CoDCon Project: FY 2019 Status Report

Nuclear Technology Research and Development

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SUMMARY

The co-decontamination (CoDCon) project was established in FY 2016 with the objectives of (a) evaluating the uncertainty in the uranium (U)/plutonium (Pu) ratio in a mixed U/Pu product from a tributyl phosphate (TBP)–based solvent extraction flowsheet and (b) developing and demonstrating on-line optical spectroscopy for real-time monitoring of key components (e.g., Pu, U, and HNO_3 concentrations) in the process solutions. We are interested in establishing the accuracy and precision to which a specific uranium-to-plutonium (U/Pu) ratio can be achieved, which for the purposes of this project is set at a U/Pu mass ratio of 7/3. The uncertainty associated with achieving this specific target U/Pu ratio is being established through multiple flowsheet tests using laboratory-scale solvent extraction equipment. In addition, optical spectroscopic techniques have been incorporated into the CoDCon solvent extraction testing system, allowing real time monitoring of all input and output process streams.

Two CoDCon flowsheet tests were successfully performed in FY 2018 using a simple dissolved fuel simulant containing only U (~1 M) and Pu (~15 mM) in nitric acid (HNO_3; ~3 M). In FY 2019, two additional flowsheet tests were performed. For the first of these (CoDCon Run 3), the dissolved fuel simulant was similar to that used in the first two tests, with the inclusion of 1 mM neptunium (Np). The second test conducted in FY 2019 (CoDCon Run 4) used a more representative dissolved fuel simulant, including addition of non-radioactive fission product elements. All tests used a bank of sixteen 2-cm centrifugal contactors. The tests involved first loading the solvent (30 vol% TBP dissolved in *n*-dodecane) with U and Pu, then the Pu was stripped from the loaded solvent with a U(IV) solution (~50 mM) and the flowsheet conditions were adjusted such that some U partitioned into the Pu-containing product stream. The amount of U accompanying the Pu was monitored in real time using optical spectroscopic techniques coupled with chemometric modeling. Based on the real-time spectroscopic measurement of the U/Pu ratio, adjustments were made to the flowrate of the fresh TBP solvent phase used to scrub U from the aqueous Pu-containing product. This proved to be a very effective way to control the U/Pu mass ratio in the product.

For CoDCon Run 3, the relative mass fractions of U and Pu in the product were 70.3 ± 0.4% U and 29.7 ± 0.4% Pu, respectively, as determined by spectrophotometric analysis. This U/Pu mass ratio was in excellent agreement with the target value of 7/3. The on-line monitoring indicated an initial excursion in the U/Pu product solution to 63% Pu, which rapidly decreased to 28% Pu. Increasing the flowrate of the fresh TBP solvent allowed adjustment of the U/Pu mass ratio to the target value of 7/3.

During CoDCon Run 4, the solvent extraction system was found to be much less stable with considerable drifting of the U/Pu ratio during the reductive stripping portion of the test. Interfacial crud was formed during the solvent loading step, leading to a process upset condition. Addition of hydrofluoric acid to the feed solution mitigated the interfacial crud formation. Cumulatively across product bottles that were collected during the reductive stripping portion of the Run 4 test, the averages were 69.7 ± 2.5 % U and 30.3 ± 2.5 % Pu.

Four CoDCon flowsheet tests have been conducted to date. In all four cases, on-line optical spectroscopy coupled with chemometric modeling of the spectral data provided real-time information regarding the U/Pu ratio in the product stream. This real-time process solution information was used to adjust the process conditions to achieve the target U/Pu mass ratio of 7/3. Although this methodology proved effective, the stability of the solvent extraction system was not always consistent from run to run. Very stable operation of the system was achieved during CoDCon Runs 2 and 3; but much more drift in the system was experienced in Runs 1 and 4. During Runs 2 and 3, significant operating periods were achieved where the standard deviation in the percent composition of the U/Pu product was very low (< 0.5%). On the other hand, in Runs 1 and 4, the standard deviations in the composition of product was

~3%. Based on the limited set of data represented by these four CoDCon tests, it is reasonable to conclude that the U/Pu ratio can be maintained within 5% of a target ratio using the laboratory-scale solvent extraction system used in this work.

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ACRONYMS

CCD	charge-coupled device
CoDCon	co-decontamination
HDPE	high-density polyethylene
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
MDD	modified direct denitration
MOx	mixed oxide
NIR	near infrared
NO_x	nitrogen oxides
Np	neptunium
PNNL	Pacific Northwest National Laboratory
Pu	plutonium
StDev	standard deviation
TBP	tributyl phosphate
U	uranium
UV-vis	ultraviolet-visible

CoDCon PROJECT: FY 2019 STATUS REPORT

1.0 Introduction

The U.S. Department of Energy Office of Nuclear Energy (DOE-NE) has tasked Pacific Northwest National Laboratory (PNNL) with testing a co-decontamination (CoDCon) flowsheet for separating a mixed uranium (U)/plutonium (Pu) product from dissolved used nuclear fuel. For Phase 1 of this project, the CoDCon testing is being performed at a scale of nominally 1 kg of U, using simulated dissolved fuel solutions containing U and Pu in concentrations expected from dissolving actual irradiated fuel in nitric acid (HNO_3). If funded, Phase 2 of the project would demonstrate the CoDCon flowsheet using irradiated nuclear fuel. The primary purpose of the project is to determine, using laboratory-scale equipment, the accuracy and precision to which a specific uranium-to-plutonium (U/Pu) ratio can be achieved in the mixed U/Pu stream. For the purpose of this project, the target U/Pu mass ratio is 7/3. Integral to this testing effort is demonstrating optical spectroscopic techniques for real-time monitoring of the concentrations of key components (e.g., Pu, U, and HNO_3) in the process solutions. The monitoring capability is critical to achieving the objective of producing a product with a U/Pu mass ratio of 7/3.

Two CoDCon flowsheet tests were performed in FY 2018.[1] Both of these tests used a surrogate dissolved fuel solution containing approximately 1000 g of U and 15 g of Pu. As previously described, this initial ratio of Pu to U is what would be expected for light water reactor fuel burned to ~57,000 GWD/MT.[2] The tests involved: (1) preparing the surrogate feed solution and associated process solutions, (2) loading the process solvent with U and Pu, (3) reductive stripping of Pu from the solvent, (4) real-time monitoring of all inlet and outlet streams including the U/Pu ratio in the Pu-containing product solution, (5) adjusting the process conditions to achieve the target U/Pu ratio, (6) off-line analysis of the process solutions, and (7) conversion of the U/Pu nitrate product solution to a mixed oxide (for the first experiment only).

During the first CoDCon flowsheet test, the relative mass fractions of U and Pu in the product were 61% and 39%, respectively. This U/Pu mass ratio was substantially lower than the target value. The low U/Pu ratio was attributed to the chemometric model incorrectly indicating the presence of U(VI) in the product solution, primarily due to an unoptimized calibration transfer between the instruments used to collect the training set and those actually used to monitor the process. Nevertheless, the relative Pu mass fraction was maintained within 3% of the mean value throughout the experiment. Adjustments were made to the chemometric model based on the results of the first test to correct the inaccurate results in the real-time analysis of the process solutions.

A slightly different flowsheet was tested in the second CoDCon run due to a mix up in the aqueous inlet lines. During the second CoDCon flowsheet test, the relative amounts of U and Pu in product solution were initially ~80% and 20%, respectively. However, after adjustments to the flowrate of the TBP solvent phase in the U re-extraction stages of the flowsheet, the target ratio was achieved, and this was maintained over approximately 2.5 h of operation. The final U/Pu nitrate solution contained 29.3 % Pu and 70.7 % U. This result demonstrated the utility of real-time spectroscopic monitoring in guiding process operations, and also showed that once steady state is achieved, a very stable U/Pu ratio can be maintained.

In this report we describe the results of two additional CoDCon flowsheet tests. The flowsheet tested in these tests was the same as that tested in the first run. For the third run, neptunium (Np) was added to the aqueous feed solution; the U and Pu concentrations were otherwise the same as for the first two

CoDCon runs. The fourth CoDCon flowsheet test used a more representative dissolved fuel simulant, including non-radioactive forms of the fission and corrosion products.

This report fulfills milestone number M3FT-19PN030109063 in the U.S. Department of Energy Office of Nuclear Energy Nuclear Technology Research and Development Program.

2.0 Testing System Description

The equipment used in the CoDCon flowsheet tests has previously been described in detail,[1-2] so only the key features of the testing system are summarized here. The solvent extraction was performed in 2-cm centrifugal contactors fabricated at Argonne National Laboratory.[3] A bank of 16 stages of the 2-cm centrifugal contactors was used. Metering pumps with variable speed controllers were used to feed the process solutions to the contactor bank. The pump flowrates were calibrated with the specific solutions used by determining the mass of solution passed over known time intervals at selected pump settings. The densities of the solutions involved were used to convert the masses collected to volumes for determining flowrates in terms of milliliters per minute (mL/min). Linear calibration lines for the flowrate versus pump setting were generated. Pulse dampeners and filters were installed between the pumps and the contactor bank.

The solvent extraction system was equipped with on-line optical spectroscopy. All spectroscopic equipment was procured from Spectra Solutions. Quartz flow-through cells (1-cm path length) were held within a machined cell holder as previously described.[1-2] Ultraviolet-visible (UV-vis) spectrophotometry and Raman spectroscopy were used in the first two CoDCon flowsheet tests. These two spectroscopic tools were also employed during the third and fourth CoDCon flowsheet tests, but near infrared (NIR) spectrophotometry was also added for these runs. The NIR spectrophotometer allowed the determination of Np in the process solutions. While the Raman and UV-vis spectrometers utilized CCD cameras capable of simultaneous measurement of 6 flow cells, the NIR CCD detector was limited to single channel interrogation. The NIR therefore required the use of a motorized multiplexor that allowed for sequential measurement of the 6 flow cells. The NIR was added to the system by bifurcating collection fibers to split signal between the UV-vis and NIR instruments. The NIR excitation signal was prefabricated into the UV-vis excitation source and allowed for the two systems to utilize the same source and excitation fibers. Addition of NIR spectrometry did not require any changes to the on-line monitoring flow cells and probes within the glove box.

3.0 CoDCon Run Number 3

3.1 Experimental Description for Run 3

3.1.1 Run 3 Solvent Extraction

Figure 3.1 presents a schematic illustration of the flowsheet tested in the third CoDCon experiment (CoDCon Run 3); Table 3.1 provides a key for the labeling of the different process streams in the solvent extraction flowsheet. This flowsheet was essentially the same flowsheet that was tested in CoDCon Run 1.[1] A key distinction between Run 1 and Run 3 was that Np was added to the aqueous feed for Run 3. No active manipulation of the Np oxidation state was made in the feed solution; a mixture of Np(V) and Np(VI) was present. The flowsheet used 32 contactor stages, but because the testing bank had only 16 stages, the solvent extraction portion of the experiment was divided into two parts. First, the solvent consisting of 30 vol% tributyl phosphate (TBP) dissolved in *n*-dodecane (hereafter simply referred to as the TBP solvent) was loaded with U and Pu; Np(VI) was also extracted at this point.

The following procedure was performed to load the TBP solvent. The flow cells monitoring the aqueous inlets at stages 12 and 16 were filled with deionized water and the spectral baselines were recorded. To remove the deionized water from the aqueous feed line, 0.5 M HNO_3 was pumped to stage 12. The 0.5 M HNO_3 line was moved to stage 16, and the aqueous feed line was connected to stage 12. All 16 contactors were turned on and 0.5 M HNO_3 (stream *A2*) was introduced into the stage 16 contactor at a flowrate of ~20 mL/min. Once the 0.5 M HNO_3 solution was observed exiting stage 1, the flowrate was adjusted to 5 mL/min.(a) Fresh TBP solvent (stream *O1*) was then pumped into stage 1 at a flowrate of ~20 mL/min; this flowrate was adjusted to 28 mL/min once the organic phase was observed to exit stage 16. Spectral baselines were obtained on the flow cells for the organic inlet (stage 1) and outlet (stage 16). At this point, the aqueous feed, containing 1.02 M $UO_2(NO_3)_2$, 0.015 M Pu, 0.0010 M Np, and 2.55 M HNO_3 (stream *A1*), was pumped into stage 12 at a flowrate of 10 mL/min. The organic phase outlet was routed to the loaded solvent collection vessel. Timed grab samples of the aqueous (raffinate) and organic (loaded solvent) outlets were periodically taken during the course of the solvent loading step. At the conclusion of the solvent loading step, both the collected raffinate and the loaded solvent were sampled for analysis. The loaded solvent (11.2 L) was mixed with 1.9 L of U/Pu-loaded solvent left over from Run 2; this combined solvent was also sampled for analysis. Following the solvent loading step, the contactor bank was cleaned out in preparation of performing the second part of the experiment.

In the second part of the experiment, the Pu was stripped from the U/Pu-loaded solvent with U(IV) in such a way that a fraction of the U followed the Pu into the U/Pu nitrate product stream. For the flow cell used to monitor the U(IV) solution inlet, the spectral baseline obtained with deionized water during the solvent loading run was used. The spectral baseline for the flow cell used to monitor the other aqueous inlet was re-established with deionized water, before switching the line to 0.1 M HNO_3. Following this, the contactor bank was filled with 0.1 M HNO_3 by pumping this solution into stage 32 (contactor #16). Once the aqueous solution was observed to exit at stage 17 (contactor #1), the 0.1 M HNO_3 flow was paused and switched to stage 24 (contactor #8). The flow of 0.1 M HNO_3 to stage 24 was adjusted to 4 mL/min (stream *A4*). Fresh TBP solvent was introduced into stage 17 (contactor #1) at a flowrate of ~20

(a) The flowrates given in this section are the target values. The actual flowrates achieved are discussed in later sections of the report.

mL/min. The spectral baselines for the flow cells monitoring the organic inlet and outlet were established when the TBP solvent came through stage 32. The flow of the fresh TBP solvent (stream *O3*) was adjusted to a target flowrate of 8.5 mL/min. The U(IV) solution was introduced into stage 32 at 14 mL/min (stream *A5*). After 15 minutes, the U/Pu-loaded TBP solvent was pumped to stage 25 (contactor #9) at a flowrate of 28 mL/min (stream *O2*). The U and Pu concentrations in the aqueous outlet from stage 17 were monitored with the UV/vis and Raman systems so that adjustments could be made to the fresh TBP solvent flowrate at stage 17 to manipulate the U/Pu product stream (stream *A6*) to the desired mass ratio of 7/3. The adjustments that were made to the fresh TBP solvent flowrate are discussed in Section 3.3.1. All the other input and output streams were also monitored as indicated in Figure 3.1.

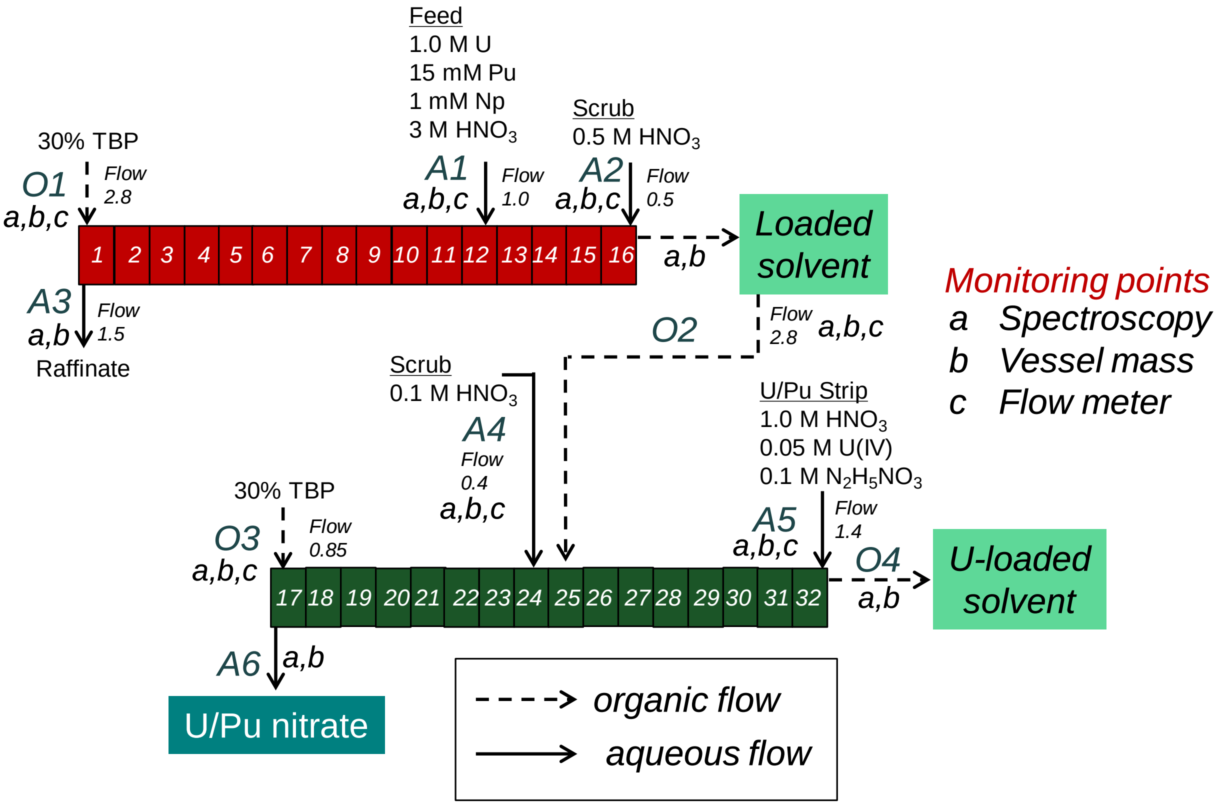

Figure 3.1. Flowsheet tested in the third CoDCon experiment (CoDCon Run 3); the numbers 1 through 32 refer to the individual 2-cm contactor stages; since only 16 contactors were available, contactors 17 through 32 were the same ones as 1 through 16, but were renumbered for the second part of the test. The flow values given are the relative flowrates for the individual process streams.

