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# Bounding the Chemistry Conditions in the HM Solvent Extraction Process Criticality Safety Analyses

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## INTRODUCTION

An approach new to the H-Canyon facility criticality safety analysis has been performed using highly detailed models of the H-Modified process mixer settlers. The HM process uses tributyl phosphate (TBP) in organic n-paraffin to extract and purify uranium from used nuclear fuel. This occurs in two cycles of counter-current solvent extraction. The aqueous stream is a weak to moderate nitric acid and the feed stock is an aqueous stream. The 1st Cycle, consisting of two 16-stage banks (A and B-Banks) and one 12-stage bank (C-Bank), is a three step process that separates uranium from the fuel matrix, fission products, and most of the transuranic actinide content. The 1st Cycle aqueous product is concentrated, adjusted for acidity and fed to the 2nd Cycle. The 2nd Cycle, consisting of one 16-stage bank (D-Bank) and one 12-stage bank (E-Bank), is a two-step process that further purifies the uranium and removes to a great extent remaining actinides and fission products

Each stage of the mixer settler banks is modeled as three unique compositions: the mixer as a combined composition of aqueous and organic components and the settler one aqueous and one organic component. This work addresses what is believed to be normal, credible abnormal, and beyond credible abnormal conditions for a particular postulated series of process parameter upsets.

The level of detail and the the source for the stage-wise compositions are both new and unique to criticality safety analyses of the HM process. Initial work was presented in Ref. 1 and has since been refined. A predictive chemistry model for flowsheet development has been used to solve the solvent extraction equations for the prescribed conditions and the output of that model was then transformed into compositions for each mixture in each stage.

The remaining question upon which to achieve consensus is if the approach was appropriately conservative by concluding the chemistry is appropriately bounded.

Computational modeling for criticality calculations was performed using KENO-VI in the SCALE 6.1 code package. Computational modeling of the chemistry was performed using the SEPHIS Modification 4 code.

## DESCRIPTION OF THE WORK

### The HM-Process Upsets Considered

Ref. 1 concluded that during an upset in a stream parameter, the process would transition to a new, though undesired, equilibrium state of operation.

The refinement of the work since Ref. 1 has focused largely on moving to a flowsheet based on 73 wt.% uranium enrichment, examining the existing procedural operating setpoints and limits for that flowsheet, and focusing on the acid concentration upsets. Current H-canyon operational requirements for confirming acid concentrations include taking multiple sample with independent verifications. This is a time intensive and time sensitive operation for the operators. Removing acidity confirmation as a criticality safety control would increase operational efficiency.

Acid concentrations upsets have been considered for the aqueous streams in all banks. This represents up to eight of the postulated inadvertent criticality scenarios associated with the HM Process. For brevity, only upsets in the B-bank and D-Bank aqueous streams are presented. Because the banks operate in sequence, changes to B-bank do not affect A-bank. Conversely, changes in B and D banks affect C and E banks, respectively.

The first cycle is nominally fed 4.5 gU/L 1.6 M acid uranyl nitrate solution at 6.13 L/min. The B-bank aqueous stream has a nominal setpoint of 1.55 M nitric acid at 6.33 L/min. The operational band is limited to 1.5 to 1.6 M acid on this stream. The second cycle is nominally fed 5.25 gU/L 5.5 M acid uranyl nitrate solution. The D-bank aqueous stream has a nominal setpoint of 0.95 M nitric acid at 3.31 L/min. The operational band is limited to 0.8 to 1.5 M acid on this stream. Once the process stream goes outside of the operational band, the operators have a short time to correct the situation or the whole process must be shut down. Being at the limits of the operational band is considered a credible abnormal, however this analysis goes beyond those conditions. The B-bank acid upset is analyzed from 0.2 M to 4.5 M nitric acid and the D-bank acid upset is analyzed from 0.05 M to 3.5 M nitric acid. These ranges are judged to be beyond the credible abnormal conditions.

Note that an upset of more than one process parameter would reflect multiple concurrent upsets which are not to be evaluated.

