RED OIL EXCURSIONS IN THE MIXED OXIDE FUEL FABRICATION FACILITY

OVERVIEW AND SUMMARY REPORT

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1. INTRODUCTION AND BACKGROUND

The U.S. Nuclear Regulatory Commission (NRC) is in the process of licensing the Mixed Oxide Fuel Fabrication Facility (MFFF) now under construction at the U.S. Department of Energy's (DOE's) Savannah River site in South Carolina. The MFFF will manufacture mixed oxide (MOX) fuel for power reactors. The MOX fuel will comprise plutonium dioxide, extracted from surplus weapons-grade plutonium, and depleted uranium dioxide, a byproduct of uranium enrichment. The proposed technology for use at the MFFF is known as solvent extraction. Therein, an organic phase, consisting of TBP (tri-butyl phosphate) dissolved in a diluent HPT (hydrogen propylene tetramer), comes in contact with an aqueous phase, a mixture of nitric acid, water, and metal nitrates, to extract and purify the metals plutonium and uranium that will be used in manufacturing MOX fuel. Solvent extraction has been employed for many years in nuclear fuel reprocessing and related activities. It has one particular hazard, known as a "red oil excursion" (ROE), an explosive, runaway nitration-oxidation reaction; it previously occurred in U.S. and foreign facilities employing processes similar to those proposed for the MFFF.

The NRC tasked Brookhaven National Laboratory (BNL) to undertake an independent analysis of issues related to the risk of a ROE in the design proposed for the MFFF; it was part of a larger program of providing technical assistance to NRC's staff on risk-informed decision-making for the fuel cycle facilities that the NRC regulates. BNL's study contains insights potentially useful in staff reviews of the MFFF License Application. However, BNL's study is meant only to convey additional information to the NRC staff and offer an independent perspective on risk. It is not intended to serve as the basis for any determinations on facility licensing made under the requirements of 10 CFR 70.

2. BACKGROUND TO THE RED OIL PHENOMENON

Red oil is a substance of non-specific composition created when an organic phase consisting of TBP and a diluent comes into contact with concentrated nitric acid under certain conditions. The red color supposedly reflects the formation of nitrated organic species, and the evolution of nitrogen dioxide, a reddish-brown gas. The oxidation of TBP and its decomposition products, i.e., red oil formation, occurs over a wide range of temperature, with the rate dependent on various parameters, such as temperature, acid concentration, length of time of contact between the organic and aqueous phases, efficiency of contact (mass transfer), and radiolysis. At temperatures below about 60^0C, the heat of reaction and the volumes of gases evolved generally are small. Of concern is the very energetic exothermic decomposition reaction and the associated over-pressurization, viz., the self-heating runaway reaction known as a ROE that is observed at higher temperatures. The focus of the red oil reaction analyzed by the BNL study was TBP-nitrate thermal reactions. Possibly, the radiolytic dissociation of organic compounds could generate more reactive species that might promote ROEs. However, the quantities of radionuclides involved in the MFFF are small compared to those in fuel reprocessing plants, and their decay rates are low so the impact of radiolysis is likely to be minor.

3. SAFETY STRATEGIES FOR RED OIL AT MFFF

There are three elements in the safety strategy and approach for coping with the possibility of ROEs proposed by the applicant in the License Application (LA) and analyzed in the accompanying Integrated Safety Analysis (ISA) Summary. Each element is implemented through a set of items relied on for safety (IROFS) that consists of active and passive engineered controls and administrative controls.

1. TBP Prevention Strategy: This strategy segregates the solvent (TBP) from acid-bearing and heated process equipment, such as evaporators, thereby ensuring that a separate phase of TBP or TBP in excess of its solubility limit that might be entrained with the aqueous phase does not experience prolonged contact with highly concentrated nitric acid at elevated temperatures. This approach is implemented through process sampling and density monitoring and control and a device for passive separation of the organic and aqueous phases. The IROFS credited for this strategy include sampling points and procedures, process-density control loops and monitors, and the slab settler, a device that separates the lighter organic phase from the heavier aqueous phase based only on their density difference.

2. Heat Transfer Strategy: This relies on passive convective and radiative heat transfer to the surrounding environment. The strategy demonstrates the adequate transfer to the room environment of heat that may be generated from all possible sources, including exothermic reactions, such as the solvent nitric acid reaction (at relatively low temperatures). Control of the temperature of the surrounding environment ensures that heat is adequately transferred during routine and pre-defined upset conditions. The IROFS credited include the geometry of process vessels, temperature sensors and control loops to detect and limit self-heating, off-gas venting to relieve pressure from any gases evolved in the reactions, and reagent sampling controls to assure use of the proper diluent.

