Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

A Chemistry Based Criticality Safety Evaluation of the HM-Process Mixer Settlers

Tracy Stover and Stephen Kessler

Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC 29803, Tracy.Stover@srs.gov

INTRODUCTION

The criticality safety of Savannah River Site's H-Canyon two cycle uranium extraction and purification process, called the HM process, is examined. Explicit Monte Carlo models of the multi-stage mixer-settlers are generated for the first time using the KENO-VI module of the SCALE 6.1 code package and spanning normal operating conditions and a wide range of potential upset conditions with stage-wise compositions based directly on SEPHIS Mod-4 chemistry models of the same conditions.

To achieve industrial scale processing, mixer-settlers are often not geometrically favorable to prevent criticality so other means must be used for criticality safety, namely control of fissile concentration and mass. Historically, the worst case upset is a reflux condition resulting from some stream flow or composition that is off from the normal operating conditions. A reflux is considered to be the state in which the fissile material is not proceeding in the desired direction, i.e. is stripping rather than extracting or vice versa. The criticality safety analyses which set the current operational limits were conducted many years ago with less sophisticated codes and only loosely tied criticality to chemistry. Those analyses conservatively assumed that a reflux changed the behavior of the mixer-settler such that the fissile content collected continuously in only three stages of the mixer-settler, at a rate based on the SEPHIS modeling, until criticality occurred. This implies that under some condition the distribution coefficient of the fissile material either goes to infinity or zero, which is not physically achievable. In such a scenario the operator would have some amount of time to react and correct the problem before sufficient fissile material built up in the mixer-settler and caused a criticality.

In reality, an upset in a stream would lead to the transition to some new, though undesired, equilibrium state of operation. The distribution coefficients would change, but would not diverge. In this work, aqueous and organic streams are modeled for both the mixer and the settler region of each stage of each bank using chemical distribution data from SEPHIS and solving the chemical equations for a wide range of operational parameters spanning normal and upset conditions. Conservative assumptions are made regarding enrichment and reflection and whole bank multiplication factor is evaluated using discrete stage-wise compositions.

DESCRIPTION OF THE WORK

HM-Process Analytical Range

The H-modified (HM) process uses tributyl phosphate (TBP) in organic n-paraffin to extract and purify uranium from spent nuclear fuel. This takes place in two cycles of counter-current solvent extraction. The aqueous stream is a weak to moderate nitric acid and the feed stock may be in either an aqueous or organic stream. The first cycle is a three stage process that separates the uranium from the fuel matrix, fission products, and most of the transuranic actinide content. The first cycle, consisting of two 16-stage banks (A and B-banks) and one 12-stage bank (C-Bank), is a three stage process that separates the uranium from the fuel matrix, fission products, and most of the transuranic actinide content. The first cycle aqueous product is then concentrated, adjusted for acidity and fed to the second cycle.

The second cycle, consisting of one 16-stage bank (D-bank) and one 12-stage bank (E-bank), is a two stage process that further purifies the uranium and removes to a great extent any remaining transuranic actinides and fission products. . A computational chemical analysis of the system was performed with SEPHIS Mod-4 in References 1 and 2.

The base case for the first cycle feed (into Stage 8 of the A-Bank) is 8.3 L/min, 0.5 M nitric acid, 8.4 g U/L, and 6 M excess nitrate from dissolution of the aluminum by nitric acid (Reference 1). The base case for the second cycle feed (into Stage 8 of the D-Bank) is 8.1 L/min, 4.5 M nitric acid, and 4.2 g U/L (Reference 2). The base case values and analyzed range for all other parameters are given in Table 1. These ranges greatly exceed the operational bounds required by References 3 and 4 and as such go beyond credible abnormal conditions.

D-Bank also includes a low flow, low concentration (0.067 L/min, 0.02 M) stream of ferrous sulfamate to strip out any remaining trace plutonium. It is conservative not to include this in the KENO models as it takes up volume otherwise occupied by fissile-bearing solution. It is included in the SEPHIS runs to ensure correct chemistry results.

