SANDIA REPORT

SAND2017-2253
Unlimited Release
Printed March 2017

CoDCon Dynamic Modeling

Benjamin B. Cipiti

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@osti.gov
Online ordering: http://www.osti.gov/scitech

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.gov
Online order: http://www.ntis.gov/search

SAND2017-2253
Unlimited Release
Printed March 2017

CoDCon Dynamic Modeling

Benjamin B. Cipiti
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0747

Abstract

The Co-Decontamination (CoDCon) Demonstration project is designed to test the separation of a mixed U and Pu product from dissolved spent nuclear fuel. The primary purpose of the project is to quantify the accuracy and precision to which a U/Pu mass ratio can be achieved without removing a pure Pu product. The system includes an on-line monitoring system using spectroscopy to monitor the ratios throughout the process. A dynamic model of the CoDCon flowsheet and on-line monitoring system was developed in order to expand the range of scenarios that can be examined for process control and determine overall measurement uncertainty. The model development and initial results are presented here.

ACKNOWLEDGMENTS

This work is supported through the U.S. Department of Energy Fuel Cycle Technologies Program. The author would like to acknowledge the CoDCon team for providing the information for building the model.

CONTENTS

FIGURES

NOMENCLATURE

AMUSE	Argonne Model for Universal Solvent Extraction
CoDCon	Co-Decontamination
MDD	Modified Direct Denitration
PUREX	Plutonium and Uranium Extraction
SSPM	Separation and Safeguards Performance Model
UV	Ultraviolet
Vis	Visible

1. INTRODUCTION

The CoDCon Demo [1] at Pacific Northwest National Laboratory seeks to test a solvent extraction process for removing U and Pu from spent nuclear fuel without separating a pure Pu product. The main goal of the project is to quantify the accuracy and precision of maintaining a specific U/Pu ratio throughout the entire process, from solvent extraction through mixed oxide production. On-line spectroscopy will be used to monitor the solutions in seven locations within the flowsheet.

Phase 1 of the testing is using simulated solutions containing U and Pu only. Phase 2 will use dissolved spent nuclear fuel. The testing is being performed using a bank of 16 2-cm centrifugal contactors.

The monitoring system uses combined Raman and UV-Vis absorbance spectroscopy to determine nitric acid, U, and Pu concentrations in multiple oxidation states. Probes will be installed in seven locations along the contactor bank. This concentration data will be used along with flow meters to determine the ratio of U/Pu throughout the process.

The purpose of modeling such a process is both to quantify measurement uncertainties and examine process control for a wider variety of process conditions. Initial testing will use a simulated fuel solution, and this can be used to help validate the dynamic model. The model can be used to explore other typical plant process conditions (such as variations in fuel feed) as well as off-normal process upsets. Of particular interest is the response of the monitoring system to changes and how quickly that data can be reported for the operator to make adjustments. The measurement uncertainties for the spectroscopic probes will change depending on the location and solution concentrations—the SSPM fully propagates the error to determine how well the product can be controlled. However, measurement uncertainties will be determined experimentally.

The Separation and Safeguards Performance Model (SSPM) [2,3] was used as the basis for developing the dynamic model. This model tracks the mass of species through a separations plant and simulates measurements that are used for materials accountancy or process monitoring. A new model was developed for this work to represent the CoDCon process. The model development is described here along with initial results.

2. BACKGROUND

2.1. CoDCon Flowsheet

The flowsheet illustrating the CoDCon Demo is shown in Figure 1 [1]. Based on development work currently in progress, the flowsheet actually tested might differ from that shown in the figure, but the flowsheet illustrated was used for the purposes of model development. The testing at PNNL will separate a mixture of U and Pu made up of 1 kg of U, and 14 g of Pu to represent the typical 1w% Pu in spent nuclear fuel from LWRs. The demo is designed to perform the separations in three steps, all on the same contactor bank. In between tests, the product solutions will be collected in vessels temporarily for feed into the next test. The tentative locations of the seven spectroscopic probes and flow meters are on the feeds to contactors 1, 8, 9, 12, and 16, as well as the outputs from contactors 1 and 16. This covers all the feeds and products for the three sets.