3. Evaporative Cooling Strategy: This approach removes heat via the evaporation of water in the aqueous phase from heated process vessels wherein some (limited) amount of TBP is expected to be present, and where there is the possibility of an exothermic nitration-oxidation reaction. This strategy depends on the large latent heat of vaporization of the aqueous phase. It requires the fulfillment of certain criteria, such as maintaining a minimum ratio of the aqueous to TBP mass, a maximum depth of the TBP layer, a maximum process-solution temperature, and an open, vented system to prevent over-pressurization so gases generated in the reaction are discharged safely. The IROFS credited for this strategy are process sampling and administrative flushing to limit the accumulation of TBP, level controls to maintain the minimum aqueous-to-TBP mass ratio, temperature controls to limit solution temperatures, and an off-gas venting system to relieve pressure from gases released in the reactions.

4. SCOPE OF THE BNL STUDY

The BNL study developed a probabilistic risk assessment (PRA) model that evaluated the failure of some of the ROE safety strategies due to internally initiated process deviations. In particular, the PRA model focused on (1) the failure of evaporative cooling in selected process vessels and (2) the failure of the TBP prevention strategy, through events, such as emulsification and the formation of a third phase, or a rag layer, eventually entailing a violation of the success criteria for evaporative cooling. The PRA is considered a limited-scope risk assessment for several reasons:

1. The analysis excluded generic risks due to external hazards, such as seismic events, internal fires, or loss of offsite power events, including station blackout. These initiating events potentially could lead to other high consequence outcomes, similar to ROEs; including them would have greatly enlarged the scope of the study, which is limited to ROEs. In addition, according to the ISA Summary, the applicant took several steps and actions by installing the IROFS to reduce to low values the likelihood of internal fires and of externally initiated event sequences, consistent with the highly unlikely category of event frequencies.

2. In analyzing the red oil reaction, the characterization of the phenomenon developed by the applicant was accepted broadly by focusing only on the thermal decomposition reactions. As noted above, the impact of radiolytic dissociation on this reaction was not considered because it was felt that radiolysis would have a minor impact in the MFFF as the concentrations and decay rates of the radionuclides involved are low.

3. The analysis did not consider failures of the heat transfer strategy. This strategy applies to the adequacy of passive heat transfer to the room environment from process vessels containing solutions at lower temperatures (about 55ºC and below); its success depends on the proper operation of room cooling, i.e., the facility's heating, ventilation, and air conditioning (HVAC) system. However, including failures of the HVAC system would have greatly enlarged the scope of the analysis, which is limited to ROE.

4. The semi-empirical model for the TBP-nitrate reactions developed by the applicant to set the success criteria for evaporative cooling safety was accepted as the basis to further evaluate the phenomenon. The applicant considers this model as conservative because it is based on the heat generated in a pure TBP-nitric acid reaction, rather than on the 30%TBP-70% HPT mixture that the MFFF will use. An independent assessment of this model was considered as beyond the scope of the BNL study.

5. QUALITATIVE ASSESSMENT OF ROE

The BNL study initially made a qualitative assessment of the factors that could contribute to a possible ROE in the various process units comprising the Aqueous Polishing (AP) Unit. There are eight process units in the AP process wherein organics and nitric acid could or might come into contact during normal operation. They are as follows: (1) Purification cycle (KPA), (2) Solvent recovery (KPB), (3) Oxalic precipitation and oxidation (KCA), (4) Oxalic mother-liquor recovery (KCD), (5) Acid recovery (KPC), (6) Aqueous waste reception (KWD), (7) Solvent waste reception (KWS), and (8) laboratory liquid-waste receipt (LGF). ROEs could occur in these eight units; the BNL study focused on Units (1) through (5) since the process conditions there place them at a higher risk of a ROE compared to Units (6) through (8). The evaluation considered the likelihood of an ROE for each of these five process units in terms of the equipment employed, the sequence of operations, and the conditions (e.g., temperature, pressure) during operations.

The sequence of operations employed in the AP unit is summarized as follows. Plutonium nitrate is fed to the purification cycle (KPA) unit, where plutonium is extracted via the solvent extraction process, which removes impurities, such as gallium and americium. Then, the purified plutonium nitrate is fed to a continuous oxalate calcination process unit (KCA) that converts it to a plutonium dioxide powder. The oxalic mother-liquors produced in the precipitation to oxalate are recycled to the oxalic mother-liquor recovery unit (KCD). The solvent is regenerated in the solvent recovery unit (KPB) and the acid is recycled in the acid recovery (KPC) unit. The liquid-waste storage tanks temporarily hold low- and high-level alpha liquids, stripped uranium and organic waste streams received from various processes in the AP process until they are pre-treated, and ultimately sent offsite for final disposal.