### SEPHIS Calculations

The SEPHIS code is designed to arrive at a predictive chemistry result for each stage for all of the banks in a cycle (either A, B, and C or D and E). The process parameters are specified including acid concentration, uranium feed concentration, flow rates, and any additional reducing or oxidizing agents. Plutonium and other fissile isotopes are expected to be negligible in the process and are neglected. Since the cycles are not in reality run at the maximum 73 wt.% uranium enrichment, this is still acceptably conservative. The user then specifies the setup of the system, i.e. into and out of which stages of which banks the various process streams flow. SEPHIS can run sequential cases automatically so one case may start at the normal condition and then sequentially run cases either going up or down in acid concentration of the upset stream, retaining the other process parameters between each case.

In examining whether the chemistry is bounded, the chemistry conditions at the allowed operational bands are compared stage-wise to the minimum and maximum chemistry conditions over the entire analyzed range. Chemistry conditions are taken to mean the uranium and acid aqueous and organic concentrations and the calculated distribution coefficient for each.

### KENO-VI Model of the Mixer Settlers

Models of the mixer settlers were made per the methodology outlined in Ref. 1, which is summarized here. The first or second cycle is modeled in SEPHIS either at the normal condition or at one of the points in the process parameter upset. SEPHIS is run to convergence at equilibrium and the stage-wise distribution of uranium and acid in both aqueous and organic phase is taken from the SEPHIS prediction. These compositions are used to construct stage-wise aqueous and organic mixtures compatible to SCALE inputs. The physical mixer settler is modeled as a stainless steel bank per the engineering drawings of the built devices. Internal components of the mixer settler are neglected which conservatively adds more fissile solution to the system. Each affected bank is modeled at each of the parameter upset points spanning the credible abnormal upset range.

### Bounding Through Validation and Bias

Only limited original experimental data prepared explicitly for the HM process is available (Refs. 3 and 4) and has been used for many decades of operation. A validation was conducted for the SEPHIS code in Ref. 5 where SEPHIS was set up to model exactly the data points of the experimental results in Refs. 3 and 4. Overall, the code tends to under-predict the distribution coefficient (ratio of a component concentration in the organic phase to its concentration in the aqueous phase). This results in conservatively high aqueous concentrations of uranium for many of the HM process cases analyzed. Since SEPHIS was originally correlated to the PUREX (plutonium uranium extraction) process which includes plutonium and runs at a much higher TBP concentration, some differences are expected.

Ref. 5 was surveyed and conservatively large uncertainties on uranium and acid concentration were chosen (30% and 10%, respectively) to represent a flat bias applied to the results. The bias is applied directly to the SEPHIS predicted uranium and acid concentrations in the acid and organic phases; the associated biased distribution coefficients are then also computed. In examining whether the chemistry is bounded, the biased results are also added to the comparison.

### Bounding Through Code Comparison

The SOLVEX code is an older, less advanced alternative to the SEPHIS code. This code performs similar process predictive chemistry, but does not have built-in distribution coefficient correlation. The user must enter not only the process parameters but also either a table or function for the program to interpolate or compute the uranium and acid distribution coefficients from. While this allows the experimental data from Refs. 3 and 4 to be directly used in the analysis, it limits the capability of performing a flexible analysis like the one done with SEPHIS.

SOLVEX cases were prepared using a combination of correlated and tabulated data from Refs. 3 and 4. SOLVEX was run only at the operational bands of the process parameter. The predicted uranium and acid concentrations in the acid and organic phases are taken from the output; the associated biased distribution coefficients are then also computed. In examining whether the chemistry is bounded, the SOLVEX results are also added to the comparison.

### Bounding through Experimental Results

Ideally, experimental data would be available to show that indeed the chemistry predictions are either acceptably accurate or conservative. This is rarely the case.

One set of experimental evaluations is available. In support of other missions, Savannah River National Laboratory (SRNL) did perform experimental analysis of an upset in the acid concentration of the D-bank aqueous stream. This was done in miniaturized versions of the mixer settlers in 2002 (Ref. 6) and those facilities are currently undergoing renovation. That study however concluded that SEPHIS was giving conservative results for acid concentration upsets over the actual observed aqueous concentration of uranium. It also concluded, not surprisingly, that D-bank was more limiting than E-bank. By virtue of their similarity, (same design and similar chemistry) this should also apply to B, C, and potentially A banks as well. SRNL has been requested to evaluate this position. This provides the potential impetus for more experimental data.