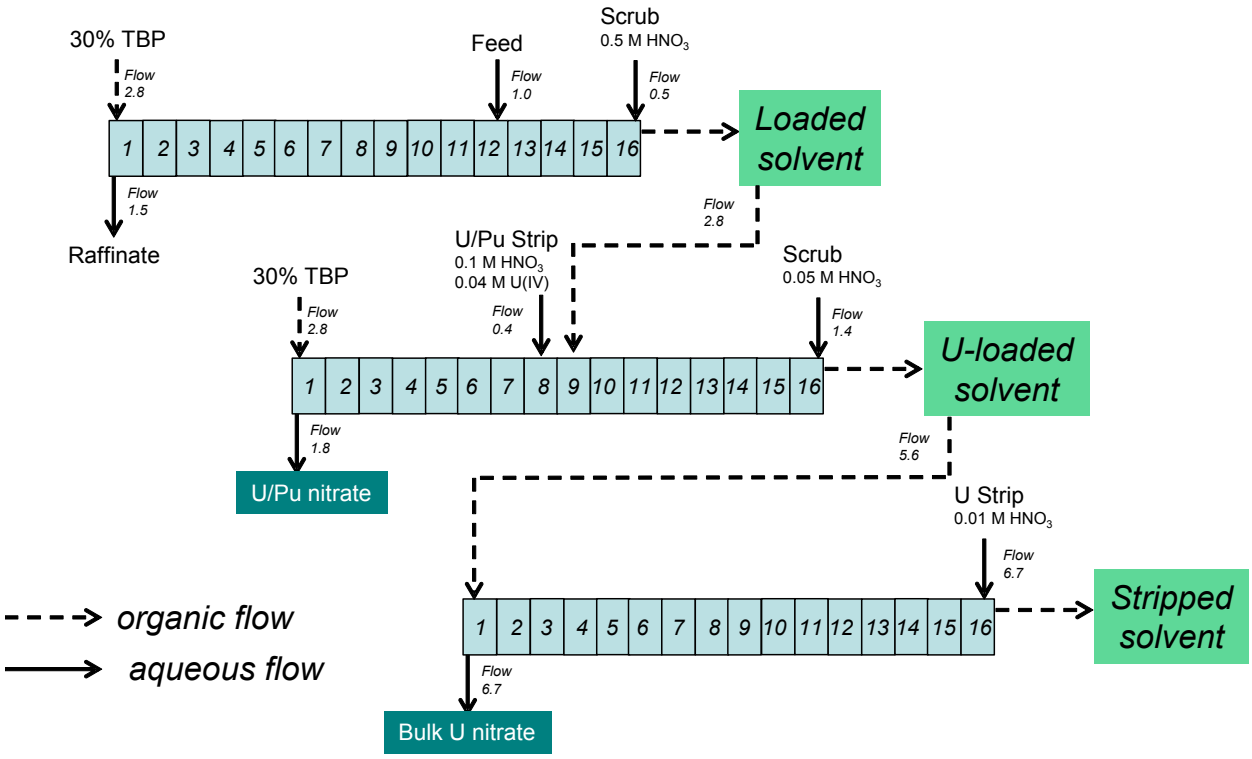

Figure 1: Proposed CoDCon flowsheet; each box represents a single stage; flow values are relative flow rates [1].

The flowsheet design was modeled using the AMUSE code at Argonne National Laboratory. The data from AMUSE was used to develop the dynamic model. The data that was provided included the concentration profiles in the contactor bank for the three tests along with the distribution ratio (D) values. The flowrate data along with the D values were used in the SSPM to develop the contactor models.

The final step in the process, after the three separation steps, is a co-conversion system to convert the product U/Pu nitrate solution to a mixed U/Pu oxide. This will be done with modified direct

denitration (MDD) as a batch process. The details of this have not been worked out yet, so it has not yet been modeled in detail.

2.2. On-line Measurements

The spectroscopic equipment used to monitor the process includes both Raman spectroscopy and UV-Vis absorbance spectroscopy [1]. Raman is used to monitor the nitric acid concentration along with UO_2^{2+} and the hydrazinium ion. UV-Vis is used to monitor the multiple oxidation states of Pu and U. Only the flow cells and fiber optic cables will be contained within the glovebox; all other components of the measurements system can be outside the glovebox. The spectroscopic systems use chemometric models to determine the concentrations within solutions.

Flowmeters are also installed at each spectroscopic measurement point. They have an accuracy of 5% and repeatability of 0.5% of the measured value. Scales will be used to monitor changes in solution level at the various vessels. The uranium nitrate and scrub/strip tanks will be on scales readable to 0.01 kg. The raffinate, Pu/U nitrate, aqueous feed, and U nitrate tanks will be on scales readable to 1 g.

2.3. Separation and Safeguards Performance Model

The Separation and Safeguards Performance Model (SSPM) is built in Matlab Simulink and has been used for a variety of safeguards and process monitoring problems. Past work has focused on reprocessing, though other facility types have been modeled. The model was originally developed to simulate safeguards system response for investigating advanced safeguards concepts, diversion scenario analysis, and examining the potential improvement of new measurement instrumentation.

