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A Parametric Study of Uranium Sensitivity in an Aqueous Separations Simulation

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INTRODUCTION

Counter current two-phase solvent extraction is carried out in the HM-process used at the H-Canyon facility at the Savannah River Site. The separation phases are an aqueous, higher density solution of uranyl nitrate in nitric acid and an organic lower density solution of tributyl phosphate in normal paraffin diluent. These two phases flow in opposite directions through banks of mixer settler stages. They are mechanically mixed in the mixing section and then expected to separate in the long settling section such that at the end organic may exit near the top of the settling section and aqueous near the bottom. Two cycles of extraction are currently carried out (Ref. 1-4). The first cycle partitions uranium from the transuranics and fission products and the second cycle purifies the uranium product.

The separations processes have an allowed range of acceptable values for the input streams' flow rates and compositions. These then determine how the material is distributed through the system during operation. In general, it is preferred to know what range of output can be expected from each process given the allowed range of inputs. For criticality safety concerns, it is of interest to know where in the process equipment fissile material is concentrating and what parameters affect that location and concentration. For process efficiency, it is of interest to know what parameters can be adjusted to increase product purity, decrease waste or cold chemical usage, or increase throughput rate. Predictive chemistry modeling of the process provides a good indication the local concentrations of uranium, plutonium, acid, and reductant in both phases of the extraction media.

Savannah River Site currently employs a predictive chemistry model called SEPHIS, of which three versions are available for use (Ref. 5) at Savannah River Site and have varying levels of functionality and complexity of use. The SEPHIS Modification 4 version is selected for this sensitivity study (Ref. 6-9).

DESCRIPTION OF THE WORK

Process Description

The Savannah River Site H-Canyon facility currently operates a uranium separation and purification process known as HM-Process which is derived from Purex process chemistry and utilizes a low tributyl phosphate (TBP) concentration due to the processing of highly enriched uranium (Ref. 1,4). Two cycles of processing are used: the first cycle (three mixer settler banks A, B, and C) separates uranium from fission products, transuranics, and the fuel matrix. The second cycle (two mixer settler banks D and E) further purifies the uranium. In both cycles, a single solvent

(TBP and normal paraffin mixture) source feeds the cycle. Also, in both cycles, process chemicals are made up and sampled before use allowing tighter control on their composition.

In the first cycle, uranium is fed to a 16-stage mixer settler (A-Bank), along with acid and solvent process streams. The uranium loaded solvent flows to the 16-stage B-Bank which has acid and solvent flows as well. The solvent then flows to the 12-stage C-Bank where the uranium is stripped from it with a dilute acid stream. Parameter ranges for the first cycle are shown in Table I.

In the second uranium cycle, uranium is fed to a 16-stage D-Bank which has acid, reducing agent, and solvent flows. The uranium loaded solvent then flows to the 12-stage E-Bank where the uranium is stripped from it with a dilute acid stream. Parameter ranges for the second cycle are shown in Table II.

Parameter Variation Methods

Each of the parameters' ranges listed above is cast as a uniform distribution between the minimum and maximum. A uniform distribution is appropriate here because any value within the range is considered acceptable to run the process. No value between the range endpoints is more or less preferred than another. Another way to view this is that any set of parameter values that fall within the acceptable range is a credible run of the process.

Two approaches are used and subsequently compared in this sensitivity study. In the first approach, a Python based script is used to generate 1000 perturbations of for each cycle in which all parameters available for perturbation are randomly perturbed within their acceptable ranges. This approach reflects reality of how the processes are run.

The second approach uses a Python based computer script to generate 150 perturbations in which all process parameters available for perturbation are held at their midpoint value except one which is allowed to be perturbed within its range. This process is repeated for each parameter in turn. This approach intends to look at the individual contribution of each parameter to the overall variation in each process. Competing effects were expected.

RESULTS AND FUTURE WORK

Previous work has shown that in these two systems, neutron multiplication, and thus criticality concern, is driven by the aqueous fissile content (Ref. 1-3,5). Therefore, the results presented here focus on the aqueous uranium content, though the predictive model SEPHIS gave results for various chemical species in both phases.

Anticipated Process Ranges

Both criticality concerns and process efficiency consideration can be addressed by knowing the expected range of fissile uranium concentration in the bank locations. Stage-wise aqueous uranium concentration is shown on Fig. 1 and 2 for the two cycles. The First Cycle product stream had a range of 1.635 to 3.977 g U/L. The Second Cycle product stream had a range of 5.250 to 8.916 g U/L. This is the most practical result of this study.