Table 3.1. Description and labels for the process streams in the CoDCon solvent extraction flowsheet.

Process stream label	***Description***
A1	Aqueous dissolved fuel simulant feed
A2	0.5 M HNO_3 scrub solution for solvent loading step
A3	Aqueous raffinate for solvent loading step
A4	0.1 M HNO_3 scrub solution for U/Pu stripping step
A5	Aqueous U(IV) solution used as Pu reductant
A6	U/Pu nitrate product stream
O1	Fresh TBP solvent for U/Pu loading
O2	U/Pu-loaded TBP solvent
O3	Fresh TBP solvent for U re-extraction
O4	Pu-depleted TBP solvent

The U/Pu nitrate aqueous product solution from stage 17 was collected in a series of nine 1-L HDPE bottles. Timed grab samples were periodically taken of the aqueous product solution from stage 17 and the Pu-depleted TBP solvent from stage 32. The masses of the various process vessels were also periodically recorded. The latter measurements were made with uncalibrated balances, so should be considered for indication only.

3.1.2 Concentration of U/Pu Nitrate Stream from Run 3

The U/Pu nitrates solutions from collection bottles 2 through 9 were combined and concentrated. Before concentrating the solutions, the hydrazine present in the solution was catalytically decomposed using a Pt catalyst.[4] For this purpose, 229 g of 1% Pt-on-silica catalyst (Sigma-Aldrich)(a) was placed in a 4 L stainless steel beaker. In batches of ~3 L, the solutions from the U/Pu nitrate product bottles were transferred into the beaker for hydrazine decomposition, which was performed by heating the mixture at 75 °C with mixing *via* sparging with compressed air. The hydrazine decomposition typically took 8 to 15 hours based on these conditions. Completion of the hydrazine decomposition was characterized by change in the solution color from blue to brown [presumably indicating oxidation of Pu(III) to Pu(IV)], and by cessation of gas evolution from the reaction vessel (the primary reaction product from the hydrazine decomposition being nitrogen[4]).

Following the hydrazine decomposition, the U/Pu nitrate solution was filtered (0.45-µm membrane), then concentrated by distillation. Because the capacity of the distillation apparatus was only 1 L, the distillation operation was conducted by repeatedly filling the vessel to ~700 mL, then concentrating to ~200 mL. Concentrating beyond this point lead to the formation of solids, which were re-dissolved by addition of concentrated HNO_3. The final volume of the concentrated U/Pu nitrate solution was 303 mL (density = 1.41 g/mL), which included volume added from rinsing of the distillation vessel with 0.5 M HNO_3. Samples of the concentrated solution were taken for analysis by spectrophotometry and ICP-MS.

(a) http://www.sigmaaldrich.com/catalog/product/aldrich/520691?lang=en&region=US

3.2 Run 3 Solvent Loading

3.2.1 Material Flows during Run 3 Solvent Loading

The flowrates for the various process streams were monitored in three ways: (1) weighing timed grab samples, (2) periodically weighing the vessels containing the process solutions, and (3) recording the signal from the flow meters. The latter method was only used for the input streams, and the first method was only practical for the outlet streams. Table 3.2 presents the flowrate data for the aqueous feed stream (*A1*) for Run 3, as determined from changes in the feed vessel mass over time.(a) The measured flowrate of 9.9 ± 0.3 mL/min(b) agreed very well with the target flowrate of 10 mL/min. Reliable data regarding the flowrate of the aqueous feed stream could not be obtained from the in line flowmeter because the data were very scattered.

Table 3.3 presents the flowrate data for the 0.5 M HNO_3 scrub solution (stream *A2*) for Run 3, as determined from changes in the scrub feed vessel mass over time. The measured flowrate of 4.3 ± 0.2 mL/min was ~15% lower than the target flowrate of 5 mL/min. The flow meter data for the 0.5 M HNO_3 scrub solution was very erratic up to 110 minutes into the loading run and reliable data could not be obtained during this time period. Past the 110-minute mark, the flow meter readings stabilized giving a flowrate of 4.4 ± 0.4 mL/min for the 0.5 M HNO_3 scrub solution. This was in excellent agreement with the flowrate obtained by changes in the scrub feed vessel mass.

Table 3.4 presents the flowrate data for the TBP solvent (stream *O1*) during the Run 3 loading step, as determined from changes in the solvent feed vessel mass over time. The measured flowrate of 27.3 ± 0.5 mL/min was slightly lower than the target flowrate of 28 mL/min, but nearly in agreement given the experimental uncertainty. The flow meter data indicated a somewhat higher flowrate for the TBP solvent—31.5 ± 1.8 mL/min.

The flowrate of the aqueous raffinate (stream *A3*) was determined by both timed grab samples and changes in the mass of the raffinate collection vessel, giving average flowrates of 12.5 ± 0.4 and 11.7 ± 1.8, respectively (Table 3.5). The two values agree within the experimental uncertainty. Based on the input flowrates—9.9 mL/min for stream *A1* and 4.3 mL/min for stream *A2*—a flowrate of 14.2 mL/min would be expected, assuming the volumes to be additive. The lower flowrate observed suggests a decrease in the aqueous solution volume upon mass transfer of the U and Pu into the organic phase, although this cannot be stated definitively.

The flowrate of the loaded solvent was also determined by both timed grab samples and changes in the mass of the loaded solvent collection vessel, giving average flowrates of 29.5 ± 0.6 and 26.3 ± 2.7, respectively (Table 3.6). The two values agree within the experimental uncertainty, but the value obtained by changes in the tank masses does appear to be lower. This is partially due to the low value obtained from the last tank mass reading, which might be anomalous. If this data point is excluded from the calculation, the flowrate obtained from changes in the loaded solvent collection vessel was 27.1 ± 1.1.

(a) For the solvent loading part of the test, the run time is defined as the total time elapsed since the start of the run, with the start time being defined as the time at which the flow of the aqueous feed with the U and Pu was commenced.

(b) Unless otherwise noted, the uncertainty values given in this report represent the standard deviations of multiple data points.

Table 3.2. Flowrates for the aqueous feed (stream *A1*) during CoDCon Run 3 solvent loading as determined by changes to the aqueous feed tank mass; target flow rate = 10.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
22	13.7	9.8
50	13.9	10.0
91	14.1	10.1
135	13.5	9.7
174	14.7	10.6
212	13.3	9.5
249	14.1	10.2
282	13.2	9.5
316	14.2	10.2
356	13.8	9.9
391	13.6	9.8
Mean	13.8 ± 0.4	9.9 ± 0.3

(a) Run time represented by the mid-point of the sampling period.

Table 3.3. Flowrates for the 0.5 M HNO_3 scrub (stream *A2*) during CoDCon Run 3 solvent loading as determined by changes to the scrub tank mass; target flow rate = 5.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
21	4.7	4.7
49	4.5	4.4
91	4.4	4.4
133	4.6	4.5
172	4.5	4.4
211	4.2	4.1
248	4.3	4.2
281	4.1	4.0
316	4.3	4.3
355	4.0	4.0
390	4.3	4.2
Mean	4.4 ± 0.2	4.3 ± 0.2

[a] Run time represented by the mid-point of the sampling period.

Table 3.4. Flowrates for the 30% TBP solvent (stream *O1*) during CoDCon Run 3 solvent loading as determined by changes to the TBP solvent tank mass; target flow rate = 28.0 mL/min..

Run time, min	***Flow, g/min***	***Flow, mL/min***
20	22.5	27.2
49	22.1	26.8
90	23.0	27.9
132	22.6	27.4
172	22.4	27.1
212	22.7	27.5
249	22.6	27.4
282	22.5	27.2
317	21.9	26.5
356	23.3	28.2
391	22.5	27.2
Mean	22.6 ± 0.4	27.3 ± 0.5

[a] Run time represented by the mid-point of the sampling period.

Table 3.5. Flowrate of aqueous raffinate (stream *A3*) during CoDCon Run 3 solvent loading, as determined with timed grab samples and from changes in the collection tank mass.

From Timed Grab Samples			***From Changes in Tank Mass***		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
27	12.6	12.1	21	11.8	10.7
63	13.6	12.7	50	12.1	11.0
109	14.1	13.2	90	14.6	13.3
145	13.5	12.5	133	13.2	12.0
173	14.2	13.3	173	15.5	14.1
230	13.0	12.1	212	11.3	10.3
264	13.3	12.5	250	15.1	13.7
295	13.1	12.2	282	9.1	8.2
332	13.1	12.3	317	12.4	11.3
376	13.7	12.7	370	13.3	12.1
404	13.2	12.3			
Mean	13.4 ± 0.5	12.5 ± 0.4	Mean	12.8 ± 1.9	11.7 ± 1.8

Table 3.6. Flowrate of loaded solvent outlet during CoDCon Run 3 solvent loading, as determined with timed grab samples and from changes in the collection tank mass.

From Timed Grab Samples			***From Changes in Tank Mass***		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
20	25.5	28.8			
58	26.2	29.3	50	25.7	27.9
102	26.4	29.4	91	24.4	26.6
138	26.8	30.4	139	25.5	27.7
190	26.3	29.4	179	22.4	24.4
226	26.8	29.8	213	25.6	27.9
259	25.9	28.6	249	25.0	27.2
291	27.4	30.4	282	25.0	27.2
328	25.6	28.7	317	25.7	27.9
373	26.5	29.6	356	25.0	27.2
400	26.5	29.7	391	17.9	19.4
Mean	26.4 ± 0.5	29.5 ± 0.6	Mean	24.2 ± 2.4	26.3 ± 2.7

The flowrate data derived from the grab samples and vessel masses during the Run 3 loading step are depicted graphically in Figure 3.2. The data obtained from vessel balances inside the glovebox tended to show significant scatter, especially the loaded solvent receipt vessel and the raffinate receipt vessel. Figure 3.2 also clearly shows the generally lower flowrate for the loaded solvent indicated by the changes in the vessel mass compared to the grab samples. As determined from the changes in the vessel masses, the flowrate of the input TBP solvent stream agrees with that of the loaded solvent.

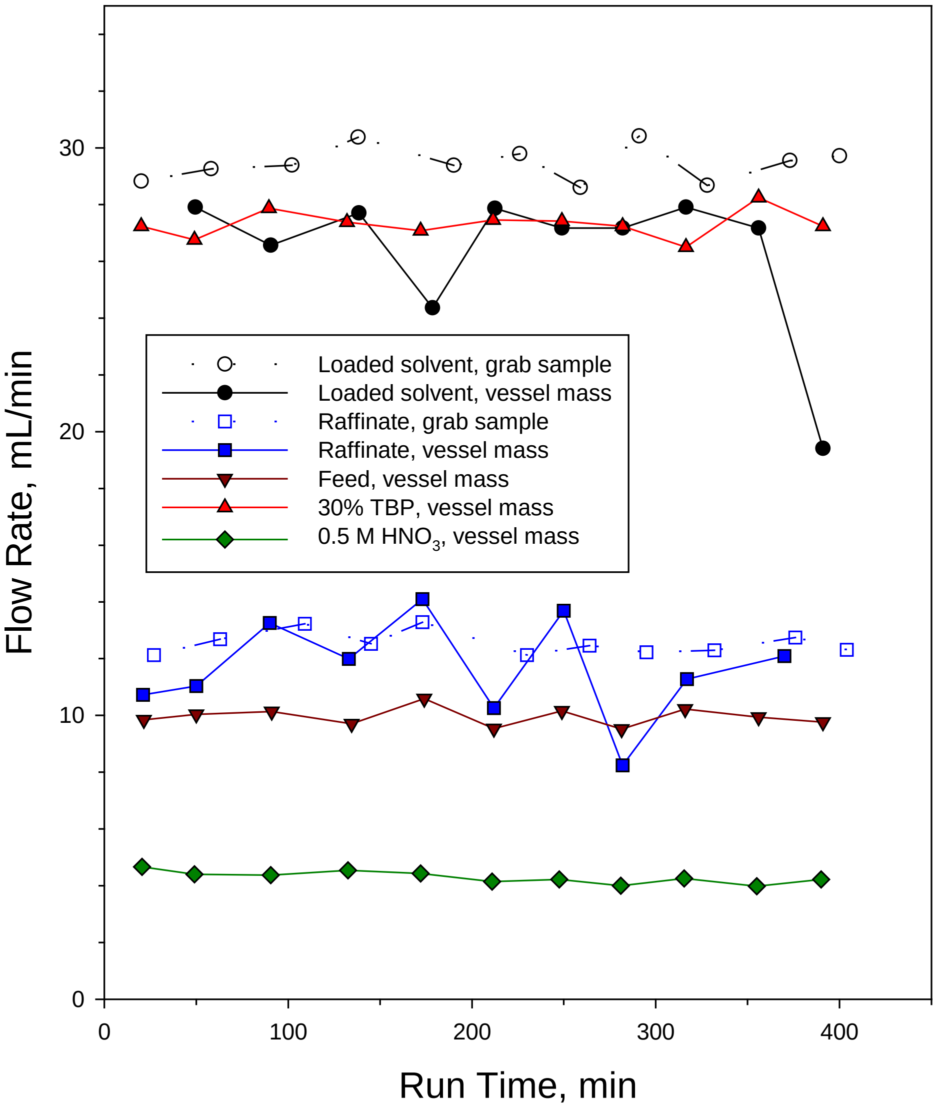

Figure 3.2. Flowrate data obtained during Run 3 solvent loading.

3.2.2 Run 3 Solvent Loading Results

After mixing with the loaded solvent left over from Run 2, the loaded solvent from Run 3 was examined by spectrophotometry. However, the Pu concentration could not be reliably determined by this technique because some Pu(VI) was initially present and reliable molar absorptivities for this species in TBP were not available. In previous tests, allowing the solvent to stand for a period of several weeks allowed the Pu(VI) to reduce to Pu(IV),[1] but this was not the case for Run 3. An attempt was made to accelerate the reduction of Pu(VI) to Pu(IV) by exposing the loaded solvent to light, but this led to an even more complicated absorption spectrum which was difficult to interpret. Because of these complications, the U, Pu, and Np concentrations in the loaded solvent were determined by ICP-MS. To do this, the U, Pu, and Np were back extracted from the loaded solvent by three successive contacts with 0.5 M $(NH_4)_2CO_3$ (organic-to-aqueous ratio = 0.17), with the aqueous phases from each contact being combined. A portion of the resulting $(NH_4)_2CO_3$ solution was acidified with HNO_3 and analyzed by ICP-MS. The loaded solvent from Run 3 was analyzed in this way both before, and after mixing with the leftover loaded solvent from Run 2. Prior to mixing, the Run 3 loaded solvent contained 290 mM U, 4.62 mM Pu, and 0.10 mM Np. After mixing with the leftover Run 2 loaded solvent, the U, Pu, and Np concentrations were 285 mM, 4.68 mM, and 0.09 mM, respectively. In addition, the HNO_3 concentration in the loaded solvent was determined by back-extraction into deionized water and titration with standard NaOH. This gave HNO_3 concentration values of 32 mM before mixing and 33 mM after mixing with the left over loaded solvent from Run 2.

3.3 Run 3 Reductive Stripping

3.3.1 Material Flows during Run 3 Reductive Stripping

Table 3.7 presents the flowrate data for the U/Pu-loaded solvent stream (*O2*) during the Run 3 reductive stripping step, as determined from changes in the feed vessel mass over time.[a] The measured flowrate of 28.1 ± 0.7 mL/min was in excellent agreement with the target flowrate of 28 mL/min. The flow meter data yielded a similar result with an average flowrate of 28.8 ± 2.4 mL/min.

