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Time Dependent Neutron Multiplication Simulation in Aqueous Separations Upsets

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INTRODUCTION

Aqueous solvent extraction of fissile material relies on the continuous mass transfer of these materials between two immiscible solutions, typically tributyl phosphate in a hydrocarbon diluent and an aqueous (commonly nitric) acid. To keep the fissile material migrating in the desired direction through the extraction process equipment requires careful control of the chemical composition and flows of the two phases.

The degree to which changes in chemistry affect the reflux of chemical species depends on the dynamics of the system – how fast the phases are flowing past each other, their contact time, settling time, and how close the acid conditions are to elution or extraction.

Of the 22 known processing criticality accidents (Ref. 1), only one has occurred within a solvent extraction system. That accident was the result of multiple concurrent, uncorrected, upset conditions that occurred over time. The slow but near total dilution of acid, missing and inactive instrumentation, and a deliberate increase in the fissile material feed rate all contributed.

In these systems, it is often assumed that without nearly immediate (on the order of a few minutes) process correction or shutdown, criticality will inevitably result from the buildup of fissile material in the equipment. While conservative and easily defensible, this position has been shown in previous work (Ref. 2, 3) to not always be physically accurate. An upset may lead to undesirable extraction conditions but may not result in a criticality. This is due to the physical limitations of the chemistry, the processing equipment, or both.

To demonstrate the dynamic behavior of a such a system a multi-physics simulation was conducted in this work. Acid concentration upsets in two solvent extraction systems were dynamically simulated. The process used is a modified PUREX using low concentration tri-butyl phosphate (TBP) as the solvent and adjusting the reducing conditions to partition (First Cycle) both neptunium and plutonium as well as fission products away from the uranium and then to concentrate and purify the uranium (Second Uranium Cycle). Uranium enrichment has no lower limit but is held to less than 73 wt.% U-235. Feed concentrations are on the order of 4-6 g U/L. The resulting chemical configurations were also dynamically simulated to calculate a time dependent k-effective for the systems. The First Cycle uses three mixer-settler banks A, B, and C with fissile feed applied to A-Bank. The Second Uranium Cycle uses two mixer-settler banks D and E with fissile feed applied to D-Bank.

SEPHIS Mod-4 (Ref. 4) was used for chemistry dynamics simulations and KENO VI in SCALE 6.1 with ENDF-B VII 238-group cross section was used for neutronics calculations.

SIMULATION APPROACH

Acid Dilution Upset Dynamic Chemistry Simulation

The operating conditions in Table I were set as chemical stream inputs to the SEPHIS program for simulation. The code was configured to simulate the cold chemical streams for one hour before introducing the uranium bearing feed. The feed was then ramped up at 5% per minute for 20 simulated minutes to its full flow value. Sometime long after equilibrium was established (after 535 simulated minutes in the First Cycle and after 325 simulated minutes in the Second Uranium Cycle) an instantaneous upset was introduced. Each of the following was simulated initiating from equilibrium normal conditions:

- Dilution of the First Cycle feed bank scrub acid from 3.70 M to 1.55 M.
- Decrease of the First Cycle feed bank solvent flow from 10.66 L/min to 5.00 L/min
- Dilution of the Second Uranium Cycle feed bank scrub acid from 0.95 M to 0.50 M.
- Decrease of the Second Uranium Cycle feed bank solvent flow from 26.02 L/min to 15.00 L/min

It is important to note that these conditions are beyond what is considered credible abnormal upsets because they represent head tank chemistry that would be disallowed for use due to pre-operational sampling and decreases in flow that would trigger multiple layers of alarms and engineered interlocks.

Acid dilution causes more of the uranium to remain in the aqueous phase. Decrease of the solvent flow increases the residence time of the solvent allowing more uranium to complex. Each upset increases the uranium in the aqueous phase which drives the neutron multiplication (Ref. 5) and which also results in product loss. That is why these upsets were chosen for simulation. The time dependent volumetric material balance is governed by the equation:

$$\frac{d\left[V_{a,j}\cdot x_j^i + V_{o,j}\cdot y_j^i\right]}{dt} = \sum_{in} A_{j,k}(t)\cdot x_{j,k}^i + \sum_{in} O_{j,k}(t)\cdot y_{j,k}^i - \sum_{out} A_{j,k}(t)\cdot x_{j,k}^i - \sum_{out} O_{j,k}(t)\cdot y_{j,k}^i$$

Where A and O are the aqueous and organic volumetric flow rates, respectively, in a single discrete stage i for any component species j in a contacting stream k. The mass transfer between phases is related by the distribution coefficient:

$$D_i^j = y_{i,out}^j / x_{i,out}^j$$

Discrete Time-Step Neutron Multiplication Simulation

The SEPHIS jobs were set to print data every five simulated minutes after the upset. This was sufficient time to allow convergence between time steps and noticeable changes in the distributions. This was also a reasonable time scale for operations to detect an incipient upset in the data trend over ten points (30 second readings are normal).