The SSPM simulates the mass flow of elements through a reprocessing plant, and models the transient nature of process operations to track inventories and flows in real time. Past work has integrated AMUSE and SSPM in order to provide more fidelity for modeling centrifugal contactors--this integration was used for the CoDCon model. Past work has also examined the use of spectroscopy data in PUREX reprocessing plants as a process monitoring technique, and these measurement models were also used for this work.

The SSPM uses user-defined measurement blocks to simulate measurements taken at various areas in the process. The model collects all the measurement data to perform material balances and calculate the error propagation. For the CoDCon project, the mass balance is not as important as tracking the error propagation and determining the transient response of changes to the process.

3. CODCON MODEL DEVELOPMENT

The CoDCon model was developed initially to simulate the test at PNNL. The model is able to be easily modified to run different fuel types or process upsets for future work. The model in Simulink is shown in Figure 2.

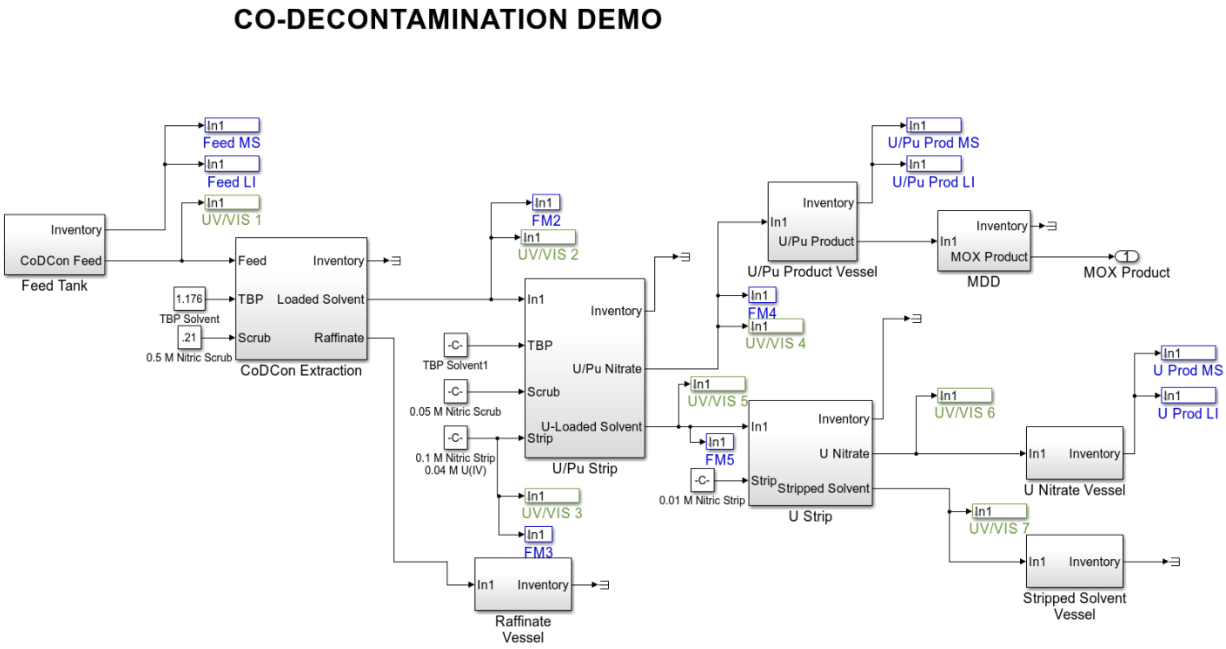

Figure 2: CoDCon model in Simulink

The grey blocks represent the key vessels or unit operations. This was simulated as a continuous process, when in fact the operations are paused in between each of the three set of tests. The three contactor banks are labeled as "CoDCon Extraction", "U/Pu Strip", and "U Strip." The rest of the blocks are feed or product vessels. The MDD co-conversion process has been added to the end, but measurements in this area are not modeled yet.

The green blocks are the spectroscopy measurements and are assumed to provide data about U and Pu concentration in real time. In reality, spectroscopy measures multiple species and oxidation states, and these data are used in detailed chemometric models to determine the concentrations. The SSPM simulates a random and systematic error for the concentration measures of U and Pu that can be updated as experimental data is obtained.

The blue blocks represent the flowmeters, level measurements, and mass ~~spec~~ measurement at various locations. These are used to set up a material balance if that is needed in the future. For now, the focus of the work is on the U/Pu ratio and error propagation.

3.1. Modeling Transient Solvent Extraction

Within each of the contactor bank blocks, the inventory (for the entire bank) is tracked in real time. An embedded Matlab function takes all of the feed flows and initial concentration data and calculates the U and Pu concentration in each stage using a mass balance and the D values provided from AMUSE. Figure 3 shows an example of the first contactor bank block.