Table 3.8 presents the flowrate data for the fresh TBP solvent (stream *O3*) during the Run 3 reductive stripping, as determined from changes in the scrub feed vessel mass over time. This parameter was adjusted during the course of the experiment to achieve and maintain the target U/Pu ratio of 7/3, but the average flowrate as determined by the change in the vessel mass was 7.0 ± 0.6 mL/min. The fresh TBP solvent stream was also monitored using an in-line flow meter; the flow meter data are summarized in Table 3.9 and are presented graphically in Figure 3.3. The agreement between the vessel mass data and the flow meter data was excellent, with the average flow of the fresh TBP solvent over the course of the experiment being identical by both methods (7.0 ± 0.6 mL/min). The flowrate in the early stages of the run were considerably lower than the initial target of 8.5 mL/min. This could be attributed to an incorrect scaling factor being applied to the flow meter data during the test, which gave flow meter readings that were biased high during the experiment (the values in Table 3.9 and Figure 3.3 were produced using the correct scaling factor). The in-line flow meter data indicated rapid response in changing of the flowrate upon changing the pump settings.

(a) For the reductive stripping part of the test, the run time is defined as the total time elapsed since the start of the run, with the start time being defined as the time at which the flow of the U/Pu-loaded solvent was commenced.

Table 3.10 presents the flowrate data for the 0.1 M HNO_3 scrub (stream *A4*) during the Run 3 reductive stripping, as determined from changes in the 0.1 M HNO_3 feed vessel mass over time. The measured flowrate of 3.3 ± 0.3 mL/min was 15 – 20 % lower than the target flowrate of 4.0 mL/min. The flow meter data agreed very well with the vessel mass data, indicating an average flowrate of 3.4 ± 0.3 mL/min over the course of the test.

Table 3.11 presents the flowrate data for the U(IV) stripping solution (stream *A5*) during the Run 3 reductive stripping, as determined from changes in the solvent feed vessel mass over time. The measured flowrate of 16.1 ± 0.3 mL/min was 15% higher than the target flowrate of 14.0 mL/min. The average flowrate determined from the flow meter data was 14.5 ± 2.0 mL/min which was more in line with the target value.

The flowrate of the aqueous U/Pu nitrate product stream (stream *A6*) was determined by both timed grab samples and by the mass of the solution collected into each product bottle, giving average flowrates of 17.8 ± 0.3 and 17.5 ± 0.4, respectively (Table 3.12). The two values agree within the experimental uncertainty. Based on the input aqueous flowrates—3.3 mL/min for stream *A4* and 16.1 mL/min for stream *A5* (determined from the vessel mass change)—a flowrate of 19.4 mL/min would be expected, assuming the volumes to be additive. If the stream *A5* flowrate determined from the flow meter is used (14.5 mL/min), then the expected flowrate for the U/Pu nitrate product stream would be 17.8 mL/min, which agrees very well with the measured values. Based on this, the 16.1 mL/min flowrate for stream *A5* appears to be biased high.

The flowrate of the Pu-depleted solvent (stream *O4*) was determined by both timed grab samples and changes in the mass of the Pu-depleted solvent collection vessel, giving average flowrates of 39.9 ± 1.6 and 36.1 ± 1.6, respectively (Table 3.13). The value obtained from the grab sample data are significantly higher than those obtained by the vessel mass data. Based on the data in Tables 3.7 and 3.8, a flowrate of ~35 mL/min would be expected for the Pu-depleted solvent, so the flowrate of 36.1 ± 1.6 is likely more correct.

Table 3.7. Flowrates for the loaded solvent (stream *O2*) during CoDCon Run 3 reductive stripping step as determined by changes to the loaded solvent tank mass; target flowrate = 28.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
21	25.0	27.2
54	26.6	28.9
85	25.0	27.2
115	26.7	29.0
146	25.8	28.1
176	25.9	28.1
205	26.7	29.0
235	25.0	27.2
265	26.7	29.0
296	25.8	28.1
326	25.9	28.1
356	25.0	27.2
386	25.9	28.2
415	25.8	28.1
Mean	25.8 ± 0.6	28.1 ± 0.7

[a] Run time represented by the mid-point of the sampling period.

Table 3.8. Flowrates for the fresh TBP solvent (stream *O3*) during CoDCon Run 3 reductive stripping step as determined by changes to the TBP solvent tank mass.

Run time, min[(a)]	***Flow, g/min***	***Flow, mL/min***
20	6.8	5.6
54	7.0	5.8
85	7.9	6.6
115	9.0	7.5
146	9.4	7.7
176	9.0	7.4
205	9.0	7.4
235	8.7	7.2
265	9.0	7.4
296	8.5	7.0
326	8.6	7.1
356	8.4	7.0
386	8.1	6.7
414	8.7	7.2
Mean	8.4 ± 0.8	7.0 ± 0.6

(a) Run time represented by the mid-point of the sampling period.

Table 3.9. Flowrates for the fresh TBP solvent (stream *O3*) during CoDCon Run 3 reductive stripping step as determined by the flow meter. The values given are the average values over the time frames indicated; the uncertainties are the associated standard deviations. These values are those obtained after correcting the scaling factor (see text).

Run time, min		***Flow, mL/min***
Start[(a)]	*End*	
0	56	5.9 ± 0.1
56	78	6.2 ± 0.2
78	93	6.6 ± 0.4
93	113	7.2 ± 0.2
113	131	7.7 ± 0.3
131	147	7.6 ± 0.3
147	160	7.5 ± 0.3
160	189	7.4 ± 0.3
189	211	7.3 ± 0.3
211	265	7.2 ± 0.4
265	321	7.1 ± 0.3
321	448	7.0 ± 0.3
0	448	7.0 ± 0.6

(a) The start times indicated correspond to the times at which adjustment was made to the flowrate of the fresh TBP solvent stream.

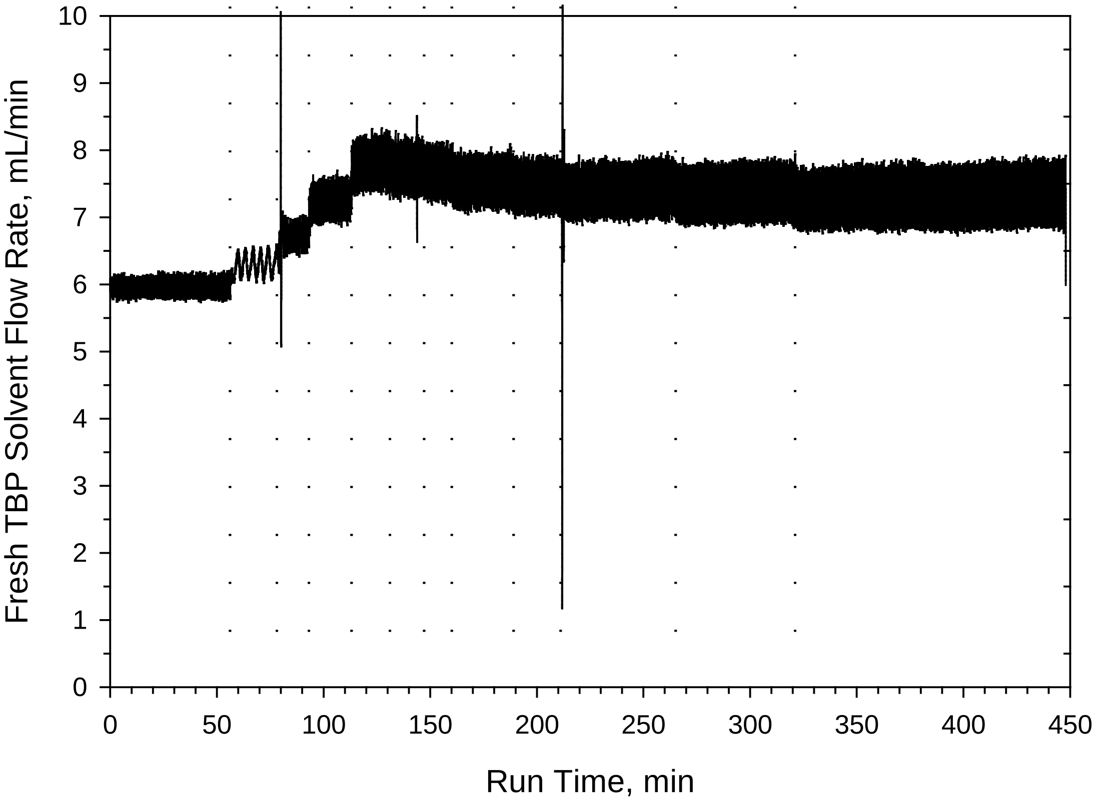

Figure 3.3. Flowrate data for the fresh TBP solvent (stream *O3*) during CoDCon Run 3 reductive stripping step as determined by the in-line flow meter; the vertical dashed lines represent the time points at which adjustments were made to the pump speed, as indicated in Table 3.9.

Table 3.10. Flowrates for the 0.1 M HNO_3 scrub (stream *A4*) during the CoDCon Run 3 reductive stripping step as determined by changes to the scrub tank mass; target flowrate = 4.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
21	3.4	3.4
54	3.4	3.4
85	3.3	3.3
131	3.3	3.2
176	4.1	4.1
205	3.4	3.4
234	3.7	3.6
265	3.2	3.2
296	3.2	3.2
325	3.2	3.2
355	3.1	3.1
386	3.4	3.4
415	3.1	3.1
Mean	3.4 ± 0.3	3.3 ± 0.3

[a] Run time represented by the mid-point of the sampling period.

Table 3.11. Flowrates for the U(IV) stripping solution (stream *A5*) during the CoDCon Run 3 reductive stripping step as determined by changes to the scrub tank mass; target flowrate = 14.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
20	17.1	16.2
53	16.9	16.1
84	17.3	16.5
114	16.7	15.9
146	17.0	16.2
176	17.1	16.3
206	16.5	15.7
235	16.8	16.0
265	16.6	15.8
297	17.4	16.6
326	16.7	15.9
355	16.9	16.1
385	16.7	15.9
414	16.8	16.0
Mean	16.9 ± 0.3	16.1 ± 0.3

(a) Run time represented by the mid-point of the sampling period.

Table 3.12. Flowrate of aqueous U/Pu nitrate product (stream *A6*) during CoDCon Run 3 reductive stripping, as determined with timed grab samples and from the masses of the U/Pu product collection bottles.

From Timed Grab Samples			***From Product Collection Bottle Masses***[(a)]		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
43	19.0	18.4	63	18.5	18.0
77	19.0	18.1	115	18.1	17.4
104	18.9	18.2	167	18.6	17.8
135	18.1	17.4	218	17.8	17.2
161	18.3	17.9	271	18.5	17.7
203	18.2	17.4	324	18.0	17.3
227	18.9	17.8	376	18.4	17.7
257	18.7	17.9	425	17.5	17.0
300	18.8	18.2			
353	18.6	17.9			
411	18.6	17.9			
446	18.2	17.4			
Mean	18.6 ± 0.3	17.8 ± 0.3	Mean	18.2 ± 0.4	17.5 ± 0.4
(a) Data listed for sequential order in which the U/Pu nitrate collection bottles were filled.					

Table 3.13. Flowrate of Pu-depleted solvent outlet (stream *O4*) during CoDCon Run 3 reductive stripping, as determined with timed grab samples and from changes in the collection tank mass.

From Timed Grab Samples			***From Changes in Tank Mass***		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
49	32.7	37.5	22	31.8	34.6
74	37.3	42.5	54	29.7	32.3
107	36.1	41.1	85	33.3	36.2
138	35.8	41.0	115	32.8	35.6
170	34.5	39.6	145	34.4	37.4
199	34.9	40.0	176	32.8	35.6
224	34.8	40.0	205	33.3	36.2
261	34.8	39.9	235	34.5	37.5
304	35.7	41.2	265	32.3	35.1
356	33.6	38.6	296	33.9	36.8
410	32.9	37.6	326	34.5	37.5
			356	34.4	37.4
			386	35.2	38.2
			415	32.3	35.1
Mean	34.8 ± 1.4	39.9 ± 1.6	Mean	33.2 ± 1.4	36.1 ± 1.6

The flowrate data derived from the grab samples and vessel masses during the Run 3 reductive stripping step are depicted graphically in Figure 3.4. Again, the lower flowrate for Pu-depleted solvent indicated by the changes in the vessel mass compared to the grab samples is evident in Figure 3.4. The other flow data appears reasonably consistent. The flowrates for the U/Pu product obtained by the grab samples and by the masses of the product bottles collected are in good agreement, as suggested by the mean values reported in Table 3.12.

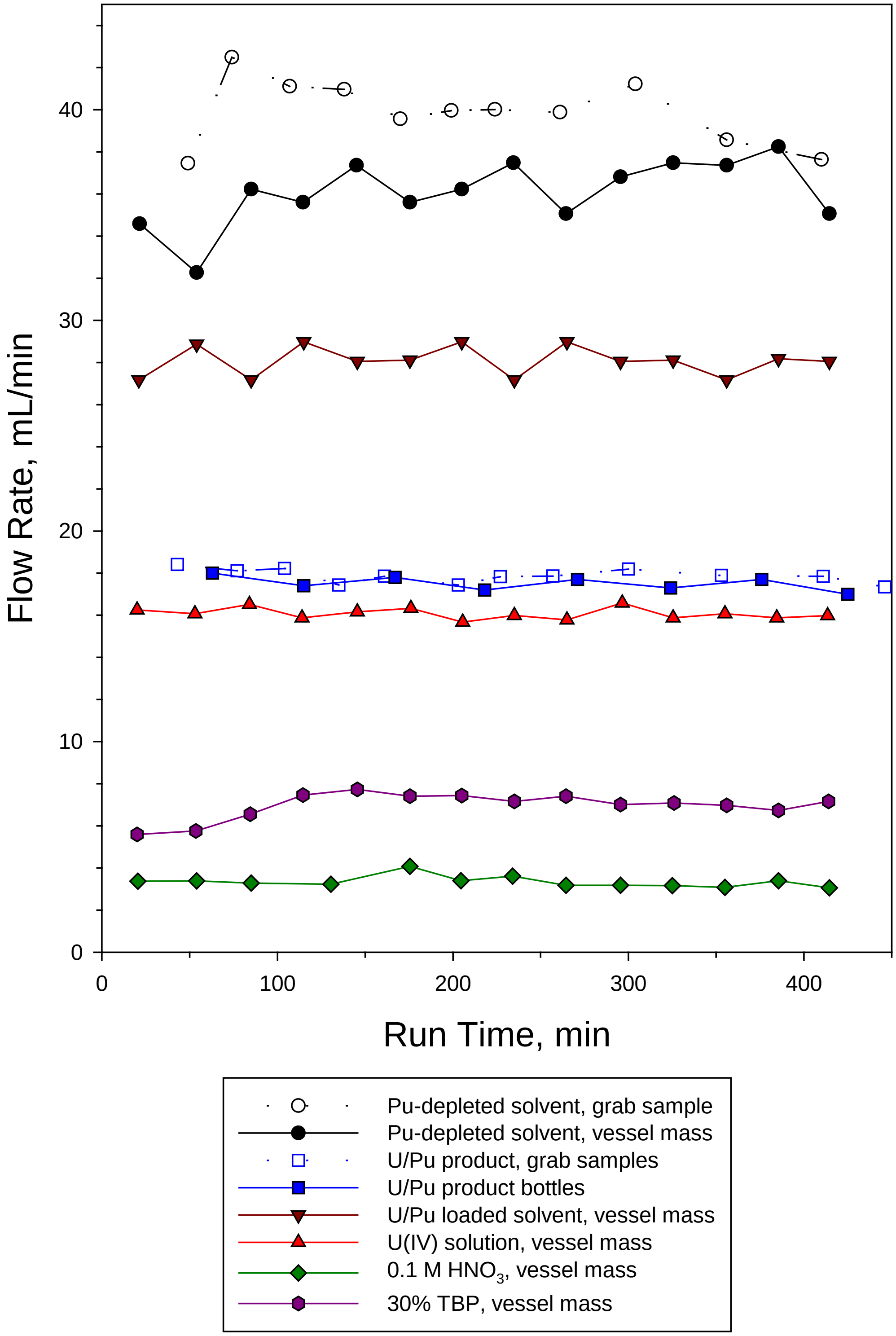

Figure 3.4. Flowrate data obtained during Run 3 reductive stripping.