The conclusions of Ref. 6 are qualitatively considered in making the case that the chemistry range possible is conservatively bounded by this analysis, and thus so is the neutron multiplication range.

## RESULTS AND CONCLUSIONS

### Criticality Results for an Acid Concentration Upset

The acid concentration upsets for the B and D banks described above were analyzed using the methodology from Ref. 1, applying the appropriate changes for the actual operational parameters for the first and second cycle using the 73 wt.% uranium flowsheet. SEPHIS was run to equilibrium conditions at the normal acid concentration, credible abnormal acid concentrations, and a number of points spanning the analyzed range. The results are shown in Fig. 1 for B-Bank upset and Fig. 2 for D-Bank upset. The k-safe was set at 0.9664 for HEU solutions based on a validation for the SCALE 6.1 KENO-VI code (Ref. 2).

The operational range and the normal condition setpoints were consistently far away from upset conditions that neared k-safe. For the entire evaluated range, k-safe was met. The multiplication followed the *combined* effect of aqueous uranium concentration and stage-wise distribution of the fissile material. The results are favorable so it is imperative to be able to conclusively state the chemistry modeled is acceptably representative of reality.

## Chemistry Bounding Results for the Upsets

Figs. 3, 4, 5, 6, 7, and 8 show the stage-wise results for the B and C bank uranium distribution coefficient, acid distribution coefficient, and aqueous uranium concentration. Likewise Figures 9, 10, 11, 12, 13, and 14 show the stage-wise results for the D and E bank uranium distribution coefficient, acid distribution coefficient, and aqueous uranium concentration. The results on each graph include the SEPHIS results at the operational bands, the minimum and maximum SEPHIS results over the analyzed range, the SEPHIS biased results at the operational bands, and the SOLVEX results at the operational bands.

Note that C and E bank plots only show stages 8 through 12 , because stages 1 through 7 have results near 0 and do not contribute to the understanding of the data.

In nearly all cases, the SOLVEX and SEPHIS results follow similar behavior. In many cases the results at the operational bounds, including those of the biased SEPHIS data, are bounded or effectively bounded by the range or values analyzed over the entire analytical range evaluated. Effectively bounded is taken to mean locations where neutron multiplication is of concern and would be bounded. Large relative variations in the nearly negligible acid entrainment in the organic phase or in locations where uranium concentration is <<1 gU/L do not contribute substantially to the multiplication of the overall system. Large variations there can be tolerated. The aqueous uranium is bounded in all but two cases and those two cases are the C and E bank biased results where the aqueous uranium concentration was *directly increased* by 30% over the predicted value.

Between the various bounding techniques it is believed that the range of analysis performed bounds at a minimum the operational bands allowed for the process. These cases have been shown to be safely subcritical.

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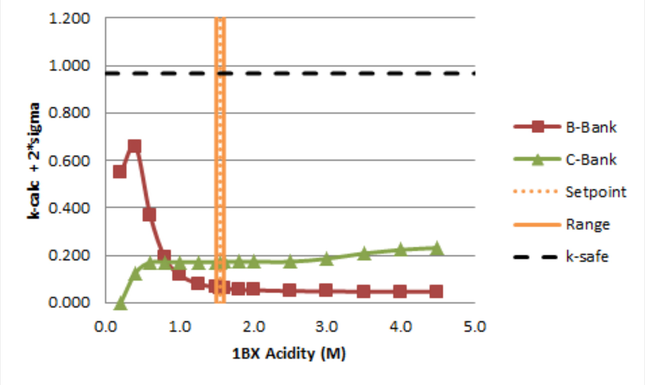

Fig. 1. Neutron multiplication of the B and C banks at various extents of upset B-bank aqueous acid concentration.