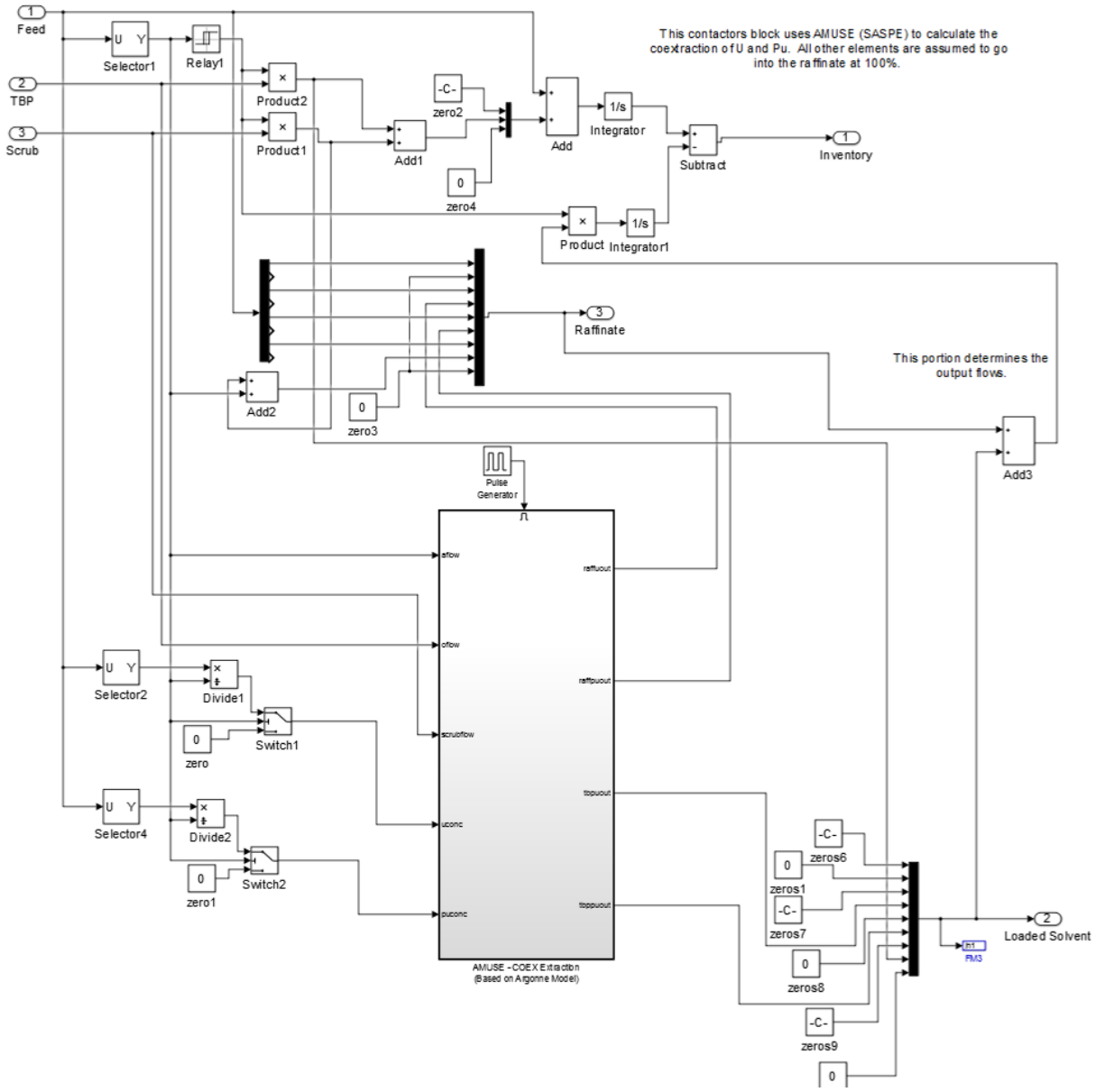

Figure 3: Example contactor bank showing the first extraction.

The actual feed and outputs can be plotted as the model runs to monitor the operation. These are mainly used to test the model and make sure the behavior is as expected.

The Feed Tank can be modified to alter the feed with time (representing, for example, variation in spent fuel feed in an actual process). The cold chemicals can also be altered easily to represent changes in flow rates. Examples are shown in the next section.

The model will continue to be updated as the experimental flowsheet design changes. Once results are generated, they will be used to update the model as needed.

3.2. Measurement Models

The key measurements that will be used in this study are the spectroscopic measurements, which use a combination of Raman and UV-Vis spectroscopy. These are modeled as blocks that measure the concentration of total U and Pu on the flow lines. The user can input the random and systematic errors for these measurements, and those values may change depending on the point in the process. Initially, all uncertainties have been set to 1% until experimental data is available from PNNL.