For each time step, the aqueous and organic compositions for each stage were collected and input to a spreadsheet. The spreadsheet back-solved the solvent extraction equations to get a mixer solution and translated the compositions into an input for KENO VI using mixer settler geometry and assumed isotopics. This was done for each of the three mixer-settler banks in the First Cycle and both banks in the Second Uranium Cycle. Time step cases were run until the chemical compositions for all the banks in the cycle reached a new equilibrium state after the upset. Multiplication factors effectively converge before chemical conditions do.

Table I: Simulation Input	
First Cycle	
First Cycle TBP (volume %)	7.5
A-Bank aqueous flow (L/min)	3.70
A-Bank aqueous acidity (M)	1.38
A-Bank feed uranium concentration (g U/L)	4.50
A-Bank feed acidity (M)	1.60
A-Bank feed flow (L/min)	6.13
A-Bank organic flow (L/min)	10.66
B-Bank aqueous flow (L/min)	18.71
B-Bank aqueous acidity (M)	1.55
B-Bank organic flow (L/min)	6.33
C-Bank aqueous flow (L/min)	7.57
C-Bank aqueous acidity (M)	0.016
Second Uranium Cycle	
Second Uranium Cycle TBP (volume %)	7.5
D-Bank aqueous flow (L/min)	3.31
D-Bank aqueous acidity (M)	0.95
D-Bank feed uranium concentration (g U/L)	5.25
D-Bank feed acidity (M)	5.50
D-Bank feed flow (L/min)	8.67
D-Bank organic flow (L/min)	26.02
E-Bank aqueous flow (L/min)	6.94
E-Bank aqueous acidity (M)	0.010

Time Discretization versus Kinetics

There are two reasons that the choice was made to simulate the problem as many discrete time steps, each considered to be a unique condition, rather than treat this as a neutron kinetics problem.

First, the system in question, as will be shown, is substantially subcritical so assumptions underlying point reactors kinetics are not appliable; this is not a reactor near critical. Second, the time scale over which process chemistry changes were predicted to occur is substantially longer than the time scale for neutron kinetics. In essence, the solutions change chemical properties over the course of many minutes while kinetics parameters such as delayed neutron half-life or mean neutron lifetime are on the order of seconds.

RESULTS

A-Bank Acid Dilution

The acid dilution primarily affects the bank in which it was introduced. The aqueous (solid line) and organic (dashed line) uranium concentration distribution in A-Bank is shown in Fig. 1 at various times. The bank upset starts with the cycle at equilibrium. At 60 minutes operators would be administratively required to shutdown the cycle (if interlocks had not already done so since the acid is outside of specification). A new equilibrium state is reached by 355 minutes after the upset. An intermediate time of 200 minutes is also shown. Table II records the calculated multiplication factor for each First Cycle banks for the upset.

Dilution of the acid causes the uranium held in the aqueous phase to increase resulting in additional fissile material in the bank. This is expected as extractability of uranium into TBP decreases with decreasing acidity. The peak concentration remains less than the feed concentration. The process is not run near the uranium saturation of the TBP so it is the TBP concentration and flow rate, and hence the residence time for the TBP, that limit extraction of uranium and other species. Since there is no change in the phase flow rates or TBP properties, there is little effect on the organic phase concentration of uranium. Even with an instantaneous change in acid concentration, the cycle is predicted to take nearly 6 hours to reach a new equilibrium point. A typical First Cycle run can last 36 to 48 hours depending on batch size. The multiplication factors predicted throughout the upset are significantly subcritical (Table II).

A-Bank Solvent Flow Decrease

The solvent flow decrease primarily affects the bank in which it was introduced, though the solvent is the feed to the next two banks. The aqueous (solid line) and organic (dashed line) uranium concentration distribution in A-Bank is shown in Fig. 2 at various times. The bank upset starts with the cycle at equilibrium. At 60 minutes operators would be administratively required to shutdown the cycle (if interlocks had not already done so since the solvent flow is outside of specification). A new equilibrium state is reached in only 120 minutes after the upset. An intermediate time of 30 minutes is also shown. Table II records the calculated multiplication factor for each First Cycle banks for the upset.