Output Parameter Distributions

This study input known uniform (i.e. flat) distributions into the code. Key output distributions are shown in Fig. 3 parts a through d. These histograms represent the result of the 1000 sample all-perturbed cases. Part (a) shows the First Cycle product distribution (i.e. C-Bank Stage 12). Part (b) shows the peak concentration stage in the B-Bank. Part (c) shows the Second Cycle product distribution (i.e. E-Bank Stage 12). Part (d) shows the peak concentration stage in the D-Bank. The only firm conclusion is that these are not uniform distribution coming out, verifying that the simulation, when all parameters are allowed to vary, is non-linear.

None of the output distributions appear to follow any statistical models such as the normal or uniform distributions. One of the distributions that appeared close to being normal was checked and was found to not be normal. By visual inspection, one of the distributions appeared to have a skewed (higher order) Weibull distribution. If time wasn't such a limiting factor, a more rigorous test of each of the distributions would have been conducted.

From the output distributions, it can be concluded that the processes involved are comprised of higher order relations. This result is expected due to the chemistry involved in this system. The higher order relations mean that creating a statistical model of the system would be challenging if possible at all. The ease of running the SEPHIS model negates the need for such a model.

Component Linearity

A simple linearity test was performed. If the model was truly linear, then for any output in any stage the result of perturbing each individual stream should sum to the result where all streams are perturbed simultaneously. If the model is weakly non-linear, this would be expected to sum to within a few percent. Table III presents examples of selected data for each of the cycles wherein individually perturbed components that resulted in the largest ranges were summed directly and by root sum of squares and then compared to the all-perturbed case. All values in Table III are range of aqueous uranium concentration in g U/L.

The First Cycle cases summed the effects of the feed uranium and acid concentrations, the A and B bank organic flow rates, and the feed flow rate. The Second Cycle cases summed the effects of the feed uranium and acid concentration, the D-bank organic flow rate, the feed flow rate, and the D-bank acid concentration.

The outputs were determined to be non-linear responses by this test.

Covariance Correlation

One final search for a correlation of the outputs was made. Distribution of the uranium between the two phases is a function of acid, reductant, TBP, and uranium concentrations. It is a chemical property that is part of the nature of the process and cannot be fundamentally changed, only controlled. An attempt was made to search for a dependence on the covariance between an output and an input parameter with respect to the distribution coefficient.

For example, given aqueous uranium concentration outputs for perturbing feed flow, the distribution coefficient of uranium in each bank stage was calculated for each case. Using the standardized covariance function in Excel the covariance of aqueous uranium concentration with respect to feed flow was plotted versus the distribution coefficient (Fig. 4a). Note both the distribution coefficient and the standardized variance values are unitless. The plots are for visual inspection to determine a trend.

Results for key parameters are shown in Fig. 4 parts a through d. No correlation was found in any of the parameters examined.

ACKNOWLEDGEMENTS

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Table I. Ranges Analyzed - First Cycle Parameters

Parameter	Description
Process feed stream	5.4 to 6.6 L/min 2.5 to 4.68 g U/L 0.00365 g Pu/L 4.45 to 7.49 M acid
A-Bank acid stream	1.3 to 1.5 L/min 3.5 to 4.3 M acid
A-Bank solvent stream	10.1 to 11.6 L/min
B-Bank acid stream	6.3 to 7.1 L/min 1.5 to 1.5 M acid 0.00375 to 0.22 M reductant
B-Bank solvent stream	18.7 to 21.5 L/min
C-Bank acid stream	7.4 to 8.5 L/min 0.005 to 0.035 M acid
TBP Concentration (all solvent streams)	7.35 to 8.10 vol.%

Table II. Ranges Analyzed - Second Cycle Parameters

Parameter	Description
Process feed stream	8.1 to 8.95 L/min 4.6 to 6.6 g U/L 3.9 to 5.8 M acid
D-Bank acid stream	3.43 to 3.79 L/min 0.825 to 1.5 M acid
D-Bank solvent stream	25.5 to 27.71 L/min
D-Bank reductant stream	0.07 to 0.08 L/min 0.02 to 0.06 M reductant
E-Bank acid stream	6.48 to 7.16 L/min 0.005 to 0.04 M acid
TBP Concentration (all solvent streams)	7.35 to 8.10 vol.%

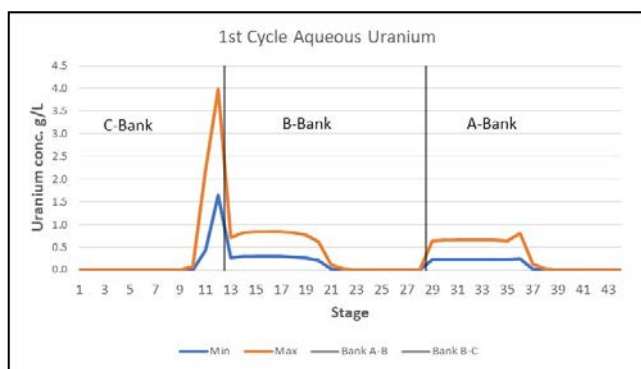


Fig. 1. Aqueous uranium concentration distribution in First Cycle extraction banks.