3.3.2 Run 3 Reductive Stripping Results

Figure 3.5 presents the relative percentages of Pu and U in the aqueous outlet stream (*A6*) during the reductive stripping portion of Run 3. The solid curves represent values that were determined from the on-line spectroscopic monitoring system. The value measured during the first ~5 minutes are not meaningful because the spectral signal is very low during that time. The rise in the relative Pu content, and its maximum of 63% at 12 minutes appears to be real, and similar spikes in the relative Pu content at the beginning of the test were observed in previous runs.[1] After this initial maximum in the Pu content, the relative Pu content dropped to ~28% within about 30 minutes. Adjustments were made as indicated in Table 3.8 and Table 3.9 to reach the target 30% Pu value. Figure 3.5 also shows the relative percentages of Pu and U in the aqueous outlet stream determined by off-line spectrophotometric analysis of the grab samples and the aqueous product bottles (*vide infra*). Excellent agreement was achieved between the on-line and off-line methods.

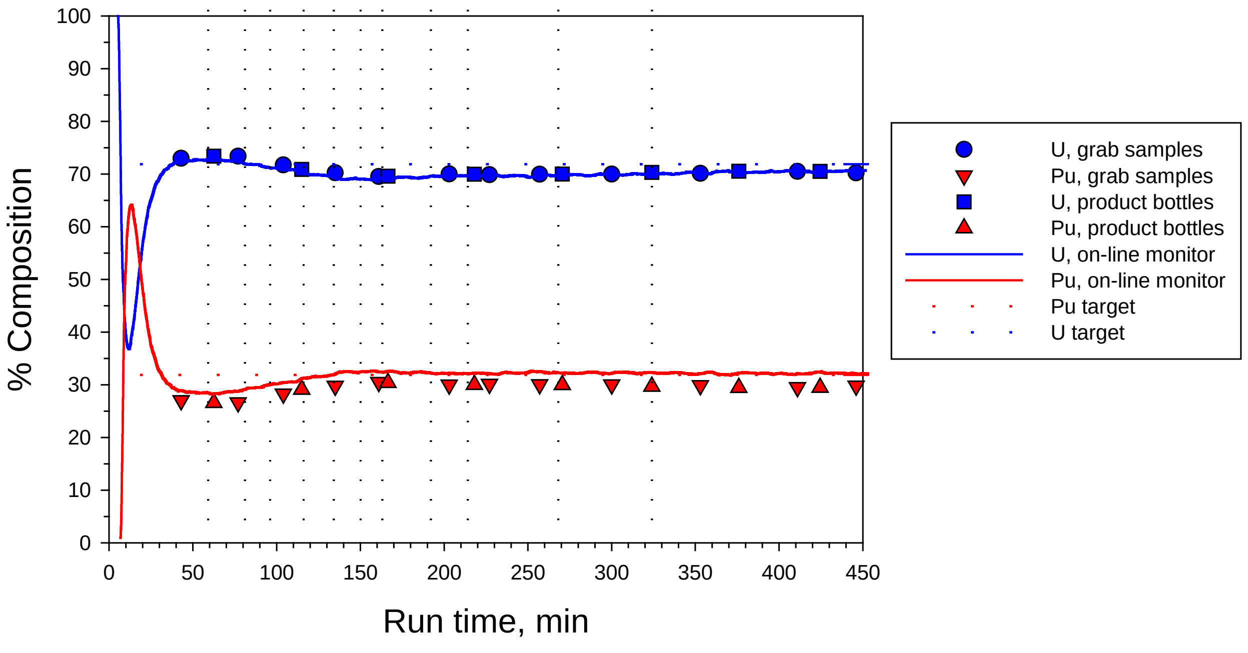

Figure 3.5. Relative percentages of Pu and U in the U/Pu product stream (*A6*) during CoDCon Run 3 as determined using the on-line spectroscopy system, and by off-line spectrophotometric analysis of grab samples and the aqueous U/Pu product bottles. The vertical dashed lines correspond to the TBP flowrate adjustments listed in Table 3.9.

In addition to the spectrophotometric analysis, selected aqueous grab samples were analyzed for U and Pu by ICP-MS (Table 3.14). The concentration values determined by ICP-MS were consistently lower than those obtained by spectrophotometry. The U concentrations were 15 – 20% lower and the Pu concentrations were consistently 6 – 8% lower when determined by ICP-MS compared to those obtained spectrophotometrically. This resulted in a composition of ~67.5% U and 32.5% Pu during the stable period of operation.

Table 3.14. Comparison of off-line spectrophotometric results to those obtained by ICP-MS for selected aqueous grab samples from stripping step of CoDCon Run 3.

Aq. grab sample #	***Run time, min***	***Spectrophotometry***				***ICP-MS***			
		[U], mM	***[Pu], mM***	***%U***	***%Pu***	***[U], mM***	***[Pu], mM***	***%U***	***%Pu***
1	43	19.6	7.2	73.0	27.0	16.1	6.6	70.7	29.3
4	135	17.9	7.6	70.2	29.8	14.8	7.1	67.5	32.5
8	257	18.0	7.7	70.0	30.0	14.5	7.1	67.0	33.0
12	446	18.5	7.8	70.2	29.8	15.1	7.2	67.5	32.5

Nine fractions were collected of the aqueous output stream (*A6*) from stage 17 during the reductive stripping part of CoDCon Run 3. The first fraction was dilute, representing the start-up of the system, and was far from steady state. For this reason, the first fraction was not considered in the analysis of the U/Pu nitrate product from the test. The individual U/Pu nitrate fractions were analyzed by spectrophotometry following the methodology described previously.[1] The results are compiled in Table 3.15, and plotted in Figure 3.5. Product bottles 3 through 9 were all within 1% of the target U/Pu ratio of 7/3; on average the relative amounts of U and Pu in these 7 product bottles was 70.3 ± 0.4% U and 29.7 ± 0.4% Pu.

Table 3.15. Spectrophotometric analytical results for the aqueous U/Pu nitrate product bottles taken during Run 3.

Product bottle number	***Run time, min***	***[HNO$_3$], M***	***[U], mM***	***[Pu], mM***	***Pu, %***	***U, %***
2	36–89	0.72	20.5	7.39	26.6	73.4
3	89–141	0.72	18.4	7.53	29.1	70.9
4	141–192	0.74	18.0	7.67	30.0	70.0
5	192–244	0.71	17.6	7.64	30.4	69.6
6	244–297	0.73	18.2	7.74	30.0	70.0
7	297–351	0.74	18.4	7.74	29.7	70.3
8	351–401	0.73	18.6	7.74	29.5	70.5
9	401–448	0.73	18.7	7.79	29.5	70.5

Figure 3.6 shows the concentration profiles for U and Pu across the reductive stripping stages of Run 3. Because each contactor was drained and sampled at the conclusion of the experiment, the stage profile shown represents the conditions at the end of the test. The data indicate good retention of U in the organic phase across stages 25 through 32. Moving from stage 25 towards the aqueous outlet at stage 17, the

effective U distribution ratios[a] decrease, and become less than 1 below stage 21. This results in the desired effect of having some U in the Pu-containing aqueous phase exiting at stage 17. The aqueous phase Pu concentration is very steady between stages 17 and 24. Effective stripping of Pu is indicated with the organic phase Pu concentrations being below detection by spectrophotometry in stages 31 and 32.

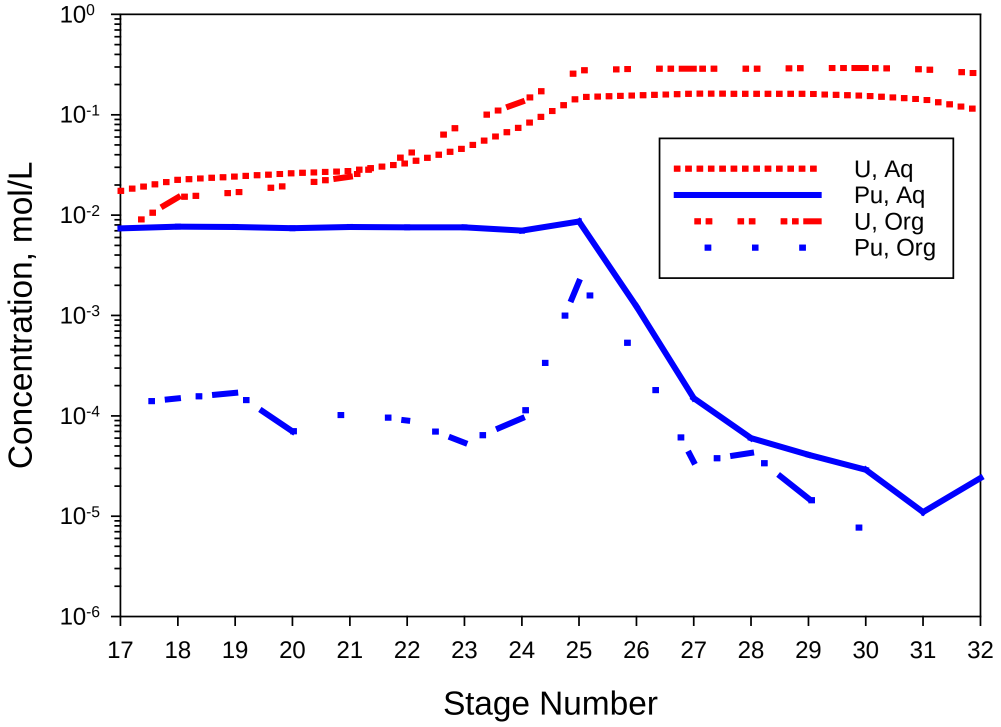

Figure 3.6. Uranium and Pu stage concentration profiles at the conclusion of the Run 3 reductive stripping step.

3.3.3 Analysis of the Concentrated Product Solution from Run 3

After combining and concentrating, the U/Pu nitrate solution was sampled for analysis by both spectrophotometry and ICP-MS. The ICP-MS data indicated the relative amounts of U and Pu to be 66.1% and 33.9%, respectively. These values were substantially different than the values of 70.7% U and 29.3% Pu obtained by spectrophotometric analysis. The difference appears to stem primarily from the U concentration determined by ICP-MS being 15 – 20% lower than that determined spectrophotometrically. This result illustrates that the primary uncertainty in the U/Pu ratio is associated with the uncertainties in the analytical methods used, rather than in operation of the centrifugal contactor system. Under the conditions of the CoDCon flowsheet, assigning an analytical uncertainty of 10% (a reasonable uncertainty for both the spectrophotometric and ICP-MS data) to the measured values results in an uncertainty of

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[a] The distribution ratio (*D*) = concentration in the organic phase divided by the concentration in the aqueous phase.

~4% in the U/Pu mass ratio. Thus, the ICP-MS and spectrophotometric results agree within such uncertainty in the analytical measurements.

3.3.4 Uranium and Plutonium Mass Balance for Run 3

The U and Pu mass balances for the reductive stripping portion of CoDCon Run 3 were assessed by evaluating the various input and output streams from this portion of the test. The input streams considered were *O2* (the U/Pu loaded solvent) and *A5* [the U(IV) stripping solution], while the output streams were *O4* (the Pu-depleted solvent) and *A6* (the U/Pu nitrate product) (Figure 3.1). The latter was distributed between the various aqueous product bottles and the aqueous grab samples. The Pu-depleted solvent was distributed between the solvent collection tank and the organic grab samples. The material remaining in the contactor bank at the conclusion of the test was not included in the mass balance calculation because volumes of the aqueous and organic phases in the contactors were not measured.

Table 3.16 summarizes the U and Pu inputs into the Run 3 reductive stripping sections. A total of 936 g of U and 14.0 g of Pu were fed into the stripping sections, based on ICP-MS analysis. The major fraction of the Pu was in the nine U/Pu nitrate product bottles. As indicated in Table 3.17, the product bottles contained 13.9 g of Pu, based on spectrophotometric analysis of the individual product bottles.. An additional 0.4 g of Pu was accounted for in the 12 aqueous grab samples that were taken during the reductive stripping test. The total 14.3 g of Pu between the product bottles and grab samples represented a 103% recovery of Pu. The majority of the U reported to the Pu-depleted solvent (stream *O4*). The volume of Pu-depleted solvent collected was 16.1 L, with a U concentration of 0.245 M (determined spectrophotometrically), indicating 992 g of U. The U/Pu product bottles contained 33.2 g U (Table 3.17) and another 21.7 g U was accounted for in the aqueous and organic grab samples taken during the test. This resulted in the recovery of 1047 g of U, representing a U mass recovery of 112%.

Table 3.16. Uranium and plutonium inputs to the reductive stripping step of CoDCon Run 3.

	Stream *O2*	**Stream *A5***
[U], mM	285	51.0
[Pu], mM	4.68	0.0
Density, g/mL	0.92	1.05
Mass in, kg	11.5	7.63
Volume in, L	12.5	7.27
Mole U in	3.56	0.37
Mass U in, g	848	88.2
Mole Pu in	0.0585	0.0
Mass Pu in, g	14.0	0.0
	Total U in, g	936
	Total Pu in, g	14.0

Table 3.17. Uranium and plutonium mass outputs from the nine U/Pu nitrate collection vessels.

Product Bottle:	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
[U], mM	5.65	20.5	18.4	18.0	17.6	33.0	18.4	18.6	18.7
[Pu], mM	3.37	7.39	7.53	7.67	7.64	7.57	7.74	7.74	7.79
Density, g/mL	0.98	1.03	1.04	1.04	1.05	1.05	1.04	1.04	1.03
Mass out, kg	0.94	0.98	0.94	0.93	0.95	0.98	0.97	0.92	0.82
Volume out, L	0.96	0.96	0.91	0.89	0.91	0.94	0.93	0.89	0.89
mMole U out	5.41	19.6	16.7	16.1	15.9	30.9	17.2	16.5	14.9
Mass U out, g	1.29	4.66	3.98	3.82	3.79	4.05	4.09	3.93	3.55
mMole Pu out	3.22	7.06	6.83	6.86	6.92	7.09	7.22	6.85	6.21
Mass Pu out, g	0.77	1.69	1.63	1.64	1.65	1.69	1.72	1.64	1.48
								Sum mass U out, g	33.2
								Sum mass Pu out, g	13.9

3.3.5 Np Behavior in CoDCon Run 3

Of the 1 g of Np in the aqueous feed to the solvent loading step, approximately 60% was in the aqueous raffinate. The remaining 40% of the Np was found in the U/Pu product. Very little Np was detected in the Pu-depleted solvent by spectrophotometry or ICP-MS. In this experiment, no active control was exerted over the Np oxidation state. The aqueous feed solution contained a mixture of Np(V) and Np(VI). Based on well-known extraction chemistry, the Np(V) was poorly extracted and routed to the aqueous raffinate. The Np(VI) was extracted into the TBP solvent phase.

The behavior of Np in the reductive stripping portion of the flowsheet is complicated. From a thermodynamics standpoint, U(IV) should reduce Np(VI) to Np(IV). Since Np(IV) is reasonably extractable by TBP, the Np should remain in the organic phase during Pu stripping, and should primarily follow the bulk U in the process. However, the reduction of Np(VI) to Np(IV) passes through Np(V). The reduction of Np(VI) to Np(V) by U(IV) is rapid, but the subsequent reduction of Np(V) to Np(IV) is slow.[5] This slow Np(V) to Np(IV) reduction rate, coupled with the relatively short residence time in the

2-cm centrifugal contactors, results in a situation in which there is incomplete reduction of Np(V) to Np(IV) in the Pu stripping stages. Indeed, the CoDCon Run 3 results suggest very little reduction to Np(IV) occurred.

The real-time optical spectroscopy allowed the identification, at least qualitatively, of Np(V) in the U/Pu product during Run 3. Figure 3.7 shows a typical NIR spectrum of the U/Pu nitrate product stream taken during stable operation of the flowsheet. Neptunium(V) is indicated by the band at 983 nm. The broad band with λ_{max} at 1075 nm in the NIR spectrum can primarily be attributed to U(IV).[6-7] However, Pu(III) also displays absorption bands in this region of the NIR.[8] The presence of Np in the U/Pu products stream was verified by the ICP-MS analysis of the combined concentrate U/Pu nitrate solution, which revealed concentrations of 350 mM U, 179 mM Pu, and 3.0 mM Np. Thus, the Np represented ~0.6% of the total actinides in the U/Pu nitrate product from Run 3. The ICP-MS analysis indicated very little Np was present in the Pu-depleted solvent (0.1 µM Np).