Flowmeters are also modeled on each of the locations where spectroscopy is installed. These measure the volumetric flow rate with an assumed 0.1% random and systematic error. Again, the uncertainties will be updated in the future.

Finally, the feed and product tanks are assumed to have both level measurements that tell total volume, and sampling for determining U and Pu concentration. This may differ in the experiment, but is modeled this way to be more consistent with vessels in actual reprocessing facilities.

The measurements are used to plot out monitoring data. The Pu/U ratio is plotted for the feed tank, U/Pu product tank, and U tank. The Pu/U ratio from the seven probes is also plotted with time. Finally, the overall measurement uncertainty on the final Pu/U ratio is also plotted.

4. MODEL RESULTS

4.1. Baseline Test

The initial baseline modeling run assumed a starting solution with a 2% Pu/U ratio. This solution was kept constant for a 2 hour run. The solvent feed rates were also held constant. The flow rates were taken directly from the Argonne AMUSE flowsheet.

Figure 4 shows the Pu/U ratios in the feed and product tanks as a function of time. The feed tank is steady at the starting concentration, and no Pu is seen in the U Tank. The U/Pu product tank sees an increase in the Pu:U ratio at startup, temporarily exceeding the target 30% Pu. This ratio then decreases and levels off to 30%. It is likely that the use of steady-state D-values is leading to this transient at startup, and it is not clear if this behavior would be expected.

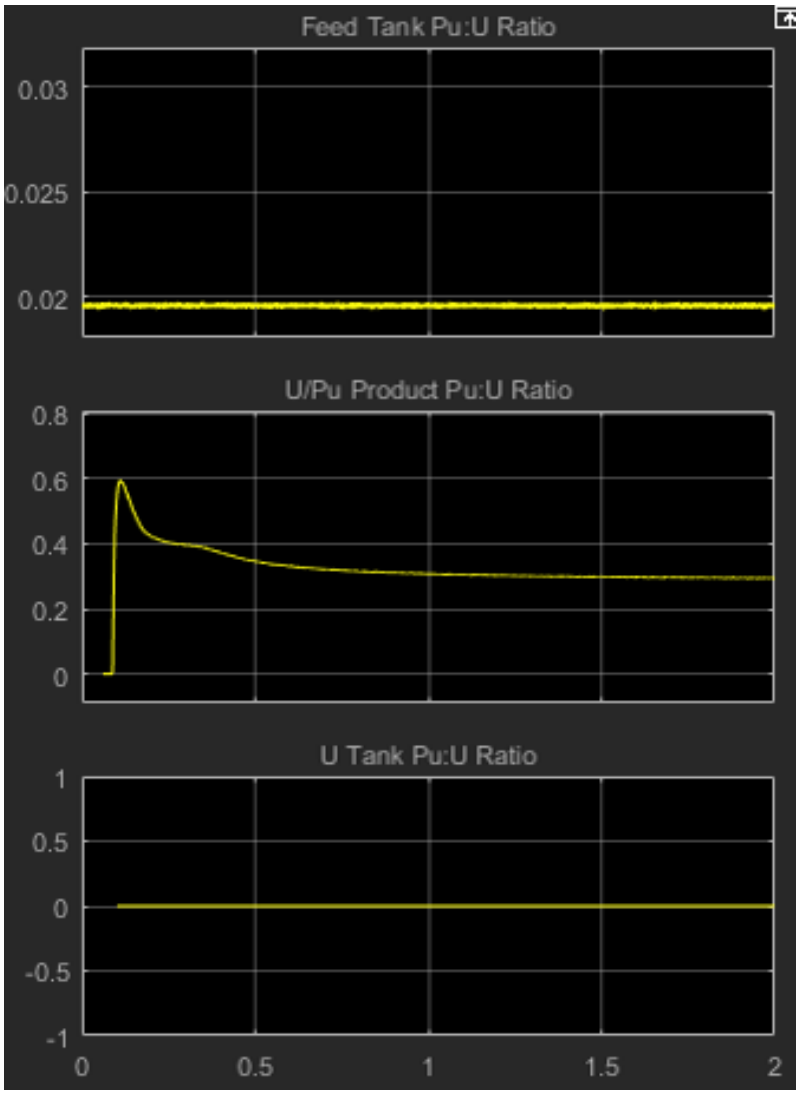

Figure 4: Pu/U ratios in feed and product tanks.