Upsets in the feed streams were not considered primarily because the feed streams are the most highly controlled process streams and also the point to which the other streams' allowable flows are referenced.

Creating Mixer-Settler Models

The mixer-settlers are individual stages arranged into either a 16-stage or 12-stage bank. The settler is a long section free of most obstructions wherein the streams can settle into an equilibrium state before moving on to the adjacent stages through flow channels at the end of the section. The settler is physically separated from the mixer by a set of baffles which help to settle the streams. The mixer section is substantially smaller and contains a false bottom, flow channels for the organic and aqueous streams including an aqueous inlet compartment, and an impeller to mix the two streams together. The KENO models employed in this study conservatively neglect the volume occupied by the impeller, baffles, and flow channeling plates which adds more fissile material to the system than is actually possible and also brings the flowing stream compositions modeled into direct contact with each other.

Table I: HM-Process Base, Operational, and Upset Properties of Streams

Parameter	Base Case	Analyzed Range
First Cycle TBP (volume %)	7.5	3 – 14
A-Bank aqueous flow (L/min)	1.9	0.1 – 5.4
A-Bank aqueous acidity (M)	3.8	0.25 to 6.5
A-Bank organic flow (L/min)	14.6	2.6 – 28.6
B-Bank aqueous flow (L/min)	8.7	1.7 – 15.7
B-Bank aqueous acidity (M)	1.5	0.2 to 4.5
B-Bank organic flow (L/min)	26.3	5.3 – 54.3
C-Bank aqueous flow (L/min)	10.4	5.4 – 10.4
C-Bank aqueous acidity (M)	0.04	0.008 – 2.5
Second Cycle TBP (volume %)	7.5	1.5 – 20.0
D-Bank aqueous flow (L/min)	2.5	0.1 – 8
D-Bank aqueous acidity (M)	0.9	0.1 – 4.5
D-Bank organic flow (L/min)	15.9	1.9 – 30
E-Bank aqueous flow (L/min)	5.8	0.2 – 12.8
E-Bank aqueous acidity (M)	0.01	0.01 – 1.81

The generic geometries of the sections of the two bank types are given on Table II (Reference 5). The thickness of the stainless steel plates that make up the body of the mixer settler are also given. The width and length of the false bottom are the same as the width and length of the mixing section. A small air pocket is modeled around the mixer-settle but an additional conservatism is added to the models in assuming water reflected boundary condition beyond that air pocket instead of a vacuum boundary.

Table II: Dimensions of the Mixer-Settlers

Parameter (all dimensions in inches)	16-Stage Bank	12-Stage Bank
Settling section height *x* width *x* length	10*x*8*x*48	12*x*12*x*108
Mixing section height *x* width *x* length	8*x*8*x*9	10*x*12*x*13.5
False bottom height	2	2
Bottom, front, and back plate thickness	0.5	0.5
Top and side plate thickness	0.25	0.25

The compositions involved are simplified into aqueous and organic, initial (in) and final (out) compositions for every stage. The aqueous and organic inlet compositions are smeared into a single composition for the mixer section. The settler section is filled with the aqueous composition on the bottom and the organic composition on the top. The height of the aqueous portion of the settler fill is determined based on the volumetric flow rate ratios of the two streams.

Solvent extraction of metals in an aqueous acid and organic solvent is a textbook problem that has been well defined. Chemistry codes, such as SEPHIS, have been developed to solve this problem specifically for nuclear chemical engineering purposes. For the purposes of generating the mixer-settler models in this work, explicit determinations of initial and final stage-wise concentrations of both streams are necessary.