BNL selected four vessels in two process units for more detailed evaluation based on the heat sources present, the heat balance, and the potential for TBP transfer, which could potentially violate any of the ROE safety strategies outlined earlier. These were (1) the first-stage evaporator in the acid recovery unit, (2) the concentrates collection tank in the acid recovery unit, (3) the second stage evaporator in the acid recovery unit, and (4) the evaporator in the oxalic mother-liquor recovery unit.

For each of these vessels, a qualitative safety review was completed, followed by a quantitative risk assessment of ROE.

1. The first stage evaporator is a natural recirculation thermosiphon-type boiler that utilizes pressurized super-heated water as a heating fluid. Distillates of nitric acid vapor from this evaporator are condensed and routed to a feed buffer pot that decouples the operation of the first evaporator from the second evaporator. The evaporator operates under vacuum. The hot water system is equipped with controls to ensure that a maximum safe temperature is not violated. Flushing the vessel every six months limits the total amount of TBP that can accumulate. The applicant applied to this vessel the red oil prevention strategy of evaporative cooling. For a ROE scenario to occur, two conditions must be met: (1) A rising process temperature that can reflect an inability to maintain the maximum safe temperature or the rupture of a heat exchanger tube and (2) failure of evaporative cooling to mitigate the event and prevent the ROE. The success criteria for evaporative cooling involve maintaining a minimum aqueous phase to TBP mass ratio, a maximum depth of the TBP layer, a maximum process solution temperature, and an open, adequately vented system. These criteria could be violated under the following conditions: equipment failures (loss of temperature control, ruptures of heat exchanger tubes, and failures of the venting system), human failures (operator’s failure to flush the system on schedule), and process failures (e.g., formation of emulsions) that could lead to excessive transfers of TBP.

2. There is a high level of alpha-emitting impurities, mainly americium, in the collection tank for concentrates drawn off from the first stage evaporator for transfer to the high alpha-liquid waste vessels. The material in this tank, cooled by a cooling water loop, is continuously mixed well to prevent the formation of any hot spots within it that could initiate a ROE. If the temperature reaches a chosen safe set point, the steam jets are shut off, and the solution volume is verified and maintained at a safe level to ensure the success of evaporative cooling. Evaporative cooling also is the red oil safety strategy for the concentrates collection tank. Its contents are flushed every six months to limit the accumulation of TBP to an amount within the criteria for successful evaporative cooling. Two conditions are necessary for a viable ROE scenario to occur: (1) a rising tank temperature due to failure or degradation of the tank cooling/mixing system and (2) the failure of evaporative cooling.

3. The second stage evaporator, a natural recirculation thermosiphon-type boiler, utilizes pressurized steam as a heating fluid. Distillate from the first stage evaporator is re-evaporated in this steam-heated evaporator. The conditions exist for an ROE in this vessel if sufficient TBP is present. Hence, the red oil safety strategy here is TBP prevention, viz., the installation of sampling instrumentation and density monitors to prevent an excessive TBP transfer from the KPA to the KPC unit. However, further analysis revealed that the possibility of the build-up of TBP in the second stage evaporator is much lower than in the first stage one, so qualitatively screening out the scenario for ROE in this vessel.

4. The evaporator in the oxalic mother-liquor recovery unit is a natural circulation thermosiphon evaporator that concentrates the mother liquors, supplied from a feeding tank. The evaporator includes a boiler used for vaporizing the feed solution and reflux from the rectification column. It has a tubular heat exchanger. The heating fluid (steam) occupies the shell side; the mother liquor for evaporation circulates in the tubes. The conditions for a ROE in this vessel readily exist only if sufficient TBP is present. Hence, TBP prevention is the red oil safety strategy applied to this evaporator. The amount of TBP entering the evaporator from the feeding tank is controlled below its solution detection limit of 50 mg/liter. This small amount of TBP is degraded fully and safely in the evaporator's aggressive environment. The BNL study conservatively assumed that a ROE could occur if the soluble TBP amount is not controlled, or if a separated phase of TBP is transferred to the evaporator. The ways in which the transfer of amounts of TBP above the solution limit could occur include either a slow accumulation of mechanically entrained droplets that eventually create a separate phase of TBP, or a severe process malfunction entailing a transfer of a large amount of solvent from the KPA unit. Both ways involve the circumvention or failure of multiple barriers, including the diluent wash pulse columns in the KPA unit and the passive slab settler at the back end of the KPA unit. Further, the process sampling controls in the KCA's batch constitution tanks ensure that the amount of soluble TBP passing through the unit downstream to the KCD evaporator remains sufficiently low. Operational failures in the pulse columns, the slab settler, and the sampling controls that could allow TBP transfer to this evaporator were analyzed quantitatively using the PRA model.

