba Product	Waste Organic
Volume	27.9 L	58.4 L	56.9 L	3.0 L
Acidity	1.4	1.4	0.04	
Am-241	0.013 g	97.6%	1.6%	0.8%
Cm-244	0.003 g	96.0%	4.0%	<0.004%
Gross alpha	250 mCi	95.8%	2.9%	1.2%
Y	0.54 g	99.89%	0.11%	
Zr	1.15 g	97.2%	2.8%	
Mo	1.20 g	>99.97%	<0.03%	
Ru	0.36 g	99.76%	0.24%	
Total	3.25 g	~98.2	~1.2	
Cs	2.59 g	<0.07%	>99.93%	
Ba	5.27 g	0.03%	99.97%	
Rb	0.68 g	<0.2%	>99.8%	
Sr	1.40 g	0.01%	99.99%	
Total	10.48 g	~0.05%	~99.95%	
Sr-90	58.4 Ci	0.095%	99.90	NM
Cs-137	70.8 Ci	0.06%	99.32%	0.62%
Eu-154	0.016 Ci	>62%	<37%	<0.4%

SUMMARY

Approximately 3.6 kg of irradiated fuel was voloxidized and dissolved to prepare a feed solution to test a suite of four solvent extraction flow sheets. These products are now available for use in the development and testing of waste forms using prototypic materials including trace contaminants. The current status of the various output streams are shown in Table XI.

Table XI. Current Status of Product Streams Produced in the First CETE Campaign

Operations	Stream	Status
Fuel Dissolution	Empty fuel hulls	In storage pending approval to ship
	Undissolved solids	Recovered on deep bed filter—In storage pending approval to ship for analysis
	Iodine	Iodine loaded AgZ shipped to Sandia National Laboratory
Coextraction and Partial Partition	U/Tc product solution	Techetium recovered by anion exchange solidified and shipped for analysis
	U/Pu/Np product solution	Uranium converted to oxide by MDD—in storage
TALSPEAK	Am/Cm product solution	In storage pending development of process to recover actinides from DTPA-lactic acid solution
	Lanthanide product solution	In storage
FPEX	Cs/Sr product solution	In storage
	Other fission products (Zr, Mo etc.)	In storage