Figure 5 shows the predicted Pu/U ratios for the seven probes along with the overall measurement uncertainty on the final Pu/U ratio (shown in the lower right plot). The behavior appears to be as expected with the more notable results being the loaded solvent and final product. The overall uncertainty on the ratio at one standard deviation levels out at 1.8%, which is a relative value, so the ratio is held at 30% +/- 0.5%. These numbers will need to be verified after better uncertainty data is found.

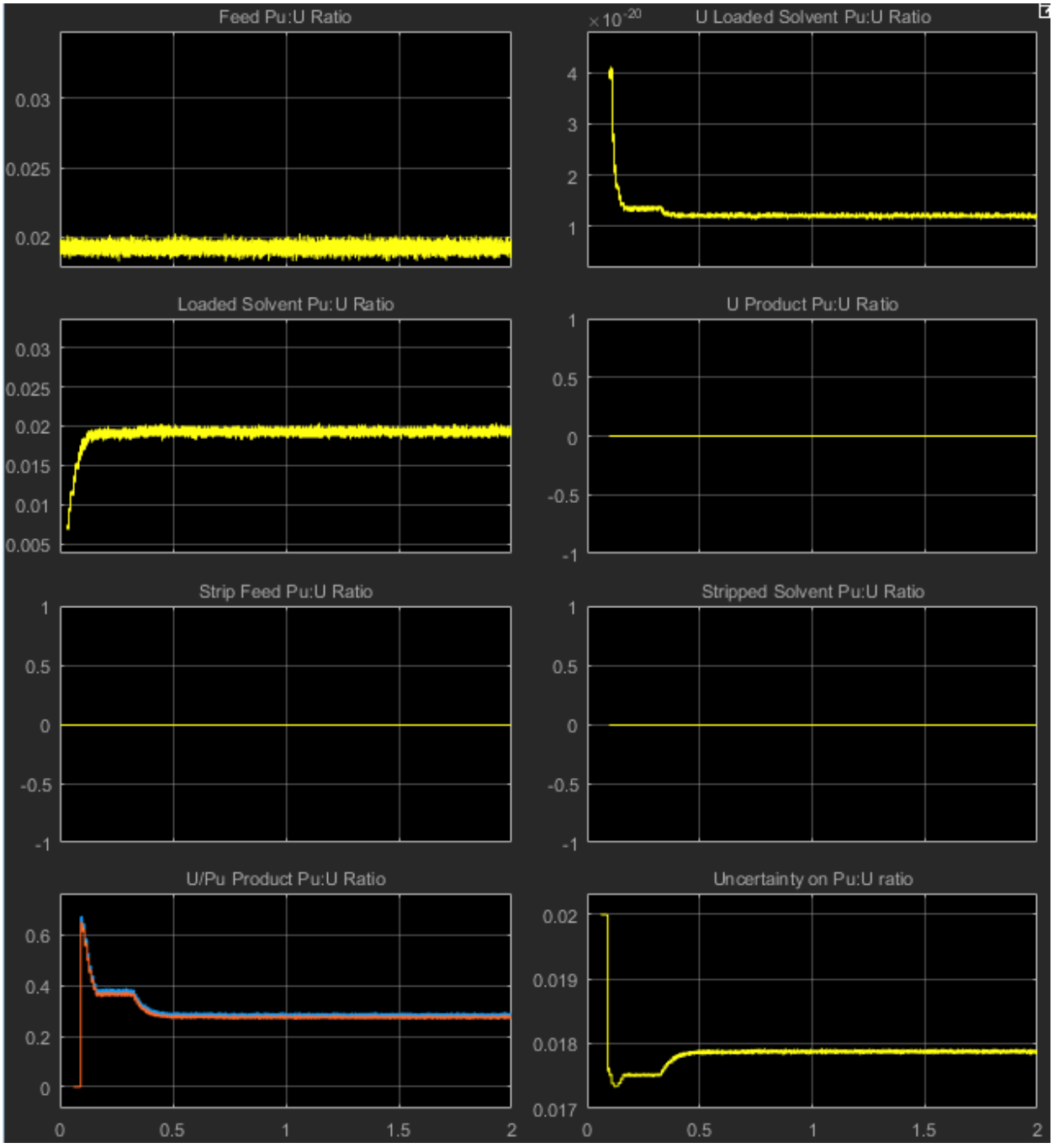

Figure 5: Predicted Pu/U ratios from spectroscopic probes and uncertainty on the final value.

4.2. Variable Test

In order to explore the transient nature of the model, and to make sure the model was able to run correctly, some variability was programmed into the model. The first variation was to change the fuel feed from a 2% Pu/U ratio to a 3% Pu/U ratio after the first hour. The second variation was to change the nitric acid scrub flowrate (in the U/Pu strip contactors) from 0.7 to 0.8 L/hr after 90 minutes.