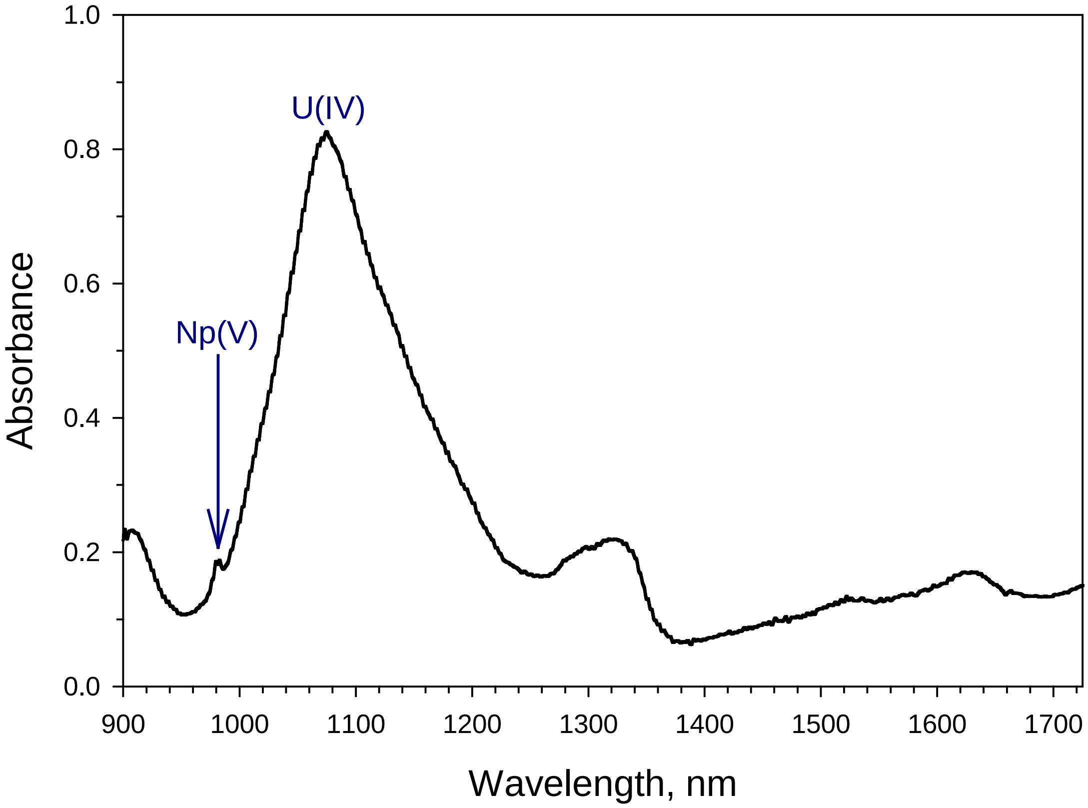

Figure 3.7. NIR spectrum of the U/Pu nitrate product stream (*A6*) at run time 250 min during the CoDCon Run 3 test.

4.0 CoDCon Run Number 4

4.1 Experimental Description for Run 4

4.1.1 Run 4 Solvent Extraction

The flowsheet tested in Run 4 (Figure 4.1) was very similar to that tested in Run 3. The flowrate of the fresh TBP stream at stage 17 (*O3*) was initially set at 8.0 mL/min. A key difference between Run 3 and Run 4 was the use of a more comprehensive dissolved fuel simulant in the latter test. The dissolved fuel simulant used for CoDCon Run 4 was intended to simulate commercial pressurized water reactor fuel with a burnup of 60 GWd/MT, and a 5-year cooling period. This was consistent with one of the scenarios considered during the case study previously performed by the DOE-NE.[9] For the purpose of this simulant, only constituents expected to have concentrations of $> 3.5 \times 10^{-4}$ M in the dissolved fuel solution were included. All concentrations were scaled proportionally to achieve a final U concentration of 1 M, consistent with the three previous CoDCon flowsheet tests. The target basis for the run was 1 kg of U at 1 M concentration for a total volume of 4.2 L. An additional 500 mL of simulant (taken prior to addition of Pu and Np) was prepared and set aside for possible future flowsheet development (e.g., to optimize Np or Tc behavior in the flowsheet). The amounts of each non-radioactive components used can be found in Table 4.1, assuming a final dilution volume of 4.7 L.

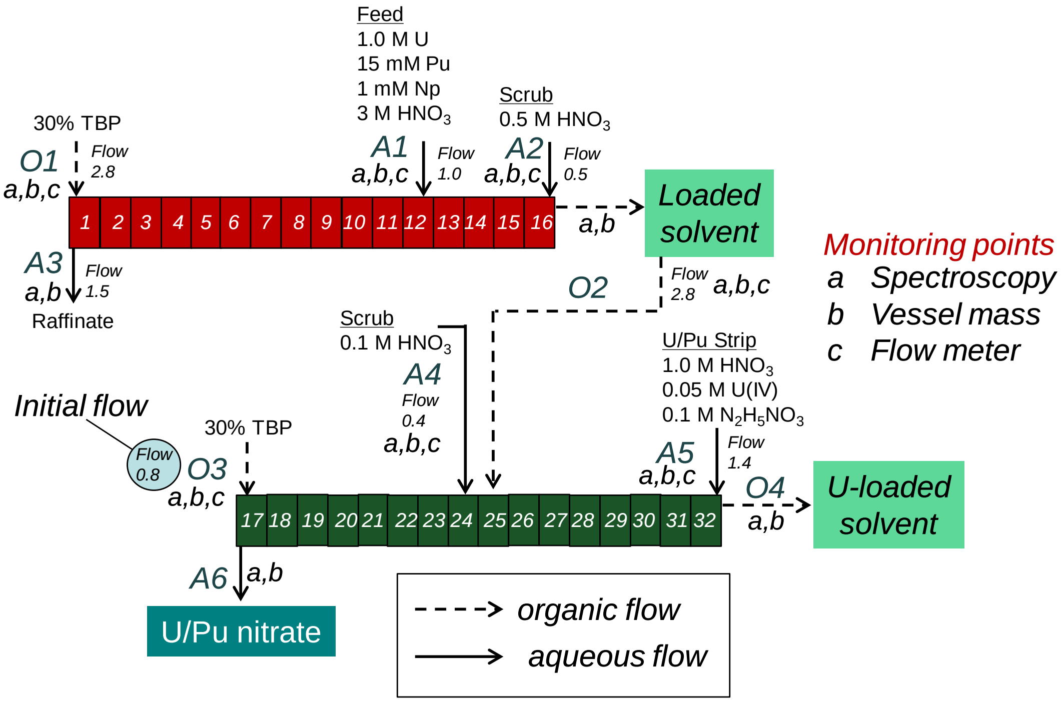

Figure 4.1. CoDCon flowsheet tested in Run 4.

Tin metal was dissolved by stirring with 2 M HNO_3 at room temperature. The $ZrO(NO_3)_2 \cdot xH_2O$ was dissolved in 1.2 M HNO_3. Both the Sn and ZrO solutions were filtered through a 0.45 µm nylon filter before adding to the dissolved fuel simulant. The remaining constituents were dissolved in 0.37 M HNO_3 with stirring and gentle heating on a hot plate set to 50 °C for 4 hours. The final solution volume was 630 mL. The solution sat for 34 days at ambient conditions in a 1 L poly bottle while awaiting the radioactive components to be prepared. During this time, a substantial amount of precipitate formed. The precipitate was found to be difficult to filter, so the bulk of the solids were separated by centrifuging, and the supernatant liquor was then vacuum filtered through a disposal 0.45 um nylon filter.

A uranyl nitrate solution was prepared by dissolving in-stock UO_2 in HNO_3 followed by filtering the solution. The concentration of U was determined spectrophotometrically to be 2.35 M, thus 1.9 L of this solution was used to prepare the CoDCon feed simulant. The acid concentration was adjusted to approximately 3 M and then thoroughly mixed with the above filtered non-radioactive solution. A portion (356 mL) of this solution was set aside for possible future flowsheet development experiments. The remaining portion (2.99 L) was taken to a radiological glovebox for addition of Np and Pu stocks. Before addition of Np and Pu, additional precipitated solids were observed in the solution. The solids were filtered, then four additional solutions were added: (1) 475 mL of 2.42 M HNO_3, 0.12 M Pu, 0.002 M Np, and 0.277 M U, (2) 180 mL of 3.3 M HNO_3, 0.38 M U, 0.016 M Np, and 0.043 M Pu, (3) 4 mL of 6.91 M HNO_3, 0.11 M Np, and (4) 550 mL of 1.05 M HNO_3. Table 4.2 shows the target concentration of each component in the dissolved fuel simulant, along with the measured composition of these components.

Table 4.1. Amounts of the non-actinide components used in preparing 4.7 L of CoDCon Run 4 feed simulant.

Formula	Mass (g) or volume (mL)	Manufacturer	Lot #
$Ce(NO)_3\bullet 6H_2O$	16.239	Acros Organics	A0385618
$Cr(NO_3)_3\bullet 9H_2O$	54.289	Aldrich	02808PG
$CsNO_3$	8.309	Aldrich	MKCG3297
$Eu(NO)_3\bullet 6H_2O$	0.917	Alfa Aesar	Q20C039
$Fe(NO)_3\bullet 9H_2O$	113.044	Sigma Aldrich	MKCG1626
$Gd(NO)_3\bullet 6H_2O$	1.043	Research Chemicals	GD-N-3-009
$La(NO)_3\bullet 6H_2O$	8.243	American Potash and Chemical Corp	PNNL # 34240
$Na_2MoO_4\bullet 2H_2O$	6.646	Sigma	30K0210
$Nd((NO)_3\bullet 6H_2O$	26.796	Aldrich	MKBG9246V
$Ni(NO)_2\bullet 6H_2O$	59.285	Sigma Aldrich	BCBV6886
118 mg/mL Pd sol'n	0.287	In-house	CMS # 110019
$Pr(NO)_3\bullet 6H_2O$	7.452	Alfa Aesar	K24U008
$RbNO_3$	1.28	Acros Organics	A0330127
$Ru(NO)(NO)_3$ sol'n (112 g/L)	22.57	In-House	
$Sm(NO)_3\bullet 6H_2O$	5.094	Research Chemicals	Sm-N-3-018
Sn metal	0.108	Fisher	912568
$Sr(NO_3)_2$	4.088	In-House	
$Na_2TeO_4\bullet 2H_2O$	0.345	Strem Chemicals	22852600
	0.764	Alfa Inorganics	020270
$Y(NO)_3\bullet 6H_2O$	4.122	Alfa Aesar	X24C026
$ZrO(NO_3)_2\bullet XH_2O$	21.548	Alfa Aesar	I10M03

Table 4.2. Composition of the dissolved fuel simulant used in CoDCon Run 4.

Component	Target Conc., mol/L	Measured Conc., mol/L
Ce	8.0×10^{-3}	8.2×10^{-3} (a)
Cr	2.9×10^{-2}	2.4×10^{-2} (b)
Cs	9.1×10^{-3}	9.21 x 10^{-3}(a)
Eu	4.4×10^{-4}	(d)
Fe	6.0×10^{-2}	2.2×10^{-1} (b)
Gd	4.9×10^{-4}	(d)
La	4.1×10^{-3}	4.1×10^{-3} (a)
Mo	5.8×10^{-3}	6.45 x 10^{-3}(a)
Nd	1.3×10^{-2}	1.4×10^{-2} (a)
Ni	4.3×10^{-2}	(d)
Pd	6.8×10^{-5}	(d)
Pr	3.6×10^{-3}	3.5×10^{-3} (a)
Rb	1.8×10^{-3}	(d)
Ru	5.6×10^{-3}	5.8 x 10^{-3}(a)
Sm	2.4×10^{-3}	2.1×10^{-3} (a)
Sn	1.9×10^{-4}	(d)
Sr	4.1×10^{-3}	(d)
Te	8.6×10^{-4}	(d)
Y	2.3×10^{-3}	(d)
Zr	1.7×10^{-2}	(d)
U	1.0×10^{0}	1.0×10^{0} (b)
Np	1.0×10^{-3}	1.0×10^{-2} (b)
Pu	1.5×10^{-2}	1.5×10^{-2} (b)
HNO_3	3.0×10^{0}	2.8×10^{0} (e)

(a) Determined by ICP-MS

(b) Determined by inductively coupled plasma optical emission spectroscopy (ICP-OES)

(c) Not measured

(d) Below the detection limit

(e) Determined by titration

The TBP solvent was loaded in the following manner. To establish the spectral baseline for the spectroscopy cell monitoring the aqueous feed solution, the cell was filled with 0.5 M HNO_3 and the spectra were recorded to establish the baseline. The inlet to this spectral cell was then switched to the aqueous feed tank and the line to the aqueous inlet at stage 12 (including the spectral cell) was filled with feed solution. The flow of feed solution was temporarily stopped once it reached the stage 12 inlet. The contactors were turned on and 0.5 M HNO_3 was pumped into the aqueous inlet at stage 16 at a rate of 20 mL/min. After 20 minutes, aqueous solution was observed exiting the contactor bank at stage 1; at this point, the flow of the 0.5 M HNO_3 scrub solution was reduced to 5.0 mL/min. Flow of the TBP solvent into stage 1 was initiated at a rate of 20 mL/min. Once the organic phase was observed to exit the contactor bank at stage 16, the solvent flowrate was increased to 28 mL/min. The spectral baseline for the organic phase outlet was established at this point, and then the aqueous feed solution was pumped into stage 12 at a rate of 10 mL/min.

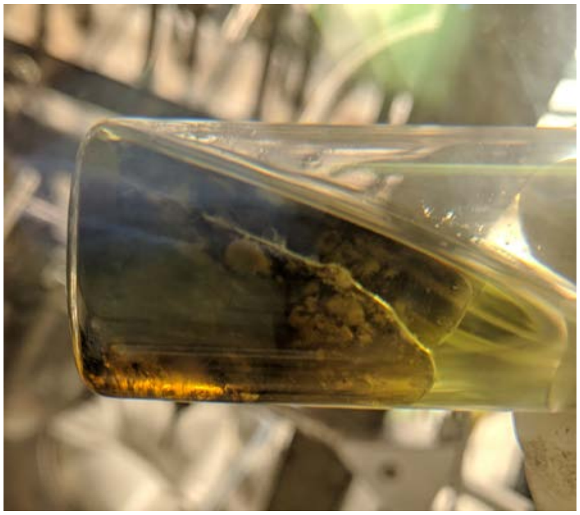

Figure 4.2. Interfacial crud in material drained from contactor 10 during the Run 4 solvent loading step.

At approximately 3.75 hours into the solvent loading run, material was discovered to be leaking out of the vent to the organic inlet on contactor 10. All flows were paused so that the cause of the leak could be investigated. The motor on contactor 10 was stopped and this contactor was drained. A considerable amount of interfacial crud was present in the contents of contactor 10 (Figure 4.2). This process was repeated for contactor 9, again with substantial crud evident. The contents of contactor 11, revealed very little interfacial crud, if any. To recover from this upset, contactors 1 through 8 were also drained. Hydrofluoric acid (1.5 mL of 48wt%) was added to the remaining aqueous feed solution to give 0.022 M HF. This was done to complex Zr, based on the hypothesis that the crud was associated with Zr. The contactors were filled again with 0.5 M HNO_3 and the TBP solvent, then the feed was reintroduced at stage 12. No further problems were encountered in the solvent loading step. At the conclusion of the solvent loading, no interfacial crud was observed in the material drained from the contactors, indicating that HF successfully suppressed the crud formation. In preparation of the Pu stripping part of the experiment, the contactor bank was flushed with 0.5 M HNO_3 and dodecane, followed by DI water, then all contactors were drained.

The Pu stripping step was performed in the following manner. The aqueous spectral baseline was established by pumping 0.1 M HNO_3 through the spectral cell leading to stage 32 (contactor 16). Once the spectral baseline was established, the flow of 0.1 M HNO_3 to stage 32 was stopped and the 0.1 M HNO_3 feed line was switched to stage 24 (contactor 8). The flowrate of the 0.1 M HNO_3 scrub solution was set to 4.0 mL/min once aqueous solution was seen to exit stage 17 (contactor 1). The organic spectral baseline was established by pumping fresh TBP solvent through the spectral cell into stage 25 (contactor 9). After the organic spectral baseline was established, the flow of fresh TBP solvent was redirected to stage 17 (contactor 1). The flowrate of fresh TBP solvent was set at 8.0 mL/min. The U(IV) solution [0.05 M U(IV)/1.0 M HNO_3/0.1 M $N_2H_5NO_3$; this solution also contained 4 mM U(VI)] was introduced at stage 32 (contactor 16) at a flowrate of 14 mL/min. After 10 minutes, the loaded solvent was introduced to stage 25 (contactor 9) at a flowrate of 28.0 mL/min. The flowrate of the fresh TBP solvent stream (*O3*) was adjusted to reach the target U/Pu ratio of 7/3. Details of these adjustments are presented in Section 4.3.1.

4.1.2 Run 4 Product Concentration

The $N_2H_5NO_3$ in the U/Pu nitrate product solution was decomposed over a Pt catalyst as previously described (e.g., see Section 3.1.2). Following $N_2H_5NO_3$ decomposition, the solution was filtered using a 0.45-µm hydrophilic polyvinylidene difluoride (PVDF) Durapore® Membrane Filter. The filtered solids were colorless after rinsing with 0.5 M HNO_3; the undissolved material was suspected to be silica from the Pt on silica catalyst used. The filtered solution was concentrated by distillation. After combining and concentrating all nine U/Pu product bottles, the final solution volume was 273 mL, with a density of 1.40 g/mL. This solution was sampled for U and Pu analysis by spectrophotometry, and for U, Pu, and Np analysis by ICP-MS.