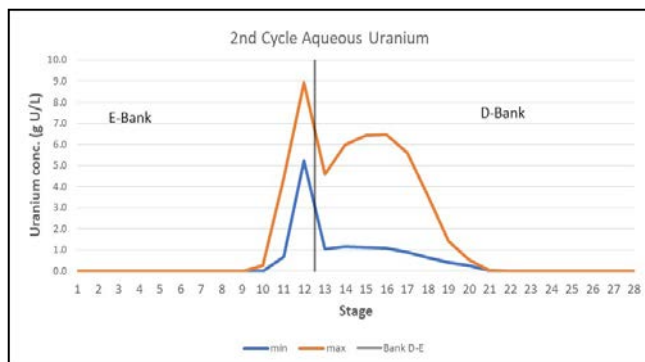


Fig. 2. Aqueous uranium concentration distribution in Second Cycle extraction banks.

Table III. Component perturbation summation in select First and Second Cycle Cases (g U/L).

Bank - Stage	All perturbed case	Sum of top contributors	Sum of squares of top contributors
A-3	0.0568	0.4336	0.2898
A-4	0.0568	0.4512	0.3005
A-5	0.0563	0.4517	0.3008
A-6	0.0553	0.4518	0.3009
A-7	0.0529	0.4518	0.3008
A-8	0.0600	0.4518	0.3004
D-4	5.380	6.074	3.710
D-5	4.718	4.834	2.725
D-6	2.9231	2.6293	1.3354
D-7	1.0141	0.9133	0.4453
D-8	0.2505	0.2735	0.1717
D-9	0.02987	0.03044	0.01669