Since the process is not run near the uranium saturation of the TBP, decreasing the flow rate increases the residence time of the TBP allowing more uranium to extract into it. The phases by nature are in a constant state of mass transfer described by the distribution of uranium between the two phases for given chemistry of each phase. For the flow rates, acidity and TBP conditions specified, the increased organic concentration results in an increased aqueous uranium concentration as well. Compared to the acid dilution upset, these new equilibrium conditions are reached faster and higher concentrations are realized but still the multiplication factors predicted throughout the upset are significantly subcritical (Table II).

D-Bank Acid Dilution

As with the First Cycle, the acid dilution primarily affects the bank in which it was introduced. The flow rates in the Second Uranium Cycle are higher than in the First Cycle so changes occur more rapidly, though still on the order of hours.

The aqueous (solid line) and organic (dashed line) uranium concentration distributions in D-Bank are shown in Fig. 3 at various times. The bank upset starts with the cycle at equilibrium. At 60 minutes operators would be administratively required to shutdown the cycle (if interlocks had not already done so since the acid is outside of specification). A new equilibrium state is reached by 180 minutes after the upset. An intermediate time of 120 minutes is also shown. Table III records the calculated multiplication factor for each Second Uranium Cycle bank for the upset.

Dilution of the acid causes the uranium held in the aqueous phase to increase. The peak concentration does exceed feed concentration and it also exceeds the ANSI/ANS 8.1 (Ref. 6) safe concentration for an infinite reflected solution. However, the banks are finite, segmented slab tanks in dry air. Second Uranium Cycle is also not run near uranium saturation of the TBP and since there is no change in the phase flow rates or TBP properties, there is little effect on the organic phase concentration of uranium. Even with an instantaneous change in acid concentration, the cycle takes 3 hours to reach a new equilibrium point. A typical Second Uranium Cycle run can last 24 to 32 hours depending on batch size. The multiplication factors predicted throughout the upset are significantly subcritical (Table III).

D-Bank Solvent Flow Decrease

As with the First Cycle, the solvent flow decrease primarily affects the bank in which it was introduced, though the solvent is the feed to the next bank. The aqueous (solid line) and organic (dashed line) uranium concentration distribution in D-Bank is shown in Fig. 4 at various times. The bank upset starts with the cycle at equilibrium. At 60 minutes operators would be administratively required to shutdown the cycle (if interlocks had not already done so since the solvent flow is outside of specification). A new equilibrium state is reached in by 240 minutes after the upset. An intermediate time of 120 minutes is also shown. Table III records the calculated multiplication factor for each Second Uranium Cycle banks for the upset.

Since the process is also not run near the uranium saturation of the TBP, decreasing the flow rate increases the residence time of the TBP allowing more uranium to extract into it. For the flow rates, acidity and TBP conditions specified, the increased organic concentration results in an increased aqueous uranium concentration as well. The effect on the aqueous concentration is more pronounced here than in the First Cycle due to the chemistry and flow balance between the two streams. However, compared to the Second Uranium Cycle acid dilution upset, these new equilibrium conditions are reached slower and with uranium lower concentrations. The multiplication factors predicted throughout the upset are significantly subcritical (Table III).

CONCLUSIONS

While only selected results are shown in this summary, chemical distributions and multiplication factors for every bank were computed for every 5 minutes of simulation time. In all of the upsets the peak uranium concentrations and peak multiplication factors for the affected bank occur at the new equilibrium state. None of the upsets approached a critical configuration. Since the upsets are beyond credible abnormal conditions these particular upsets can potentially be ruled out as criticality scenarios requiring controls.

More significantly, this work successfully demonstrates time dependent coupling of the neutronic and chemistry simulation systems. SEPHIS variants are some of the few nuclear solvent extraction codes that can simulate dynamic conditions; most compute only equilibrium conditions. Future development could automate the data handling between the two systems.

At the time of this writing, mission changes have suspended the Second Uranium Cycle and the First Cycle is planned to cease operation within the next year. Therefore, future development of this methodology specifically related to these processes is unlikely at this time.

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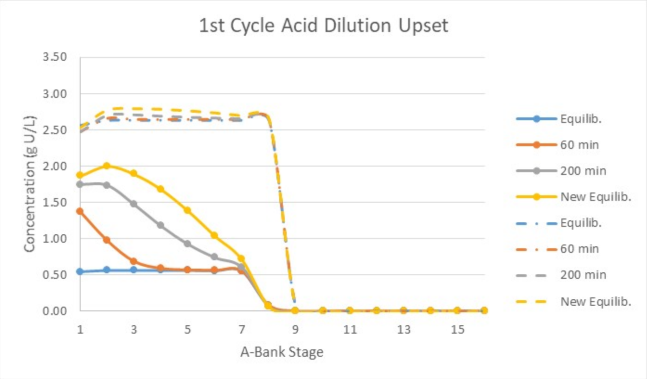

Fig. 1. A-Bank uranium distribution at various times during acid dilution upset. Solid line is aqueous phase, dashed line is organic phase.