The solution of the chemical equations may begin by considering a single stage with aqueous inputs and outputs (labeled *x*) and organic inputs and outputs (labeled *y*). At any point, given the aqueous flow S and the organic flow E to the mixer settler plus any organic feed Fs or aqueous feed Fa, the inlet and outlet concentrations (also considered initial and final, respectively) of species j can be determined by

$$y_{i,in}^{j} = y_{i,out}^{j} + \left(\frac{E+Fa}{S+Fs}\right)\left(x_{i,out}^{j} - x_{i,in}^{j}\right) \qquad (1)$$

Using the distribution coefficient relationship $D_i^j = y_{i,out}^j / x_{i,out}^j$ and knowing that the stages are connected sequentially such that $y_{i,in}^j = y_{i+1,out}^j$. So long as the user defines an aqueous and organic stream as boundary conditions, this becomes a tri-diagonal matrix system of equations that can be easily solved for the initial and final streams for any component *j* (e.g. j = uranium). This solution does represent a single state in time taken as the equilibrium condition. The distribution coefficients are calculated from the SEPHIS outputs. SEPHIS outputs stage-wise final concentrations at the equilibrium conditions (or at any user requested time). The distribution coefficients, which are tailored for the specific condition being analyzed, are computed directly from this by simply dividing the organic concentration by the aqueous concentration.

A spreadsheet was set up to automatically create these three SCALE-compatible input compositions for each stage after the stage-wise concentrations were solved. The spreadsheet also uses the densities and isotopics of the stream constituent species (Tables III and IV). The spreadsheet user also can define and manipulate the mixer settler geometry. This information is then translated into compositions and geometries and KENO input decks are automatically set up, ready to be copied and pasted.

The base case TBP is 7.5 volume percent of the input organic stream which results in a combined TPB and n-paraffin density of 0.7743 g/cm^3. In perturbation cases adjusting the TBP volume percent, the density is also adjusted accordingly.

Using this information and the uranium and nitric acid stage-wise concentrations, three compositions for each stage are constructed each composed of H, C, O, P, N, U-235, and U-238 in weight percent of the composition.

Table III: Primary Organic Species in HM Process

Name	Chemical Formula	Density (g/cm^3)
Tributyl Phosphate (TBP)	$C_{12}H_{27}O_4P$	0.9727
Nitric Acid	HNO_3	1.55
n-paraffin:	--	--
20% dodecane	$C_{12}H_{26}$	0.749
40% tridecane	$C_{13}H_{28}$	0.756
40% tetradecane	$C_{14}H_{30}$	0.763
Uranyl nitrate	$UO_2(NO_3)_2$	2.203

Table IV: Primary Aqueous Species in HM Process

Name	Chemical Formula	Density (g/cm^3)
Water	H_2O	0.9982
Nitric Acid	HNO_3	1.55
Uranyl Nitrate (aqueous)	$UO_2(NO_3)_2 * 6(H_2O)$	2.4183**

The first step is to determine the volumes of the streams, which is done using the volumetric flow rates and the volume k where k is either the mixer volume or the settler volume.

$$V^k_{organic} = \frac{E + Fs}{E + Fs + S + Fa} V_k \qquad (2)$$

$$V^k_{aqueous} = \frac{S + Fa}{E + Fs + S + Fa} V_k \qquad (3)$$

As a note, $V^k_{aqueous}$ for k= settler is divided by the surface area of the settler to give a height of the aqueous component within the settler so that the remaining height is the organic component.

The mass of uranium in grams and the number of moles of nitric acid is then given by

$$M^k_U = V^k_{organic} * y^U_{i,l} + V^k_{aqueous} * x^U_{i,l} \qquad (4)$$

$$M^k_{acid} = V^k_{organic} * y^{acid}_{i,l} + V^k_{aqueous} * x^{acid}_{i,l} \qquad (5)$$

Where l is the "in" for the mixer and "out" for the settler. The mass of the acids is then simply the number of moles times the molecular weight of n_{acid} = 63.01284 g/mole (based on values from *Table of the Nuclides* 17th Edition).

