Elimination of Acid Based Criticality Scenarios in the HM-Process

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INTRODUCTION

Over the last two years, Savannah River Nuclear Solutions Criticality Safety has placed considerable effort on reanalyzing the H-Modified (HM) process postulated criticality scenarios using modern Monte Carlo simulation enhanced with modern predictive chemistry. Reflux induced criticality events believed to be credible based on conservative assumptions and limited modeling have been shown to be not credible due to the nature of the chemistry of the process and explicit modeling of the mixer settler. Initial phases of these efforts have been reported to the criticality safety community in Ref. 1 and 2. This summary marks the first successful elimination of events from the H-Canyon criticality safety analysis which have been shown to be not credible with this new approach. Two postulated criticality scenarios based upon loss of control the nitric acid concentration in 2nd Uranium cycle are eliminated.

Since this is a new methodological approach for the facility, additional levels of expert judgement and validation through experimental data were necessary. This summary is meant to describe both the analytical work and the administrative path taken to achieve this result.

Computational modeling was performed using KENO-VI in the SCALE 6.1 code package (Ref 3) and SEPHIS-P (Ref. 4).

DESCRIPTION OF THE WORK

Process Description

The HM process, a derivative of the PUREX process, uses low concentration 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 uranyl nitrate stream. The 1st Cycle performs removal of fission products and most of the transuranic content. The second cycle is the focus of this work. The 1st Cycle uranium aqueous product is concentrated, adjusted for acidity and fed to the 2nd Cycle. The 2nd Cycle, consisting of one 16-stage mixer-settler bank (D-Bank) and one 12-stage mixer-settler bank (E-Bank), is a two-step process that further purifies the uranium and removes to a great extent any remaining actinides and fission products.

Postulated Events

Two postulated criticality events currently part of the H-Canyon safety analysis from the 2nd Cycle are considered. In one event, the aqueous acid fed to the D-Bank becomes diluted. When the acidity decreases below the minimum limit, uranium is no longer extracted into the organic solvent and continues to concentrate in the aqueous phase resulting in a potential criticality event in the D-Bank. In the second event, the aqueous acid fed to the D-Bank increases above the maximum limit. The organic solution leaving the D-Bank enters the E-bank with a larger than normal acid carryover and increases the acidity of the E-Bank which is supposed to be low acid so the uranium is stripped back into the aqueous. Instead, more uranium is retained in the organic, penetrates deeper into the E-Bank at higher than expected concentrations, and possibly causes a criticality.

Normal and Credible Abnormal Conditions

The second cycle is nominally fed 5.25 g U/L 5.5 M acid uranyl nitrate solution. The uranium has been limited to 73 wt.% enrichment per the established flowsheet and is verified by sample analysis. The D-bank aqueous stream has a nominal 0.95 M nitric acid at a setpoint of 3.31 L/min. The operational band for nitric acid is 0.8 to 1.5 M acid on this stream. The organic solvent is 7.5 volume percent TBP and 92.5 volume percent normal paraffin. In this analysis, the setpoint is considered the normal operating condition and the credible abnormal condition is the limits of the operational band. This is because once the process stream goes outside of the operational band, the operators must correct the situation or the entire process must be shut down. This analysis goes beyond those conditions. The D-bank acid upset is analyzed from 0.05 M to 3.5 M nitric acid. These ranges are judged to be far beyond the credible abnormal conditions.

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

KENO-VI Validation and Determination of k_{SAFE}

A validation for the SCALE 6.1 KENO-VI code for HEU solution systems, based on benchmarks from the International Criticality Safety Benchmark Evaluation Project Handbook, was performed in Ref. 3. Using a conservative bias for this type of system and an additional subcritical margin, the k_{SAFE} assumed for this work was 0.9564.

SEPHIS-P Validation

The SEPHIS predictive chemistry program has been in use for many decades at the Savannah River Site. Originally developed in FORTRAN, it has recently been ported to the modern programming language Python (Ref. 4) and is now called SEPHIS-P. This version was validated to be equivalent to the FORTRAN version. This was necessary because the FORTRAN version was validated for use in simulation of the HM-Process in Ref. 5 by comparing it directly to the experimental data for the development of the HM-Process in Ref. 6 and 7.

Experimental Basis

Despite the longevity of use, the SEPHIS-P program is a simulation tool that has been used for flowsheet development. Historically, flowsheets developed using it have been directly supported by experimental validation from Savannah River National Laboratory (SRNL) before they are implemented in the facility. This is because no simulation is perfect and SEPHIS-P does introduce bias into the calculated results compared to experimental data. Ref. 2 sought a number of means to ensure that any such bias was given adequate margin by extending the analysis far beyond credible abnormal conditions.

Upon internal review of the various chemistry bounding methods proposed in Ref. 2, it was concluded that the acceptably conservative path was to experimentally evaluate process upsets and determine how well SEPHIS-P predicted the chemical behavior of the system in those upsets. Ref. 8 is such an analysis, wherein acid upsets to the D-Bank aqueous stream were experimentally evaluated using a miniaturized mixer-settler system available at SRNL.