4.2 Run 4 Solvent Loading

4.2.1 Material Flows during Run 4 Solvent Loading

As in the previous CoDCon tests, the flowrates of the input process streams were monitored by periodically measuring the vessel masses and using flow meters. The flowrates of the output streams were measured by changes in the vessel masses over time and by weighing timed grab samples. The masses of the grab samples were converted to volumes by measuring the solution densities. Because the balances monitoring the vessel masses were not calibrated, the flowrates derived in this manner are considered for indication only.

Table 4.3 lists the flowrate data for the aqueous feed stream during the Run 4 solvent loading, as determined by changes in the feed vessel mass over time. The mean flowrate value of 10.2 ± 1.1 mL/min determined from the vessel mass agrees very well with the intended flowrate of 10 mL/min. The average aqueous feed flowrate determined by the in-line flowmeter (10.4 ± 0.7 mL/min) also agreed well with the intended flowrate.

Table 4.4 lists the flowrate data for the 0.5 M HNO_3 scrub stream during the Run 4 solvent loading, as determined by changes in the 0.5 M HNO_3 vessel mass over time. The mean flowrate value of 3.4 ± 0.8 mL/min determined from the vessel mass was significantly lower than the intended flowrate of 5.0 mL/min. The in-line flowmeter also indicated that the 0.5 M HNO_3 scrub flowrate was lower than intended with a mean value of 3.6 ± 0.3. Shortly before introducing the feed solution to the contactor bank, a spot check of the 0.5 M HNO_3 scrub flowrate was performed by collecting a sample of the 0.5 M HNO_3 solution over a period of 2 minutes. A total of 9.4 mL (9.6 g) of 0.5 M HNO_3 solution was collected over this 2-minute period, indicating a flowrate of 4.7 mL/min. The pump for the 0.5 M HNO_3 scrub solution was kept at this setting, so it is not obvious why the lower flowrate was indicated by the changes in the vessel mass and the flowmeter.

The flowrate for the TBP solvent during the Run 4 solvent loading step, as determined by changes in the vessel mass, are presented in Table 4.5. The flowrate value of 27.6 ± 2.2 mL/min agreed well with the intended flowrate of 28 mL/min. Over the first ~70 minutes of solvent loading, the TBP solvent flowrate was indicated to be somewhat greater than intended; 29.0 ± 0.3 mL/min as indicated by the flowmeter (a value consistent with the first three entries in Table 4.5). The TBP solvent flowrate was adjusted accordingly to a value of 27.6 ± 0.7 mL/min (flowmeter) or 26.7 ± 1.0 mL/min (vessel mass).

The flowrate of the Run 4 aqueous raffinate (stream *A3*) was determined by both timed grab samples and changes in the mass of the raffinate collection vessel, giving average flowrates of 12.3 ± 0.4 and 12.8

± 1.8, respectively (Table 4.6). The two values agree within the experimental uncertainty. Based on the input flowrates—10.2 mL/min for stream *A1* and 3.4 mL/min for stream *A2*—a flowrate of 13.6 mL/min would be expected, assuming the volumes to be additive. As was the case with Run 3, the lower flowrate observed for the aqueous raffinate suggests a decrease in the aqueous solution volume upon mass transfer of the U and Pu into the organic phase; although, this cannot be definitively concluded given the uncertainties in the experimental measurements.

The flowrate of the loaded solvent was also determined by both timed grab samples and changes in the mass of the loaded solvent collection vessel, giving average flowrates of 27.8 ± 1.5 and 26.7 ± 1.6, respectively (Table 4.7). The two values agree within the experimental uncertainty.

Table 4.3. Flowrates for the aqueous feed (stream *A1*) during CoDCon Run 4 solvent loading as determined by changes to the aqueous feed tank mass; target flowrate = 10.0 mL/min.

Run time, min[(a)]	***Flow, g/min***	***Flow, mL/min***
15	13.5	9.3
42	14.8	10.2
72	17.9	12.3
105	14.6	10.1
136	14.7	10.1
173	14.8	10.2
210	12.1	8.3
263	16.6	11.4
292	13.0	9.0
339	14.6	10.1
382	14.3	9.9
398	16.0	11.0
Mean	14.7 ± 1.6	10.2 ± 1.1

(a) Run time represented by the mid-point of the sampling period.

Table 4.4. Flowrates for the 0.5 M HNO_3 scrub (stream *A2*) during CoDCon Run 4 solvent loading as determined by changes to the scrub tank mass; target flowrate = 5.0 mL/min.

Run time, min[(a)]	***Flow, g/min***	***Flow, mL/min***
15	5.2	4.9
42	5.4	4.2
72	3.0	2.8
104	4.4	4.2
135	3.3	3.2
173	2.5	2.4
210	2.6	2.5
262	4.0	3.8
293	3.9	3.7
339	2.7	2.6
382	3.0	2.9
Mean	3.6 ± 0.9	3.4 ± 0.8

(a) Run time represented by the mid-point of the sampling period.

Table 4.5. Flowrates for the 30% TBP solvent (stream *O1*) during CoDCon Run 4 solvent loading as determined by changes to the TBP solvent tank mass; target flowrate = 28.0 mL/min.

Run time, min[(a)]	***Flow, g/min***	***Flow, mL/min***
15	23.9	29.0
42	23.6	28.6
72	27.7	33.5
104	22.3	27.0
137	22.6	27.3
173	22.1	26.8
210	20.5	24.8
263	22.9	27.7
293	22.4	27.1
338	22.3	27.0
381	22.3	27.0
400	20.9	25.3
Mean	22.8 ± 1.8	27.6 ± 2.2

(a) Run time represented by the mid-point of the sampling period.

Table 4.6. Flowrate of aqueous raffinate (stream *A3*) during CoDCon Run 4 solvent loading, as determined with timed grab samples and from changes in the collection tank mass.

From Timed Grab Samples			***From Changes in Tank Mass***		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
63	13.2	11.9	15	9.8	9.6
94	14.6	13.1	42	12.9	12.7
143	14.2	12.7	72	15.1	14.8
183	13.5	12.1	104	13.3	13.1
244	12.1	11.6	136	16.8	16.5
271	13.8	12.5	173	10.6	10.4
301	13.6	12.2	210	11.3	11.2
334	13.8	12.3	263	12.6	12.4
361	14.0	12.5	293	13.5	13.3
388	13.7	12.2	339	12.8	12.6
			382	13.0	12.8
			399	12.9	13.7
Mean	13.7 ± 0.7	12.3 ± 0.4	Mean	13.0 ± 1.9	12.8 ± 1.8

Table 4.7. Flowrate of loaded solvent outlet during CoDCon Run 4 solvent loading, as determined with timed grab samples and from changes in the collection tank mass.

From Timed Grab Samples			***From Changes in Tank Mass***		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
67	28.3	30.9	(a)		
97	25.1	27.2	104	25.0	27.2
147	24.7	26.8	136	25.0	27.2
187	22.9	24.9	173	23.7	25.7
240	25.4	27.9	210	22.0	23.9
274	26.2	28.4	263	25.9	28.1
301	25.0	27.6	293	25.8	28.1
334	26.6	29.0	339	25.0	27.2
365	25.3	27.5	382	26.1	28.4
388	25.6	27.6	399	22.7	24.7
Mean	25.5 ± 1.4	27.8 ± 1.5	Mean	24.6 ± 1.5	26.7 ± 1.6

(a) The first readings for the loaded solvent tank were discarded due to a balance malfunction.

Figure 4.3 graphically depicts the flowrate data derived from the grab samples and vessel masses during the Run 4 loading step. The data obtained from vessel balances inside the glovebox tended to show significant scatter, which was also observed during Run 3. However, unlike Run 3, the flowrates of the loaded solvent (both by grab sample and vessel mass) and the input TBP solvent (by vessel mass) were in general agreement.

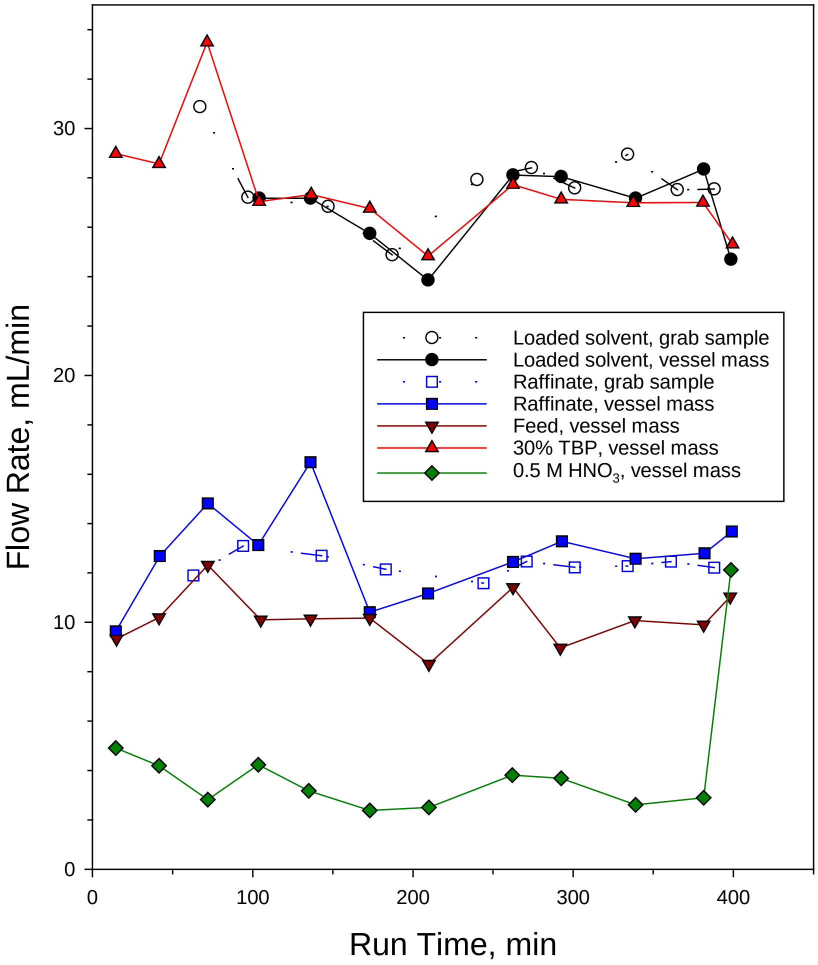

Figure 4.3. Flowrate data obtained during Run 4 solvent loading.

4.2.2 Run 4 Solvent Loading Results

Following mixing of the loaded solvent obtained during Run 4 with the loaded solvent left over from Run 3, the combined solvent consisted of 0.34 M U and 5.1 mM Pu, as determined spectrophotometrically. Back extraction of the mixed loaded solvent with ammonium carbonate solution, followed by ICP-MS analysis of the resulting aqueous phase (post acidification), gave a similar result—0.34 M U and 4.5 mM Pu. The HNO_3 concentration in the solvent was measured to be 0.026 M by titration.

Figure 4.4 compares the UV-vis spectra of the aqueous feed solution (simulated dissolved fuel) and the aqueous raffinate from the Run 4 solvent loading step. Below 460 nm, the spectrum of the feed solution is saturated from the U(VI) absorption, as well as the absorbance contribution from Ru(III). Chromium(III) also contributes substantially to the absorbance between 350 and 650 nm. However in the visible region, bands are evident for Pu(IV) (e.g., 660, 708, and 857 nm), Pu(VI) (832 nm), and Nd(III) (e.g., 579 and 742 nm). As expected, after extraction all bands associated with Pu(IV) were absent in the spectrum of the raffinate, and those associated with Nd were still evident. Surprisingly, some Pu(VI) was still evident in the spectrum of the aqueous raffinate. The presence of Pu(VI) in the raffinate is believed to be associated with the upset condition (i.e., crud formation) that occurred during the Run 4 solvent loading. Selected aqueous grab samples taken before and after the upset condition were carefully examined by spectrophotometry. This included treatment of the sample with Ce(IV) to oxidize all Pu present in the sample to Pu(VI) which is more easily detected by spectrophotometry. In all cases before and after the process upset, there was no spectral evidence for Pu in the aqueous grab samples. This suggests that retention of Pu(VI) in the aqueous raffinate occurred near to, or during, the process upset condition.

The spectrum of the aqueous raffinate evolved over time (Figure 4.4). One day after performing the loading step, the spectrum indicated an elevated baseline. After 24 days, the spectral baseline had decreased considerably. This suggests that a highly colored species was converted into a less colored species over time. No detailed investigation of this phenomenon was performed.

The amount of Np in the aqueous feed solution processed was determined to be 1.00 g by ICP-MS analysis of the aqueous feed solution. ICP-MS analysis indicated 0.23 g of Np remained in the aqueous raffinate following solvent loading, representing ~23% of the Np. This suggests that ~77% of the Np in the feed solution was in the form of extractable Np(VI). If this was the case, the Np concentration in the loaded solvent would have been 0.28 mM. ICP-MS analysis of the loaded solvent after mixing of the solvent left over from Run 3 gave a value of 0.22 mM Np. This contrasts to Run 3 in which only ~40 % of the Np was in the extractable Np(VI) state (Section 3.3.5). Conversion of the majority of the Np to the +6 oxidation state likely occurred during concentration of the product from Run 3 for recycle into Run 4.

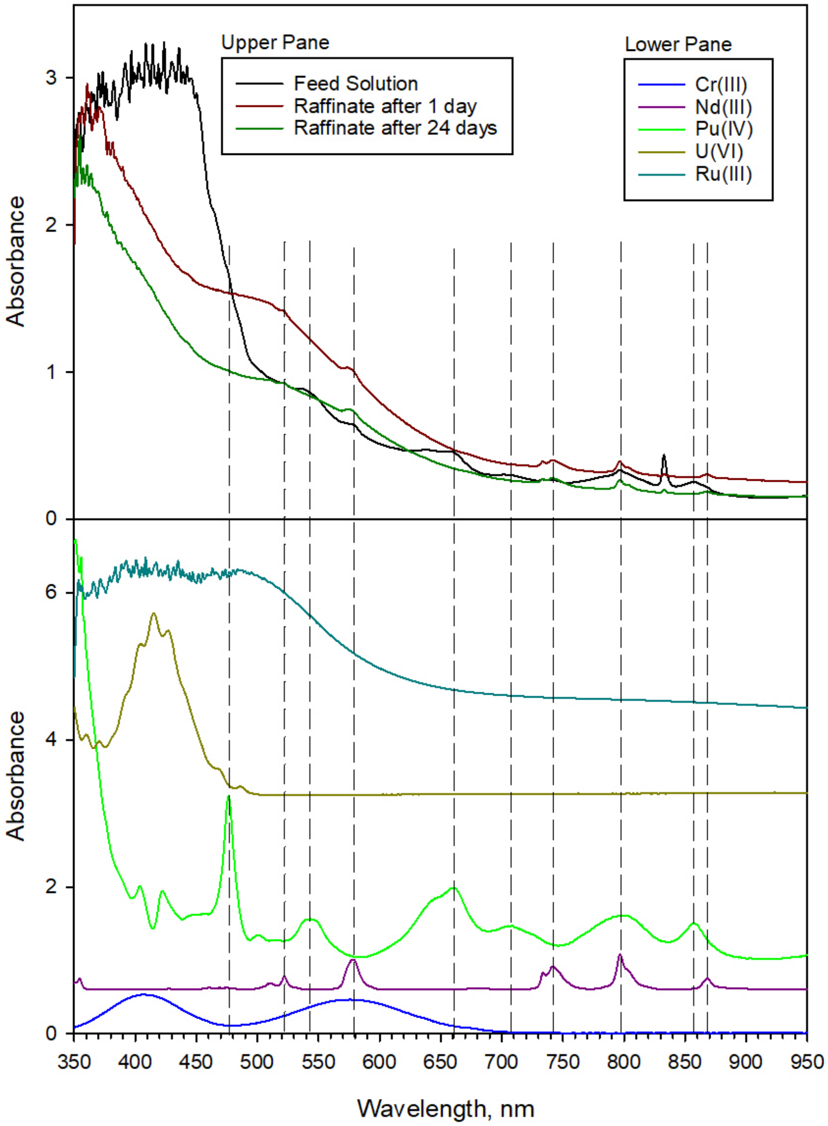

Figure 4.4. UV-vis spectra of the aqueous feed and raffinate from the Run 4 solvent loading (upper pane), and of Cr(III), Pu(IV), U(VI), and [Ru(NO)(NO_3)$_3$] in 3 M HNO_3, and Nd(III) in 6 M HNO_3 (lower pane).