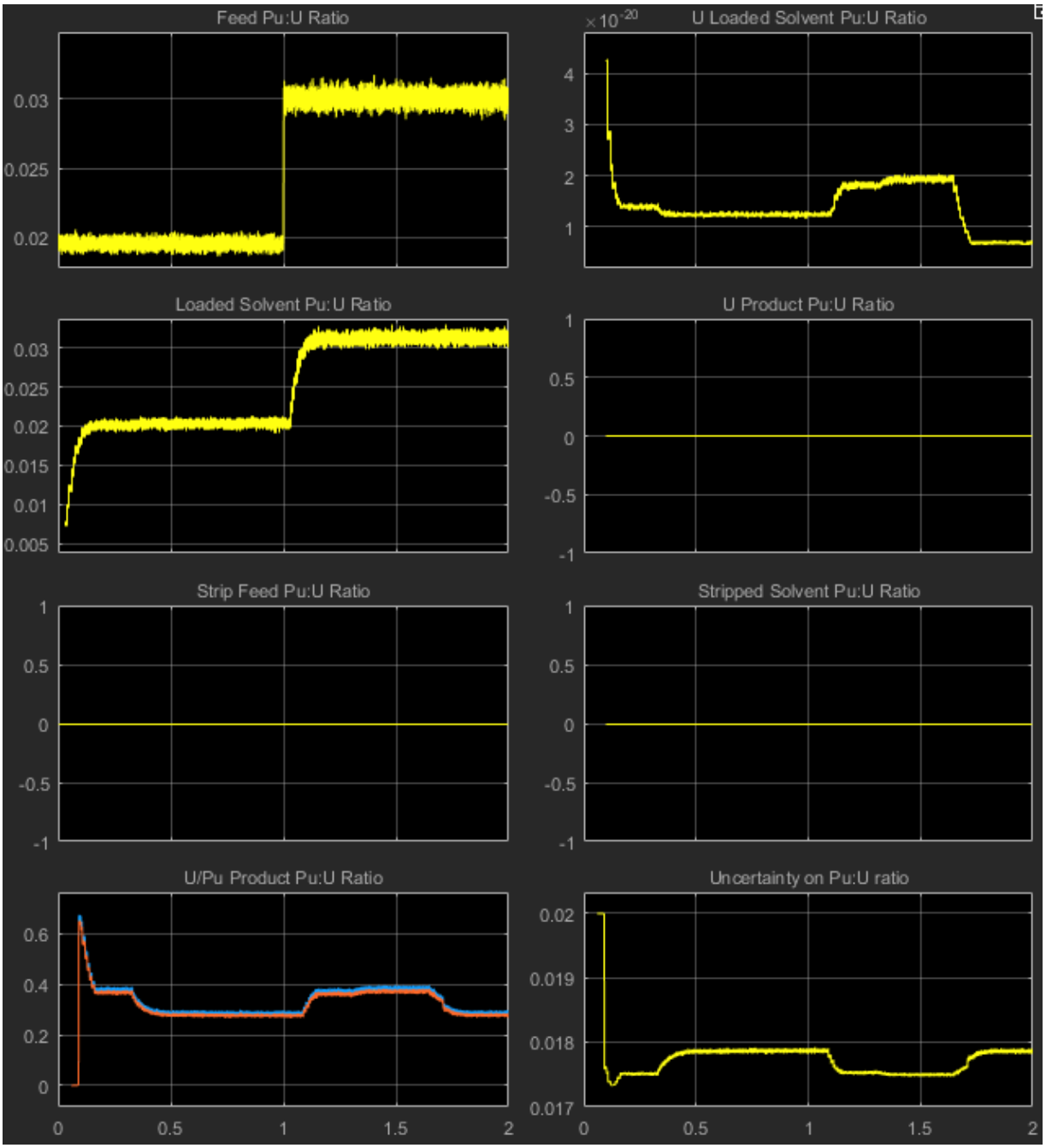

Figure 6: Pu/U ratios from the spectroscopic probes

Figure 6 shows the results from the spectroscopic probes. The change in the feed solution at hour 1 increases the Pu/U ratio of the loaded solvent and the final product. This value went over 30% to about 38%. The subsequent change in the nitric acid scrub flowrate was then able to bring the ratio back down to 30%. This particular scenario was modeled to show how the process can be controlled during normal process variation. On-line monitoring should provide timely data so that such transients can be responded to quickly.

Figure 7 shows the final Pu/U ratio in the product tank. Since this measurement is from a mixture, it smears out the change in the Pu/U ratio. The ratio does increase slightly after the fuel change, but then starts to go back down after the process change.