The mass of the uranyl nitrate in the organic ($UO_2(NO_3)_2$ called M_{UN}) and aqueous streams ($UO_2(NO_3)_2 * 6(H_2O)$ called M_{UNaq}) is then given by

$$M^k_{UN} = V^k_{organic} * y^U_{i,l} / f_{UN} \qquad (6)$$

$$M^k_{UNaq} = V^k_{organic} * x^U_{i,l} / f_{UNaq} \qquad (7)$$

Where f_{UN} and f_{UNaq} are the mass fractions of uranium in each compound. The mass of the TBP and n-paraffin (called M_{TBP+n}) is given by

$$M^k_{TBP+n} = \left\{ V^k_{organic} - M_{UN} / \rho_{UN} - \left(V^k_{organic} * y^{acid}_{i,l} * n_{acid} \right) / \rho_{acid} \right\} * \rho_{TBP+n} \qquad (8)$$

Where ρ_{TBP+n} is the density of the combined TBP and n-paraffin organic stream, ρ_{UN} is the density of $UO_2(NO_3)_2$, and ρ_{acid} is the density of nitric acid.

Similarly the mass of the water in the aqueous stream (called M_{H2O}) is given by

$$M^k_{H2O} = \left\{ V^k_{aqueous} - M_{UNaq} / \rho_{UNaq} - \left(V^k_{aqueous} * x^{acid}_{i,l} * n_{acid} \right) / \rho_{acid} \right\} * \rho_{h2O} \qquad (9)$$

Where ρ_{h2O} is the density of water.

SCALE composition inputs in weight percent also require a density of the composition. The composition density in stage *i* section *k* is calculated by

$$\rho^k_i = \frac{M^k_{UN} + M^k_{UNaq} + M^k_{TBP+n} + M^k_{H2O} + N^k_{acid} n_{acid}}{V^k_{aqueous} + V^k_{organic}} \qquad (10)$$

For k = mixer, l = in and the equations above are evaluated as written to give a mixed aqueous and organic composition. For k = settler, l = out and the equations are solved twice, once for organic and once for aqueous compositions by zeroing out the unneeded components. Having now three compositions each with a known mass of known molecular species, the atom fractions and atomic weights of H, C, O, P, N, and U that compose each species are used to determine the weight percent of each element in the composition. Uranium is in turn further broken into U-235 and U-238 isotopics by its enrichment. The only remaining components of the SCALE composition input are the alphanumeric identifier and a temperature, which is assumed to be 318 K. A conservatism is added by assuming the uranium is 95 weight percent U-235. H-Canyon's HM Process is nominally designed for 73 weight percent.

RESULTS AND CONCLUSIONS

The base and upset cases for each of the banks were modeled. All multiplication factor results are the calculated eigenvalue (k-calc) plus two times the Monte Carlo uncertainty (sigma). The multiplication factor for the banks under the base case conditions are A-Bank: 0.353, B-Bank: 0.167, C-Bank: 0.185, D-Bank: 0.241, and E-Bank: 0.205. Fig. 1 shows a scatter plot of all of the multiplication factor results. Of 15 upsets examined only 1 had results that approached critical (Fig. 2). The upset of interest is the flow rate of the clean organic stream entering the A-Bank; the base case condition is marked with a red circle and the range maintained during normal operations marked with an orange rectangle.

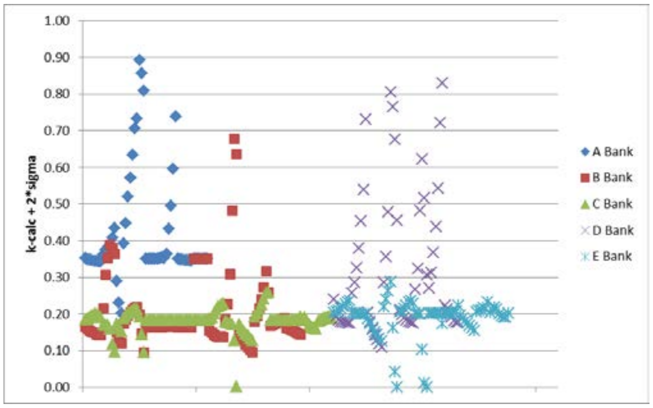

Fig. 1: Multiplication factor from all examined cases.