4.3 Run 4 Reductive Stripping

4.3.1 Material Flows during Run 4 Reductive Stripping

The flowrates of the various process streams during the reductive stripping step of Run 4 are summarized in Table 4.8 through Table 4.14 and in Figure 4.5. Table 4.8 lists the flowrate data for the loaded solvent stream entering stage 25 during the reductive stripping step of CoDCon Run 4. The average flowrate of the loaded solvent, as determined by changes in the tank mass over time, was 27.9 ± 0.8 mL/min. This value was in excellent agreement with the target flowrate of 28.0 mL/min for the loaded solvent.

Table 4.9 lists the flowrate data for the fresh TBP solvent stream entering stage 17 during the reductive stripping step of CoDCon Run 4, as determined by changes in the tank mass over time. The average flowrate of the fresh TBP solvent was 11.7 ± 1.5 mL/min. In this case, the average flowrate is not particularly significant since the flowrate of the fresh TBP solvent was intentionally varied during the course of the experiment to adjust the U/Pu ratio in the product stream (*A6*) to the target of 7/3. Table 4.10 presents the flowrate data for the fresh TBP solvent as the average flowrates indicated by the in-line flowmeter during the time intervals representing the different pump settings for this process stream. The adjustments made to the fresh TBP solvent flowrate are discussed further in Section 4.3.2.

The flowrates for the 0.1 M HNO_3 scrub stream (*A4*) and for the U(IV) stripping solution (*A5*) were consistent with the target values of 4.0 mL/min and 14.0 mL/min, respectively. Table 4.11 indicates the 0.1 M HNO_3 scrub stream flowrate was 4.1 ± 0.2 mL/min, and Table 4.12 indicates the flowrate of the U(IV) solution was 13.7 ± 0.7 mL/min. Both these values were determined by tracking changes in the vessel masses over time.

The flowrate of the U/Pu nitrate product stream (*A6*) was determined by measuring the masses of timed grab samples, and by the masses of the solution accumulated in the individual product collection bottles (Table 4.13). The former method resulted in a value of 16.6 ± 0.3 mL/min, and the latter method resulted in a value of 16.5 ± 0.3 mL/min, indicating excellent agreement between the two methods. The sum of the two aqueous input streams to the reductive stripping step (streams *A4* + *A5*) was 17.8 mL/min; so, it appears the volumes of these two streams are not additive.

The flowrate of the Pu-depleted solvent (*O4*) was determined by grab samples and by changes in the solvent collection vessel over time (Table 4.14). In terms of the average flowrate, the two methods agreed within experimental uncertainty, with a flowrate of 36.4 ± 1.8 mL/min indicated by the grab samples and 38.5 ± 2.5 mL/min indicated by changes in the vessel mass. However, the grab samples typically indicated slightly lower flowrate for the Pu-depleted solvent compared to the change in the vessel mass, as can be seen in Figure 4.5.

Table 4.8. Flowrates for the loaded solvent (stream *O2*) during CoDCon Run 4 reductive stripping step as determined by changes to the loaded solvent tank mass; target flowrate = 28.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
13	26.2	28.6
37	25.0	27.3
66	25.9	28.3
94	25.0	27.3
124	25.0	27.3
156	26.6	29.1
188	24.2	26.5
218	26.7	29.2
249	25.8	28.2
280	24.2	26.5
311	25.8	28.2
343	25.0	27.36
375	25.9	28.3
405	25.8	28.2
428	25.5	27.9
Mean	25.5 ± 0.8	27.9 ± 0.8

(a) Run time represented by the mid-point of the sampling period.

Table 4.9. Flowrates for the fresh TBP solvent (stream *O3*) during CoDCon Run 4 reductive stripping step as determined by changes to the TBP solvent tank mass.

Run time, min[(a)]	***Flow, g/min***	***Flow, mL/min***
14	7.6	9.2
38	7.8	9.4
66	8.6	10.4
94	8.6	10.4
125	9.4	11.4
157	9.7	11.7
188	10.6	12.9
218	11.3	13.7
249	10.6	12.9
280	11.0	13.3
311	10.3	12.5
343	10.3	12.5
374	10.7	13.0
404	10.0	12.1
444	8.1	9.8
Mean	9.6 ± 1.2	11.7 ± 1.5

(a) Run time represented by the mid-point of the sampling period.

Table 4.10. Flowrates for the fresh TBP solvent (stream *O3*) during CoDCon Run 4 reductive stripping step as determined by the flowmeter. The values given are the average values over the time frames indicated; the uncertainties are the associated standard deviations.

Run time, min		***Flow, mL/min***
Start[(a)]	*End*	
0	33	7.8 ± 1.2
34	50	8.1 ± 1.4
51	65	8.6 ± 1.4
66	105	9.5 ± 0.8
106	138	9.7 ± 0.2
139	153	10.2 ± 0.3
154	168	10.6 ± 0.3
169	183	11.5 ± 0.5
184	280	12.1 ± 0.4
281	293	11.8 ± 0.5
294	355	11.5 ± 0.5
356	367	11.8 ± 0.6
368	388	11.2 ± 0.6
389	406	10.7 ± 0.6
407	419	9.7 ± 0.6
420	472	8.6 ± 0.9

(b) The start times indicated correspond to the times at which adjustment was made to the flowrate of the fresh TBP solvent stream.

Table 4.11. Flowrates for the 0.1 M HNO_3 scrub (stream *A4*) during the CoDCon Run 4 reductive stripping step as determined by changes to the scrub tank mass; target flowrate = 4.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
13	3.81	3.75
37	4.44	4.37
66	4.19	4.13
95	4.29	4.22
124	4.67	4.59
155	4.06	4.00
187	4.19	4.13
217	4.00	3.94
248	4.06	4.00
280	3.87	3.81
311	4.06	4.00
344	4.24	4.18
374	4.07	4.01
403	4.06	4.00
443	4.04	3.98
Mean	4.1 ± 0.2	4.1 ± 0.2

(a) Run time represented by the mid-point of the sampling period.

Table 4.12. Flowrates for the U(IV) stripping solution (stream *A5*) during the CoDCon Run 4 reductive stripping step as determined by changes to the scrub tank mass; target flowrate = 14.0 mL/min.

Run time, min	***Flow, g/min***	***Flow, mL/min***
14	11.9	11.1
37	14.6	13.6
65	14.8	13.8
93	15.4	14.3
123	14.7	13.7
156	14.7	13.7
188	14.8	13.8
217	14.7	13.7
248	14.7	13.7
280	15.0	14.0
312	14.8	13.8
344	15.2	14.1
375	14.5	13.5
404	14.7	13.7
443	15.1	14.1
Mean	14.6 ± 0.8	13.7 ± 0.7

(a) Run time represented by the mid-point of the sampling period.

Table 4.13. Flowrate of aqueous U/Pu nitrate product (stream *A6*) during CoDCon Run 4 reductive stripping, as determined with timed grab samples and from the masses of the U/Pu product collection bottles.

From Timed Grab Samples			***From Product Collection Bottle Masses***[(a)]		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
17	18.3	17.5	55	17.2	16.4
45	17.8	16.9	111	17.5	16.7
72	17.8	16.9	164	17.6	17.0
103	17.5	16.6	220	17.2	16.5
132	17.6	16.9	276	17.2	16.4
184	17.2	16.4	334	17.1	16.2
219	17.1	16.3	390	16.8	16.1
268	17.2	16.4	445	17.2	16.3
336	17.3	16.4			
384	17.4	16.8			
410	16.9	16.2			
450	17.5	16.8			
Mean	17.4 ± 0.3	16.6 ± 0.3	Mean	17.2 ± 0.2	16.5 ± 0.3

(a) Data listed for sequential order in which the U/Pu nitrate collection bottles were filled.

Table 4.14. Flowrate of Pu-depleted solvent outlet (stream *O4*) during CoDCon Run 4 reductive stripping, as determined with timed grab samples and from changes in the collection tank mass.

From Timed Grab Samples			***From Changes in Tank Mass***		
Sampling run time, min	***Measured flow, g/min***	***Measured flow, mL/min***	***Sampling run time, min***	***Measured flow, g/min***	***Measured flow, mL/min***
21	34.4	37.6	13	28.6	32.4
48	30.2	33.1	37	31.5	35.7
72	31.1	34.9	65	31.7	35.9
103	32.2	36.3	94	35.7	40.5
135	31.7	35.7	125	33.3	37.8
186	32.0	36.2	157	35.5	40.3
221	32.8	36.0	187	36.7	41.6
270	35.5	40.1	217	33.3	37.8
339	33.8	38.4	248	35.9	40.8
386	32.2	36.5	280	35.5	40.3
414	31.9	36.0	311	35.5	40.3
450	31.8	35.8	343	33.8	38.4
			374	35.2	39.9
			404	34.8	39.5
			427	31.9	36.2
Mean	32.5 ± 1.5	36.4 ± 1.8	Mean	33.9 ± 2.2	38.5 ± 2.5

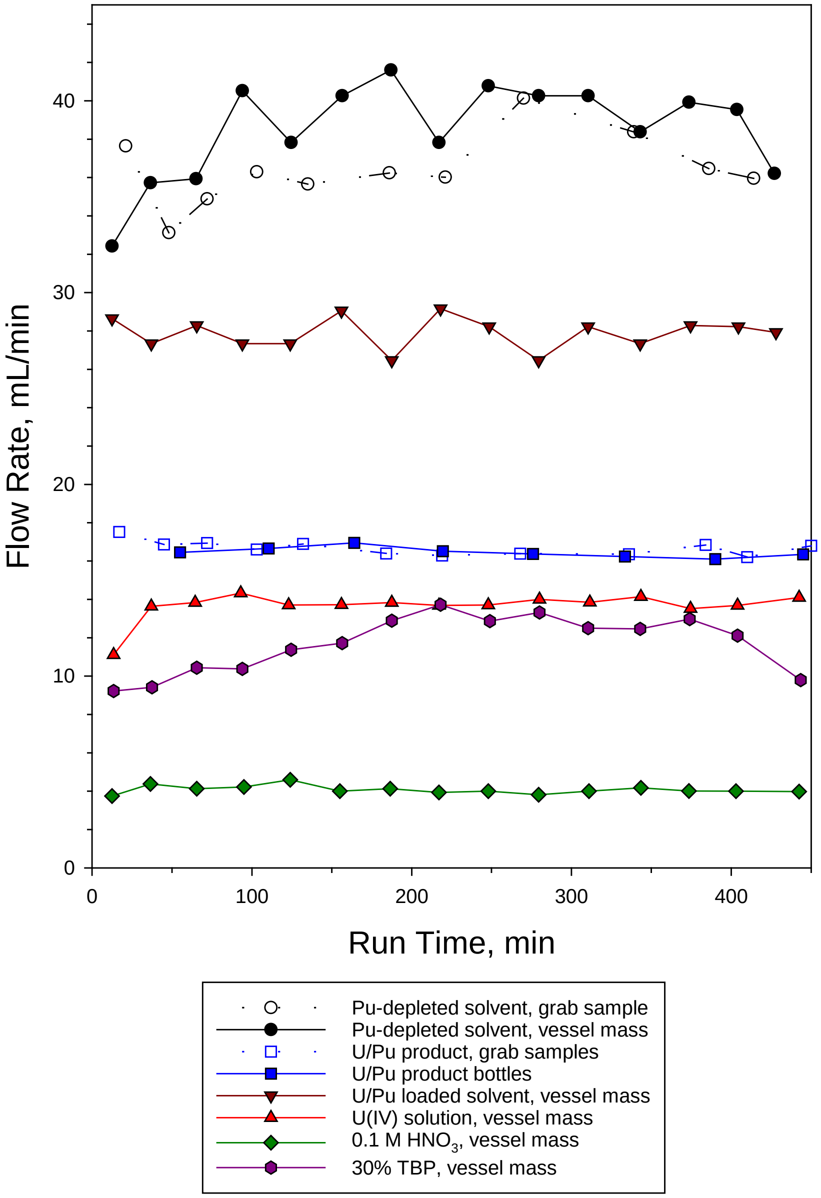

Figure 4.5. Flowrate data obtained during Run 4 reductive stripping.

4.3.2 Run 4 Reductive Stripping Results

Figure 4.6 shows the relative composition of the U/Pu nitrate product stream from Run 4 over the course of the flowsheet test. The relative Pu and U fractions in the product determined by the on-line monitoring system agree very well with those determined by off-line spectrophotometric analysis. At various points in the process, the on-line monitoring system indicated spikes in the Pu fraction (with corresponding decreases in the U fraction). These spikes reflected changes in both the Pu and U concentrations in the solutions (Figure 4.7). Such spikes were not observed in any other CoDCon test run, and the origin of this behavior is not obvious. The spikes did not occur after approximately 230 minutes into the run, however considerable drifting from the target U/Pu ratio did continue throughout the run. This drifting might have been due to changes in the ambient temperature affecting the instrument performance. During the course of the experiment the room temperature varied from 18 to 31 °C. However, the fact that the drifting was also indicated by the off-line spectrophotometric grab sample analysis suggests there was some factor other than temperature affecting the system performance. Disregarding the first grab sample taken near the startup of the test, the average U and Pu fractions across the grab samples were 70.1 ± 3.1 % and 29.9 ± 3.1 %, respectively.

Disregarding the first product collection bottle, which contained mostly solutions from the startup of the solvent extraction system, the relative U and Pu fractions in each product collection bottle are given in Table 4.15. Comparing to Table 3.15, the data in Table 4.15 indicate much greater variability from the target U/Pu ratio during Run 4 compared to Run 3. Product bottle 5 represents the point at which the target ratio was initially achieved. The average U and Pu fractions for product bottles 5 through 9 was 68.0 ± 1.1 % U and 35.0 ± 1.1 % Pu. Overall for product bottles 2 through 9, the averages were 69.7 ± 2.5 % U and 30.3 ± 2.5 % Pu. Clearly, the uncertainty in the U/Pu ratio was significantly greater in Run 4, than that observed during the stable stages of Run 3.

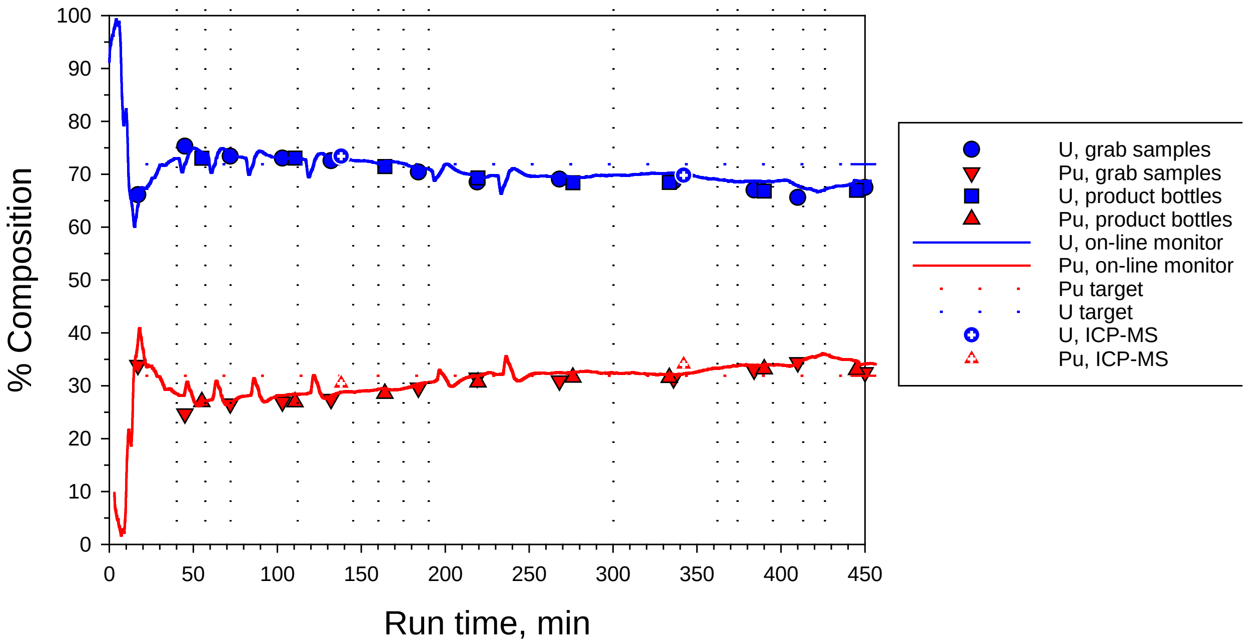

Figure 4.6. Relative percentages of Pu and U in the U/Pu product stream (*A6*) during CoDCon Run 4 as determined using the on-line spectroscopy system, and by off-line spectrophotometric analysis of grab samples and the aqueous U/Pu product bottles. ICP-MS results for selected samples are also shown. The vertical dashed lines correspond to the TBP flowrate adjustments listed in Table 4.10.