SEPHIS-P had already been found to be acceptable for use in flowsheet development (Ref. 5) provided the user was aware of the bias inherent in the code. The distribution coefficient correlation, which was developed based on PUREX data at higher TBP concentrations and different fissile species and acid concentrations, tends to under predict the distribution coefficient for uranium. This means that the uranium concentration in the aqueous phase tends to be overestimated. In many cases this is conservative for criticality purposes as the neutron multiplication changes tend to follow changes in the aqueous phase uranium concentration and bank-wise distribution of uranium in the aqueous phase. Evaluation in Ref. 8 of the uranium distribution between aqueous and organic phases at the various acid concentrations examined indicated that SEPHIS-P was overestimating the amount of uranium retained in the aqueous phase. Moreover, SRNL concluded that for criticality safety concerns SEPHIS returns conservative results for acid concentration upsets in the D-Bank 2nd Cycle chemistry (Ref. 8). Only the D-Bank was examined as the experimenters found it was more limiting than the E-Bank in 2nd Cycle.

SEPHIS Calculations

The SEPHIS-P code is designed to arrive at a predictive chemistry result for each stage for all of the banks in a cycle. The process parameters are specified including acid concentration, uranium feed concentration, flow rates, and any additional reducing or oxidizing agents. 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-P 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.

KENO-VI Model of the Mixer Settlers

Models of the mixer settlers were made per the methodology outlined in Ref. 1 and 2, which is summarized here. The 2nd Cycle is modeled in SEPHIS-P either at the normal condition or at one of the points in the process parameter upset. SEPHIS-P is run to convergence at equilibrium and the stage-wise distribution of uranium and acid in both aqueous and organic phases is taken from the SEPHIS-P 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 analyzed upset range. Additionally, a reducing agent that was modeled in SEPHIS-P to ensure the correct chemical behavior is conservatively neglected in the SCALE models because it also acts an uncredited neutron poison. 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. While SEPHIS-P makes no isotopic distinction in the chemistry the uranium modeled in SCALE is 73 wt.% enriched which is the upper limit of the enrichment seen in the HM-process and is a protected assumption for the facility. Plutonium and other fissile isotopes are expected to be negligible in the process and are neglected. Since the cycles are not operated at the maximum 73 wt.% enrichment, this is still acceptably conservative.

The interface level in the settler section of the KENO models was held at 50% aqueous and 50% organic phases. This is judged to be conservative since normally the organic can be as much as 66% of the settling section, by volume, yet the aqueous phase is what drives neutron multiplication. As an additional check, and because interface level cannot be known in every stage, a second set of models was run with the aqueous and organic phases artificially doubled in height. This effectively bounds any uncertainty on interface level because this fills each stage to the maximum physical limit possible with each phase.

RESULTS

Uranium Concentration Behavior

The SEPHIS-P predicted total uranium concentration in each stage of the D-Bank and E-Bank is shown in Fig. 1 and Fig. 2, respectively. Note only Stages 8 through 12 are shown for the E-bank as the uranium concentration drops to effectively 0 beyond that. The credible abnormal high and low acid are marked by the darker "upper" and "lower" data series. The beyond credible abnormal high and low acid are marked by the lighter "max" and "min" data series.

Neutron Multiplication of the Banks

The stage-wise aqueous and organic chemistry predicted by SEPHIS-P was translated into compositions inputs for KENO for each stage of each bank for each upset condition. The KENO model results for each bank, across the range of upset conditions, is shown in Fig. 3. All cases for the nominal interface height, including the beyond credible abnormal cases, were below k_{SAFE}. Only at the very low acid in the D-Bank did significant reflux begin to show a uranium accumulation that significantly increased multiplication.

The doubled-height interface cases are also shown on Fig. 3 by the "2x" labeled series. These cases conservatively over-exaggerate the uncertainty in the interface level of the individual stages by doubling the height, and therefore the volume, of each phase in the settling section. The mixing section volume is adjusted accordingly. Test cases, not shown, confirm that realistically varying the interface level (aqueous and organic volume fraction in thirds within the design height of the stage) produces results bounded by the double volume cases and in some instances bounded by the 50% volume fraction normal height results shown on Fig. 3. Even most of the double volume cases satisfied k_{SAFE}. Only the multiple upset condition of double volume beyond credibly low acid exceeded k_{SAFE}. That configuration is not achievable to even approach this situation, the bank would need to have no organic feed whatsoever and the acid be diluted to the concentration of process water. Therefore, the D-Bank acid upset cannot achieve a critical configuration.

Approval Process

The approval and concurrence process for this effort is worthwhile to discuss. Normal nuclear criticality safety evaluations authored at Savannah River Nuclear Solutions have a well-defined authorship, technical review, verification, and approval process from the criticality engineer up through the facility management. This is supported by a definition of the problem that is readily obtained from process descriptions, engineering drawings, facility walk downs, or through directly sampling of fissile material systems.