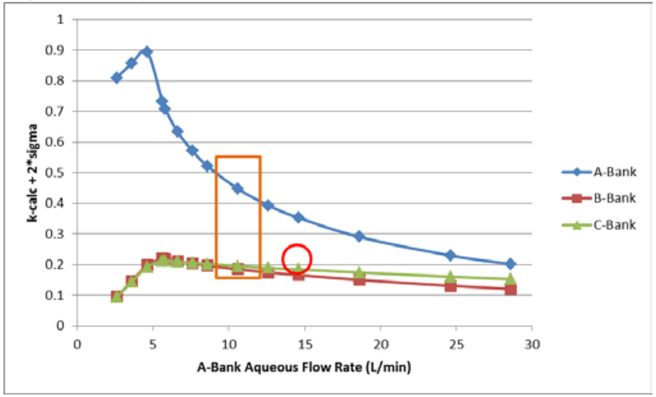

Fig. 2: Upset in the A-Bank organic stream flow rate.

Since the A-bank organic flow rate upset had the potential to challenge criticality, this condition was further examined. As modeled, the peak occurred at 4.6 L/min with a multiplication factor of 0.894. However, if the water boundary condition is removed and replaced with vacuum, the multiplication factor drops to 0.867. If the U-235 enrichment is dropped from 95 weight percent to 73 however, the multiplication factor reduces to 0.384 and if the water boundary is removed at 73 weight percent the multiplication factor is only 0.375. This should put into perspective the other cases shown in Fig. 1.

All results showed subcriticality across a wide range of conditions even with the conservative assumptions made. Given these results, none of the conditions in any mixer-settler bank will result in a criticality for uranium enrichments up to 95 weight percent. The ranges of upsets examined are beyond the operational tolerances maintained so it is incredible that some extreme conditions could occur since operators would have to shut down once outside tolerance. The external conditions around the mixer-settler have only a minor effect due to the thick steel construction.

With this knowledge, postulated criticality accidents resulting in the mixer-settler can now be concluded to be incredible under the nominal and credible abnormal HM process chemistry and may be eliminated from the safety analysis. An alternative use of this information is to update the nominal chemistry to allow for increased ranges of operation. Future work may look at perturbations in the feed streams. The one shortcoming of this analysis is the lack of consideration of upsets in the process temperature. Unfortunately, current versions of SEPHIS produce less reliable results with low TBP concentrations when the temperature is significantly varied.

NOMENCLATURE

x = aqueous stream concentration
y = organic stream concentration
D = distribution coefficient
E = organic volumetric flow rate
Fa, Fs = organic and aqueous feed streams, respectively
S = aqueous volumetric flow rate
ρ = density
M = mass
V = volume
N, n = number of moles and molar weight, respectively
f = mass fraction of element in compound

Subscripts and Superscripts

i = stage number
j = component (e.g. uranium, nitric acid, etc.)
k = section (mixer or settler)

REFERENCES

1. W.G. DYER, “First Cycle SEPHIS Modeling of the H-Canyon HM Process”, NMS-ETS-98-0075, Savannah River Site (1998).
2. W.G. DYER, “Second Uranium Cycle SEPHIS Modeling of the H-Canyon HMN Process for Reflux Conditions and Neutron Monitor Placement”, NMS-ETS-2000-00059, Savannah River Site (2000).
3. C.D. NGUYEN, “First Cycle Operating Ranges and PPL’s for HEU-Metals Material”, X-CLC-H-00074 Rev. 21, Savannah River Site (2009).
4. W.M. BENNETT, “Second Uranium Cycle Operating Ranges for Processing Materials with Maximum

Enrichment of 73 Wt.% U-235", X-CLC-H-00121 Rev. 10, Savannah River Site (2015).

5. M.L. HYDER, et. al., "Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant", DP-1500, Savannah River Site, (1979)