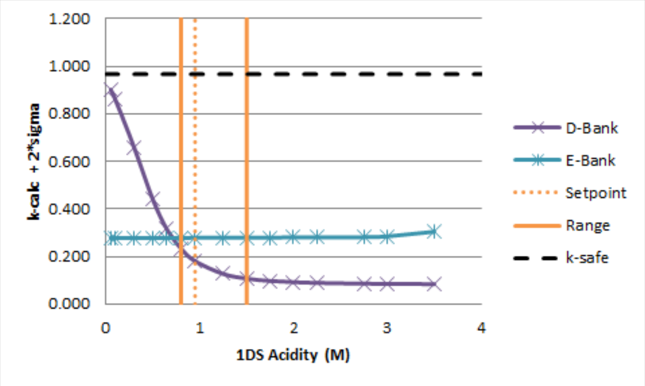

Fig. 2. Neutron multiplication of the D and E banks at various extents of upset E-bank aqueous acid concentration.

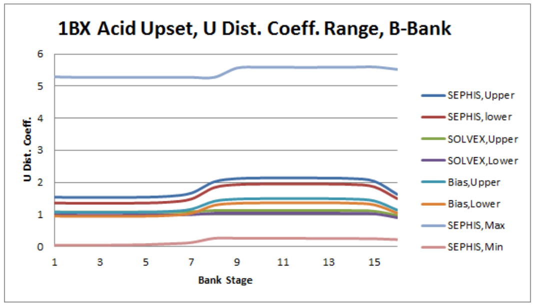

Fig. 3. B-bank uranium distribution coefficient.

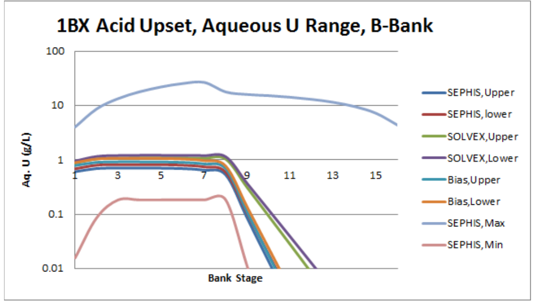

Fig. 4. B-bank aqueous uranium concentration.

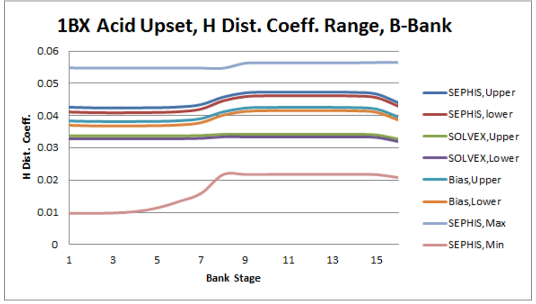

Fig. 5. B-bank acid distribution coefficient.

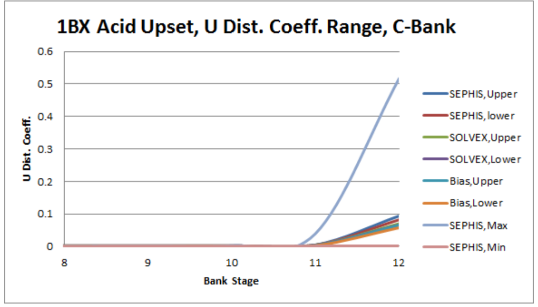

Fig. 6. C-bank uranium distribution coefficient.

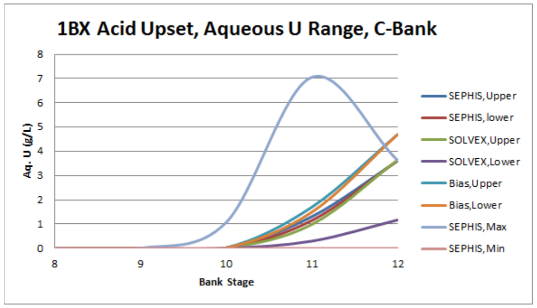

Fig. 7. C-bank aqueous uranium concentration.