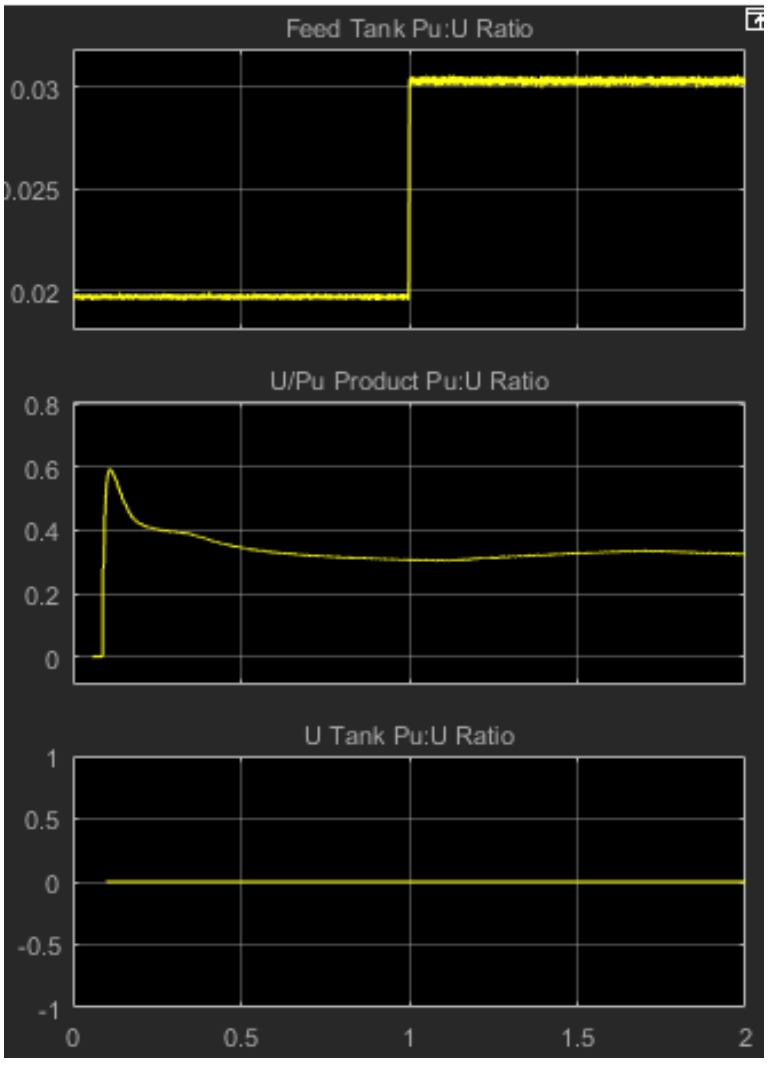

Figure 7: Feed and product tank ratios for the variable test.

5. DISCUSSION & CONCLUSION

The initial dynamic model development for the CoDCon testing has been presented. An initial model has been developed using Matlab Simulink and based on the flowsheet data provided by the CoDCon team. The model appears to be generating correct results, but will need to be validated with the experimental data from the testing at PNNL. This report outlines the progress to date, but the model will continue to be developed and updated as experimental data becomes available.

Initial results confirm that the process is able to produce a product with a 30% Pu/ 70% U. A variable test was also examined using the model to explore the transient nature of the system to process changes. This example demonstrated how tweaking the flowrates of cold chemicals could be used to keep the product at the correct range. Future work can explore these variables in more detail.

6. REFERENCES

1. G.J. Lumetta et al., "CoDCon Project: Design of the Phase ~~I~~ 1 Testing System," FCRD-MRWFD-2017-00359 (PNNL-26173), Pacific Northwest National Laboratory, January 2017.
2. B.B. Cipiti, "Safeguards Performance Modeling: New Approaches for Safeguards by Design," Institute of Nuclear Materials Management Annual Meeting, Atlanta, GA, July 2016.
3. B.B. Cipiti, "Integrated Accountability and Process Monitoring Methods for Reprocessing," 9th International Conference on Facility Operations – Safeguards Interface, Savannah, Georgia, September 23-28, 2012.

DISTRIBUTION

2 Department of Energy
Attn: James Bresee & Patricia Paviet

1 Pacific Northwest National Laboratory
Attn: Gregg Lumetta

2 Idaho National Laboratory
Attn: Terry Todd & Jack Law

1 Oak Ridge National Laboratory
Attn: Emory Collins

1 Argonne National Laboratory
Attn: Candido Pereira

1 Savannah River National Laboratory
Attn: Tracy Rudisill

1	MS0747	Sylvia Saltzstein	6225
1	MS0899	Technical Library	9536 (electronic copy)


Sandia National Laboratories