This work however had aspects outside of that scope. The mixer-settler banks are readily detailed on engineering drawings. The process flowsheets specify the normal operating bands of the process chemistry. However, that information alone is not sufficient to develop the KENO inputs. The flowsheet parameters and mixer-settler geometry are however sufficient to develop inputs to SEPHIS-P. SEPHIS-P is not a code that is normally run by criticality safety.

For approval of this work, the author first had to learn use of SEPHIS-P under the direction of an experienced user. Next, facility Engineering personnel who are familiar with the chemical engineering of the HM-Process and who regularly use SEPHIS-P were tasked to review the analysis. They verified SEPHIS-P modeling was done according to the facility process flowsheets and described the upset and problem parameter ranges criticality safety was interested in. Next, SRNL analytical chemists familiar with the HM-Process, SEPHIS-P and its biases, and the nature of this work were asked to review the analysis. They concurred that SEPHIS-P was used appropriately to model the process and that the results, per experimental analysis (Ref. 8) would be conservative for the particular upset analyzed herein. The caveat to that is other upsets will likely require experimental confirmation of SEPHIS-P predictions. This will fall under future work.

With these two approvals, management was satisfied that the chemistry analysis was done properly and that user of SEPHIS-P for KENO input was acceptable. A formal qualification to run KENO is part of the training requirements for the site's criticality safety engineers, so the KENO modeling portion of this work was accepted per the training program.

This approval process was above and beyond normal nuclear criticality safety evaluations for the site, but necessarily so because of the unique application of the SEPHIS-P software.

Conclusion and Future Work

The immediate product of this work is that two events can be removed in the next revision of the H-Canyon safety analysis. This will relieve some operational burden, sampling requirements, and move the facility closer to being able to downgrade the functional classification of some process instrumentation.

This approach also paved the way for future analyses of this nature to eliminate more postulated criticality events from the mixer-settler banks. This work addressed only 2 of the currently 36 events. With SRNL experimental support, this method will be applied to analysis of other process upsets.

ACKNOWLEDGMENTS

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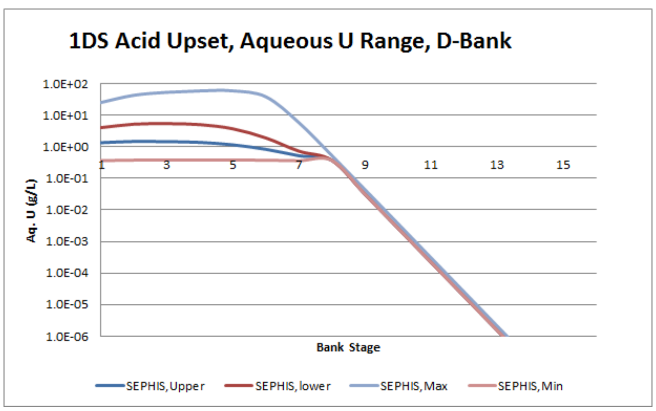

Fig 1. D-Bank Aqueous Uranium Prediction.

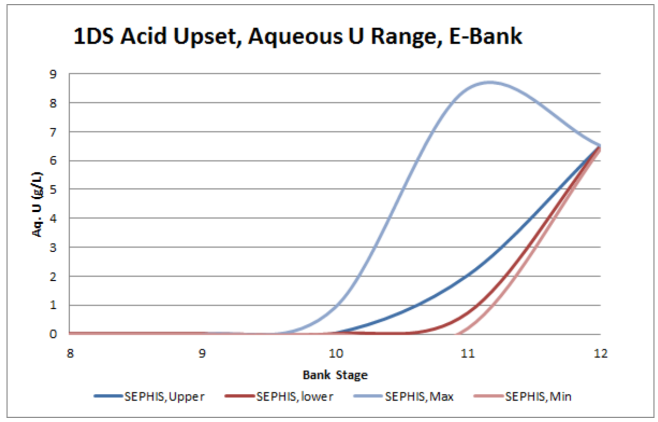

Fig 2. E-Bank Aqueous Uranium Prediction.

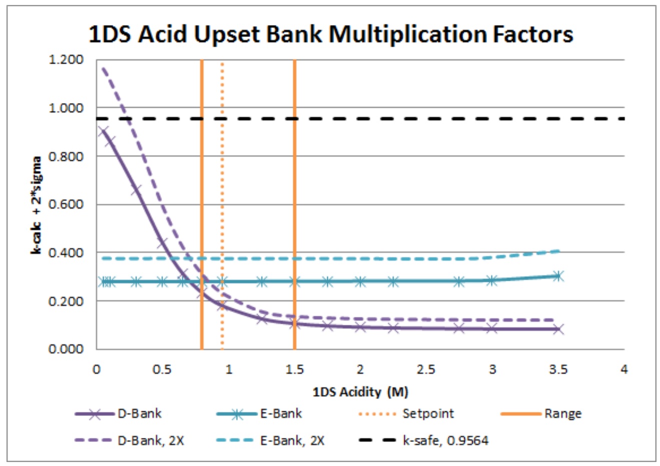

Fig 3. Neutron Multiplication of D and E Banks During Upset Conditions.

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