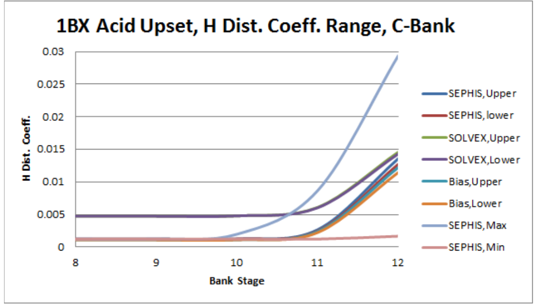

Fig. 8. C-bank acid distribution coefficient.

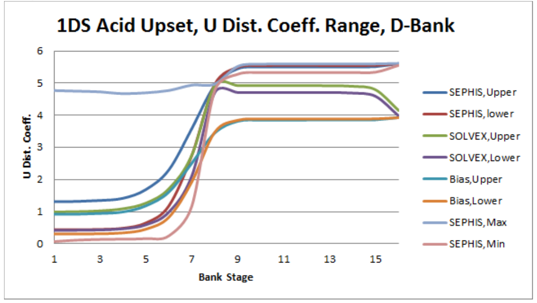

Fig. 9. D-bank uranium distribution coefficient.

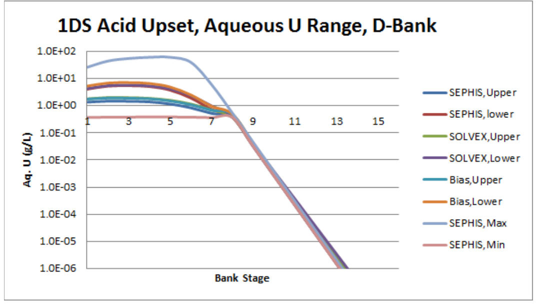

Fig. 10. D-bank aqueous uranium concentration.

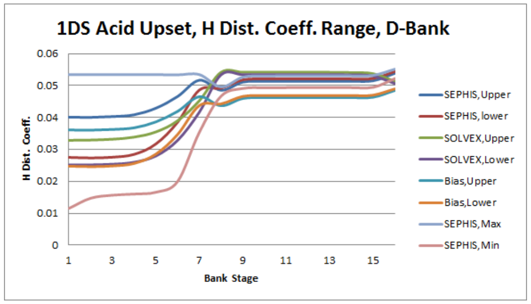

Fig. 11. D-bank acid distribution coefficient.

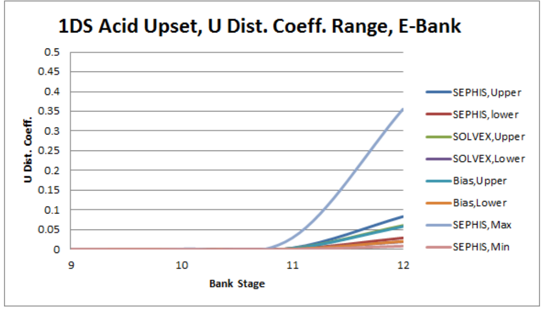

Fig. 12. E-bank uranium distribution coefficient.

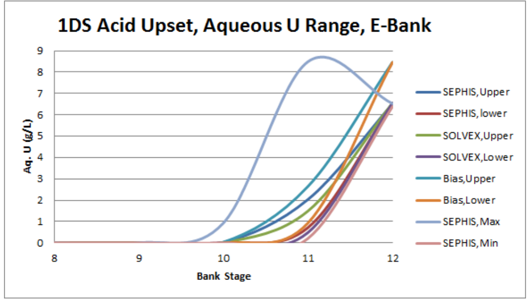

Fig. 13. E-bank aqueous uranium concentration.

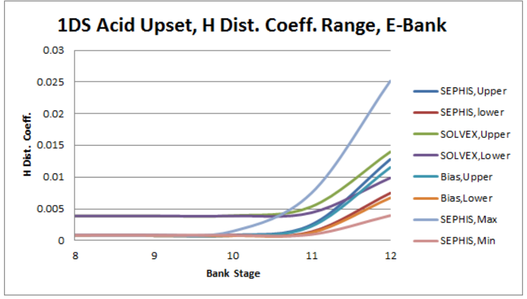

Fig. 14. E-bank acid distribution coefficient.