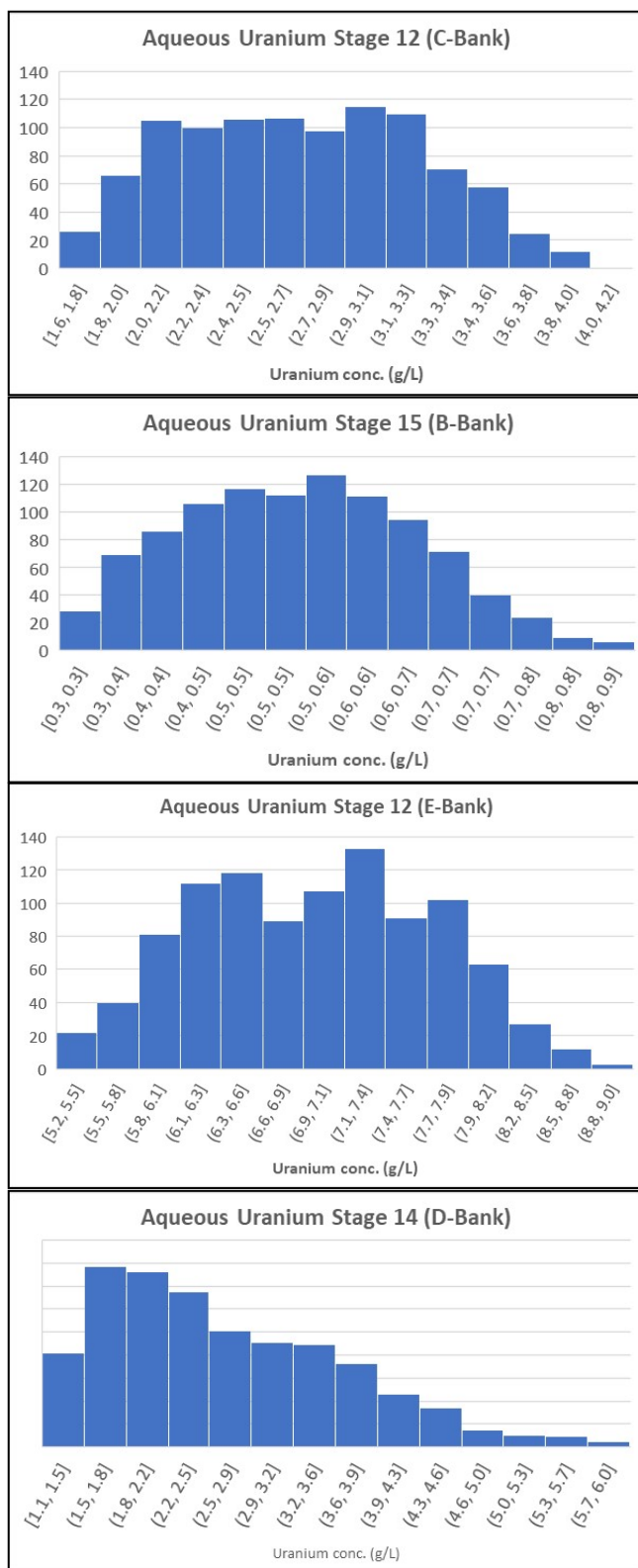


Fig. 3. From top (a) First Cycle product distribution, (b) peak concentration stage in the B-Bank, (c) Second Cycle product distribution, (d) peak concentration stage in the D-Bank

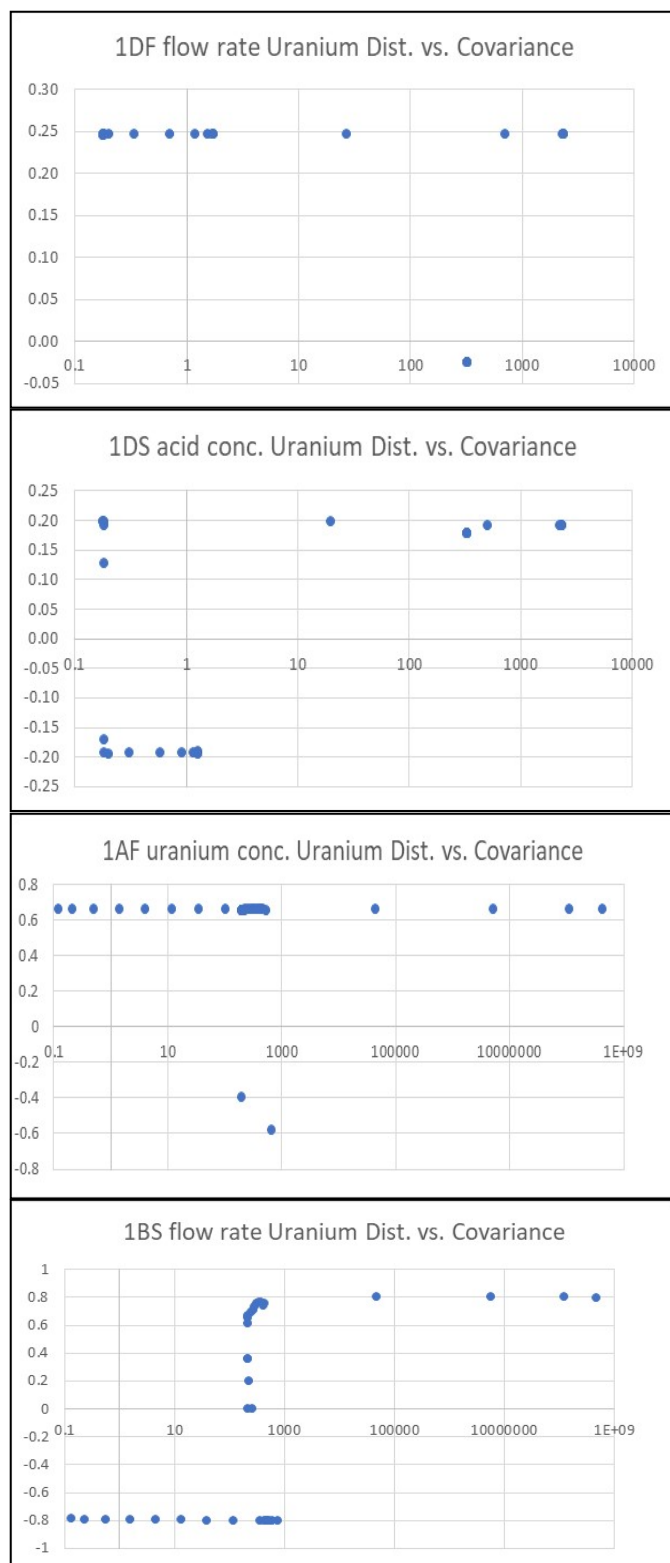


Fig. 4. Covariance of the aqueous uranium concentration with respect to (from top) (a) D-Bank feed flow rate, (b) D-bank acid stream concentration, (c) A-Bank uranium concentration in the feed stream, and (d) B-Bank solvent flow rate. All values plotted versus distribution coefficient.