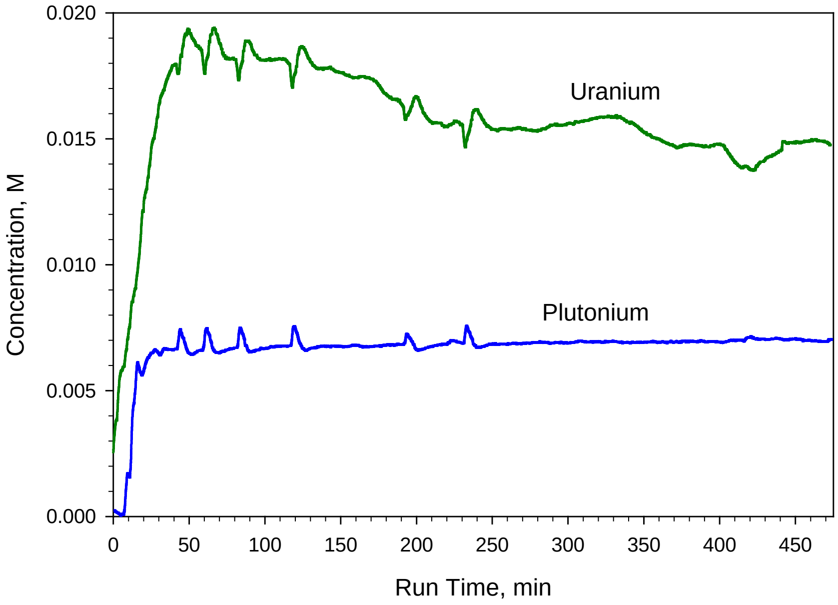

Figure 4.7. Solution concentrations of Pu and U in the U/Pu product stream (*A6*) during CoDCon Run 4 as determined using the on-line spectroscopy system.

Table 4.15. Spectrophotometric analytical results for the aqueous U/Pu nitrate product bottles taken during Run 4.

Product bottle number	***Run time, min***	***[HNO$_3$], M***	***[U], mM***	***[Pu], mM***	***Pu, %***	***U, %***
2	26–84	0.71	19.8	7.29	26.9	73.1
3	84–137	0.73	20.0	7.34	26.9	73.1
4	137–191	0.72	18.7	7.41	28.5	71.5
5	191–248	0.69	16.8	7.40	30.7	69.3
6	248–304	0.69	16.2	7.46	31.6	68.5
7	304–363	0.69	16.4	7.53	31.5	68.5
8	363–417	0.70	15.3	7.57	33.3	66.8
9	417–472	0.73	15.6	7.66	33.0	67.0

Selected aqueous grab samples were analyzed for U and Pu by ICP-MS (Table 4.16). Agreement between the ICP-MS and spectrophotometric values was much better in the case of Run 4 than Run 3. In the case of Run 4, the ICP-MS determined U concentrations were only 4 – 6% lower than those determined by spectrophotometry. The Pu concentrations were within 3% by the two different methods.

Table 4.16. Comparison of off-line spectrophotometric results to those obtained by ICP-MS for selected aqueous grab samples, and Product Bottle 8 from stripping step of CoDCon Run 4.

Aq. grab sample #	***Run time, min***	***Spectrophotometry***				***ICP-MS***			
		[U], mM	***[Pu], mM***	***%U***	***%Pu***	***[U], mM***	***[Pu], mM***	***%U***	***%Pu***
5	344	19.6	7.4	72.6	27.4	18.7	7.4	71.5	28.5
9	361	16.9	7.5	68.7	31.3	15.6	7.3	67.9	32.1
Product Bottle 8	390	15.3	7.6	66.8	33.2	14.8	7.5	66.2	33.8

The concentration profiles for U, Pu, and HNO_3 during the CoDCon Run 4 reductive stripping step are presented in Figure 4.8. These represent the stage profiles at the conclusion of the test. The U profile indicates excellent retention of the bulk U in the organic phase in stages 25 through 32. The effective U distribution ratios decreased from stage 25 to stage 17. The uranium *D* values cross over between stages 20 and 21, with the *D* values less than 1 below stage 20. This decrease in the uranium *D* value leads to the desired effect of having some U in the aqueous phase exiting stage 17. The aqueous phase Pu concentrations are relatively flat in stages 17 to 24, and the corresponding organic phase Pu concentrations were also very low in these stages. The Pu concentrations drop to low levels in both phase from stage 25 to stage 32. The increase in the aqueous phase Pu concentration at stage 29 is believed to be an anomaly.

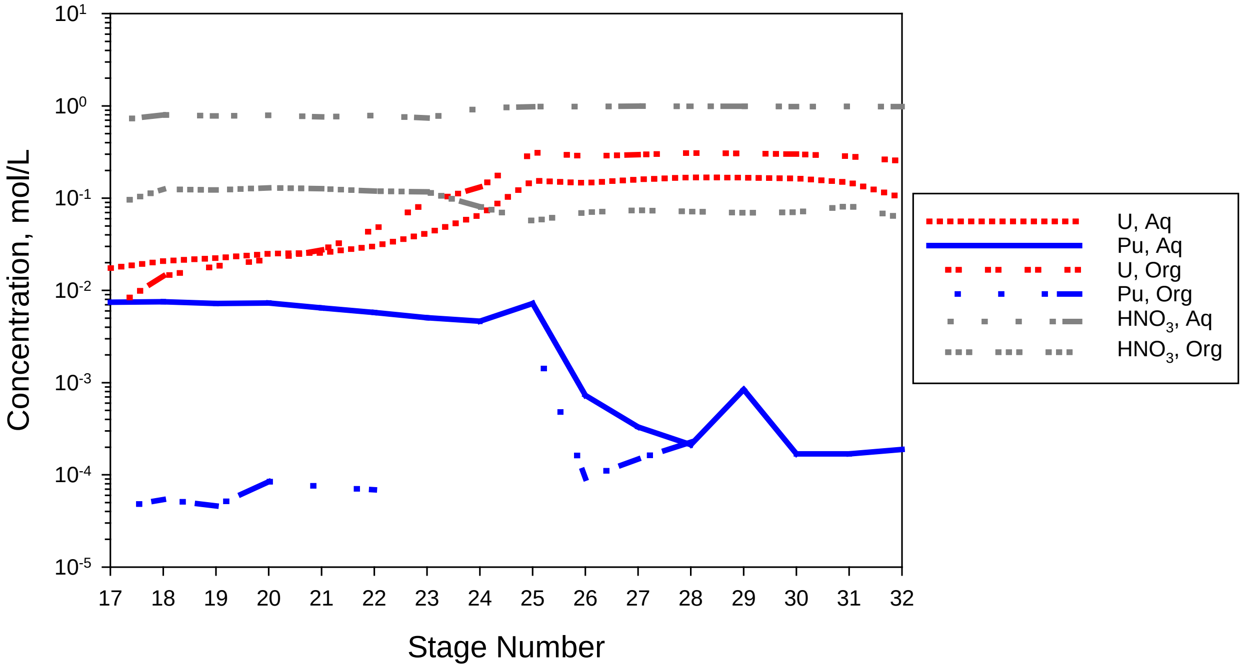

Figure 4.8. Stage concentration profiles for U, Pu, and HNO_3 during the reductive stripping portion of CoDCon Run 4. The gaps in the organic-phase Pu concentrations represent points at which the Pu concentration was below the spectrophotometric detection limit.

4.3.3 Run 4 Uranium and Plutonium Mass Balance

The U and Pu mass balances for the reductive stripping portion of CoDCon Run 4 was assessed by evaluating the various input and output streams from this portion of the test. The input streams considered were *O2* (the U/Pu loaded solvent) and *A5* [the U(IV) stripping solution], while the output streams were *O4* (the Pu-depleted solvent) and *A6* (the U/Pu nitrate product) (Figure 4.1). The U and Pu contained in the various grab samples taken, and in the organic and aqueous phases held up in the contactors at the conclusion of the flowsheet test, were also considered in determining the mass balances from the Run 4 reductive stripping step. Table 4.17 summarizes the U and Pu inputs into the Run 4 reductive stripping sections. The data presented are based on spectrophotometric analysis of the various process solutions. A total of 1151 g of U and 15.8 g of Pu were fed into the stripping sections. The major fraction of the Pu was in the nine U/Pu nitrate product bottles. As indicated in Table 4.18, the product bottles contained 13.4 g of Pu. An additional 0.3 g of Pu was accounted for in the 12 aqueous grab samples that were taken during the reductive stripping test, and 0.1 g of Pu was accounted for as hold up in the contactor bank at the conclusion of the experiment. The total 13.8 g of Pu between the product bottles, grab samples, and contactor drains represented an 87% recovery of Pu.(a) As expected, the major portion of the U reported to the Pu-depleted solvent (stream *O4*). The volume of Pu-depleted solvent collected was 17.7 L, with a U concentration of 0.244 M (determined spectrophotometrically), indicating 1028 g of U. The U/Pu product bottles contained 30.9 g U (Table 4.18). Another 20.8 g U was accounted for in the aqueous and organic grab samples taken during the test, and 10.7 g U was found in the contactor hold up at the conclusion of the test. This resulted in the recovery of 1090 g of U, representing a U mass recovery of 95%.

The data presented in Table 4.18—30.9 g U and 13.4 g Pu cumulative in the product bottles—provides verification of the assessment made regarding the data in Table 4.15. The data in Table 4.18 indicates a cumulative 69.8 % U and 30.2 % Pu. Thus overall, the U/Pu ratio in the product was very close to the target value. The same result is obtained averaging the values in Table 4.15 across product collection bottles 1 through 9, but examination of the data in that way reveals that the extent of variability in the U and Pu percentages is ~ 3%.

(a) Reassessment of the Pu mass recovery by ICP-MS analysis of the combined and concentrated U/Pu product suggested 100% recovery of Pu from the U/Pu/Np-loaded solvent.

Table 4.17. Uranium and plutonium inputs to the reductive stripping step of CoDCon Run 4.

	Stream *O2*	**Stream *A5***
[U], mM	342	53.5
[Pu], mM	5.09	0
Density, g/mL	0.91	1.07
Mass in, kg	11.95	6.8/1
Volume in, L	13.1	6.36
Mole U in	4.50	0.340
Mass U in, g	1070	80.9
Mole Pu in	0.661	0
Mass Pu in, g	15.8	0
	Total U in, g	1151
	Total Pu in, g	15.8

Table 4.18. Uranium and plutonium mass outputs from the nine U/Pu nitrate collection vessels from CoDCon Run 4.

Product Bottle:	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
[U], mM	3.33	19.8	20.0	18.7	16.8	16.2	16.4	15.3	15.6
[Pu], mM	1.8	7.29	7.34	7.41	7.40	7.46	7.53	7.57	7.66
Density, g/mL	1.02	1.05	1.05	1.04	1.04	1.05	1.05	1.05	1.05
Mass out, kg	0.98	1.00	0.91	0.96	0.95	0.96	1.01	0.91	0.93
Volume out, L	0.96	0.95	0.87	0.93	0.91	0.92	0.96	0.87	0.88
mMole U out	3.2	18.9	17.3	17.4	15.3	14.9	15.7	13.3	13.8
Mass U out, g	0.76	4.51	4.12	4.13	3.64	3.54	3.75	3.17	3.28
mMole Pu out	1.7	6.95	6.36	6.89	6.73	6.84	7.21	6.58	6.76
Mass Pu out, g	0.41	1.66	1.52	1.65	1.61	1.63	1.72	1.57	1.62
Sum mass U out, g									30.9
Sum mass Pu out, g									13.4

4.3.4 Analysis of Concentrated Product Solution from Run 4

The concentrated U/Pu product from Run 4 (combination of all 9 U/Pu product collection bottles) was analyzed by ICP-MS and by spectrophotometry. The ICP-MS analysis indicated the concentrated product solution to contain 557 mM U and 237 mM Pu, giving a U/Pu mass distribution of 70.0% U and 30.0% Pu. This again indicated that, despite of the considerable drift experienced during the Run 4 test, the target U/Pu mass ratio of 7/3 was achieved in the product. The spectrophotometric analysis of the concentrated product also indicated that the concentrated product was close to the target ratio, with 69.7% U and 30.3% Pu. However, the U and Pu concentrations measured spectrophotometrically were about 10% lower than the values obtained by ICP-MS, with values of 500 mM U and 216 mM Pu.

ICP-MS analysis of the mixed loaded solvent fed to the stripping stages in Run 4, indicated that the loaded solvent contained 0.68 g of Np (0.22 mM). Analysis of the concentrated product indicated 0.58 g

Np in the combined and concentrated U/Pu product solution, representing 85% of the Np that entered the stripping section. This would suggest 15% of the Np would have been in the Pu-depleted solvent along with the bulk U. However, ICP-MS indicated very little Np in the Pu-depleted solvent (0.001 mM Np or about 4 mg Np). A more rigorous accounting of Np would be warranted in future CoDCon experiments.

5.0 Conclusions and Recommendations

Four CoDCon flowsheet tests have been conducted to date. In all four cases, on-line optical spectroscopy, coupled with chemometric modeling of the spectral data, provided real-time information regarding the U/Pu ratio in the product stream. This real-time process solution information was used to manipulate the process conditions to achieve the targeted U/Pu mass ratio of 7/3. Although this methodology proved effective, the stability of the solvent extraction system was not always consistent from run to run. Very stable operation of the system was achieved during CoDCon Runs 2 and 3; but much more drift in the system was experienced in Runs 1 and 4.

Table 5.1 provides a comparison of the results from the four CoDCon flowsheet tests in terms of the U and Pu fractions in the product bottles. For Runs 2[1] and 3, the data presented in Table 5.1 represent the average composition of the product bottles taken during the most stable period of operation (representing three product bottles for run 2 and seven product bottles for run 3). As can be seen, during these stable periods of operation the standard deviation in the percent composition was very low (< 0.5%). On the other hand, stable periods of operation were more elusive in Runs 1[1] and 4. In these cases, the standard deviations in the composition of product was ~3%. Based on the limited set of data represented by these four CoDCon tests, it is reasonable to conclude that the U/Pu ratio can be maintained within 5% of a target ratio using the laboratory-scale solvent extraction system used in this work.(a)

Table 5.1. Comparison of the U and Pu fractions in the product bottles from the four CoDCon flowsheet tests.

Run #	***U, %***	***Pu, %***	***Standard Deviation, %***
1	61.4	38.6	2.8
2	70.4	29.6	0.1
3	70.3	29.7	0.4
4	69.7	30.3	2.5

Based on the accomplishments of the CoDCon project to date, the following ideas should be pursued to further advance this field.

1. *Automated Process Control.* During the CoDCon flowsheet tests performed to date, the flowrate adjustments needed to reach the target U/Pu ratio were performed manually by the researchers. Coupling of the on-line spectroscopic monitoring data to an automated flowrate control system would allow more accurate control over the U/Pu ratio, and the system would automatically adjust to drifting in the performance of the process equipment.
2. *Improve Robustness of Chemometric Model.* The on-line monitoring system currently requires periodic collection of reference spectra, requiring intervention by the system operators. New data analysis algorithms developed by PNNL in collaboration with Eigenvector Research can eliminate the need to collect the daily reference spectra. Incorporation of these algorithms into the

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(a) The reason for the low relative U content of the product from Run 1 has previously been discussed.[1] It was attributed to a false indication of U(VI) in the U/Pu nitrate product stream by the chemometric model. This issue was subsequently corrected.

chemometric model will allow the model to simulate the reference spectrum, drastically improving the ease of application both in the laboratory and industrial settings.

3. *Real Time Mass Balance*. The on-line monitoring system developed in the CoDCon process offers the opportunity to track the flow of special nuclear materials within a radiochemical separations process in real time. Integration of the optical spectroscopic data with vessel mass data and flowmeter data would provide a mechanism to track the plutonium and uranium material flows in real time.
4. *Neptunium and Technetium Management.* The routing of neptunium and technetium within the CoDCon flowsheet has not been rigorously defined. Various options are available for managing these radioactive species within the flowsheet, depending on their intended disposition in the nuclear fuel cycle. Evaluation of the options is needed.
5. *Demonstration with Irradiated Fuel.* All CoDCon testing to date has been performed using simulated dissolved fuel solutions. The results of these studies should be verified through testing with actual irradiated nuclear fuel. Demonstration of the real-time optical spectroscopic techniques in a hot cell environment would represent a major milestone in the development of this technology. The CoDCon demonstration with irradiated fuel would also provide opportunity to test other technologies developed under the Materials Recovery and Waste Form Development Campaign, including new off-gas treatment methods and new waste forms.

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