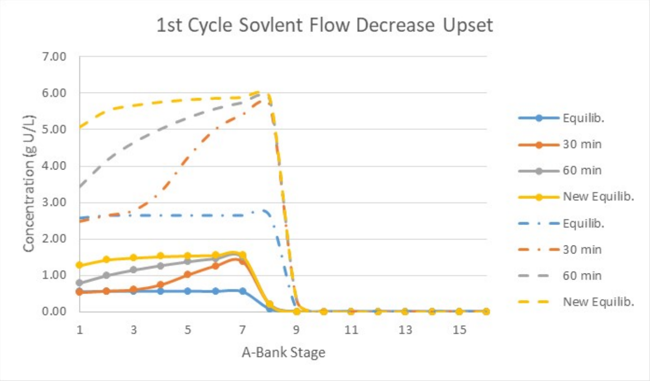

Fig. 2. A-Bank uranium distribution at various times during solvent flow decrease upset. Solid line is aqueous phase, dashed line is organic phase.

Table II: First Cycle k-calculated			
A-Bank Acid Dilution Upset			
Time	*A-Bank*	*B-Bank*	*C-Bank*
Equilibrium	0.1207	0.0627	0.1718
60 min	0.1272	0.0631	0.1719
200 min	0.1418	0.0630	0.1717
355 min (new equilibrium)	0.1492	0.0631	0.1718
A-Bank Solvent Flow Decrease Upset			
Time	*A-Bank*	*B-Bank*	*C-Bank*
Equilibrium	0.1207	0.0626	0.1718
30 min	0.2426	0.0790	0.1716
60 min	0.2451	0.0791	0.1719
120 min (new equilibrium)	0.2462	0.0803	0.1718

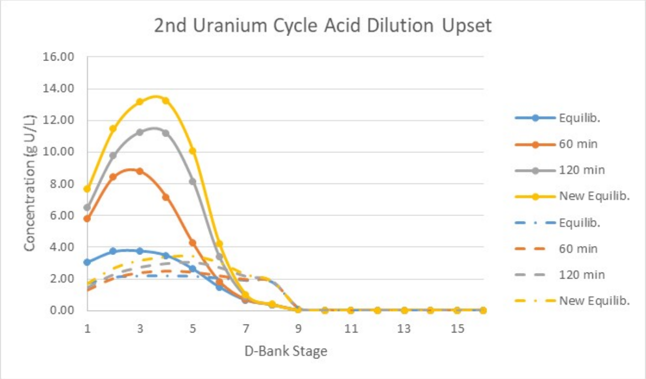

Fig. 3. D-Bank uranium distribution at various times during acid dilution upset. Solid line is aqueous phase, dashed line is organic phase.

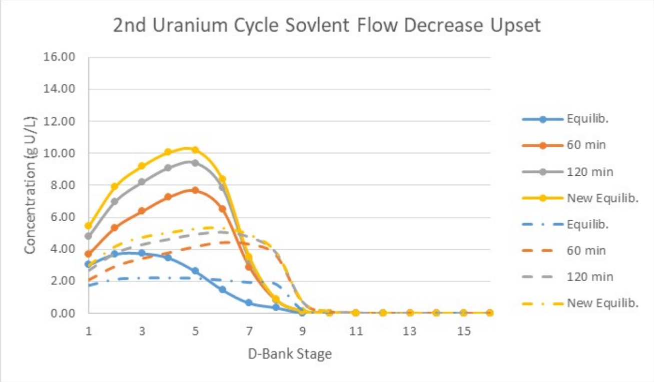

Fig. 4. D-Bank uranium distribution at various times during solvent flow decrease upset. Solid line is aqueous phase, dashed line is organic phase.

Table III: Second Uranium Cycle k-calculated		
D-Bank Acid Dilution Upset		
Time	*D-Bank*	*E-Bank*
Equilibrium	0.1805	0.2780
30 min	0.3301	0.2769
60 min	0.3965	0.2774
120 min	0.4358	0.2774
180 min (new equilibrium)	0.4371	0.2766
D-Bank Solvent Flow Decrease Upset		
Time	*D-Bank*	*E-Bank*
Equilibrium	0.1808	0.2786
30 min	0.3619	0.2776
60 min	0.3778	0.2775
120 min	0.3910	0.2776
240 min (new equilibrium)	0.3961	0.2782