6. QUANTITATIVE ASSESSMENT OF ROE

Quantitative evaluation was accomplished by delineating accident sequences, presented in the form of event trees and fault trees, to gain further insights into possible combinations of failures that could lead to ROE in the process vessels selected after the qualitative assessment. Quantification, using the SAPHIRE code, gave the point frequency of a ROE and a 5th percentile and 95th percentile frequency to show the range of uncertainty.

The ROE scenario in the first stage evaporator was modeled under two conditions of TBP accumulation: (1) normal accumulation of TBP, i.e., the accretion of a small amount by mechanical entrainment with the aqueous phase and (2) the upset accumulation of TBP, resulting from a severe process malfunction, such as the formation of an emulsion that transfers large quantities of solvent.

Under the first condition, a high solution temperature and failure of the evaporative cooling strategy is necessary for a ROE to occur. The initiating event for this scenario is the increase in solution temperature that can lead to a ROE should the evaporative cooling strategy fail. This initiating event might result from loss of temperature control or a rupture of the heat exchanger tube. The following events in the event tree model the different ways whereby the various success criteria for evaporative cooling, viz., maintaining the required aqueous to TBP mass ratio and the TBP layer thickness, are violated. The first is the operator's failure to flush the vessel at the end of six months, a period assumed conservatively to cause the unavailability of evaporative cooling for six months until the next scheduled flushing. The second can happen due to a number of failures of equipment needed to maintain control of the TBP's level. The last event in the tree represents the success/failure of venting to ensure the maintenance of the solution's temperature below a safe level. Venting is provided by a two-train system consisting of fans and HEPA filters with an additional standby fan. There are two ROE sequences for this scenario; in the first, the level control is successful but venting fails, while in the second, sufficient TBP accumulates to violate the criteria for evaporative cooling. The dominant contributor in the first sequence is common cause failure of plugging of the two sets of HEPA filters. In the second sequence, the dominant contributor is human error, viz., the failure of the operator to carry out the vessel's six monthly flush.

Under the second condition, multiple failures of the barriers that prevent excessive TBP transfer must occur before the violation of the criteria for evaporative cooling. The transfer is assumed to begin with a severe process malfunction, such as the formation of an emulsion in the initial pulse extraction column in the KPA unit. Following this, the diluent washing pulse columns that remove the TBP also could fail to break up the organics entrained in the aqueous phase, or in inducing a manual termination of TBP transfer. Very limited data formed the basis of assigning failure probabilities for these events. Further barriers to the transfer of organics are afforded by sampling controls that detect TBP and density controls that detect HPT. Failure of these controls was modeled via standard fault tree modeling. The initiating event for this scenario again is a loss of temperature control or rupture of a heat exchanger tube engendering a rise in solution temperature. The top events in the event trees relate to the success/failure of the various pulse columns in breaking up entrained organic material, followed by the success/failure of the sampling and density controls. Venting is not modeled as the amount of TBP assumed to be transferred in the upset accumulation condition would violate the criteria for the success of evaporative cooling. The following are the dominant contributors to the ROE in this case: the ineffectiveness of density controls, common cause failure of the density transmitter, failure of sampling analysis, failures in the diluent wash column, and malfunctions of the pulse extraction column.

The assumptions in the PRA model for ROE in the concentrates collection tank are as follows.

1. Failure to provide cooling flow to the tank's heat exchanger could heat up the tank and initiate evaporative cooling (failures of the HVAC system that also could do so were not modeled; it was assumed that the facility's response to HVAC failure would be to shutdown the KPC unit).

2. Failure of spray mixing inside the tank could create hot spots eventually initiating evaporative cooling.

3. Should the amount of TBP in the tank increase from an inadvertent transfer, then loss of cooling or mixing would lead to a ROE because the criteria for evaporative cooling would be violated.

The initiating event is the loss of cooling or of mixing. The event related to the transfer of separate phase TBP was estimated using the approach developed earlier for the failure of the first stage evaporator, due to the common pathways for transporting separate phase TBP to the process vessels in the acid recovery unit. Maintenance of level control addresses the operator's actions needed to provide aqueous makeup to maintain the criteria for success of evaporative cooling on the appropriate branches under conditions (1) and (2) above. The last event in the tree represents the success/failure of venting to maintain the solution temperature at a safe level to prevent a ROE. There are four ROE sequences. Two involve the transfer of large amounts of TBP to the tank after malfunctions in the pulsed extraction columns and subsequent failures of the sampling and density controls; they are very similar to the scenarios under upset accumulation in the first stage evaporator and the dominant contributors are similar. The dominant contributor in the venting failure sequence is common cause failure of plugging of the HEPA filters. In the remaining sequence, it is the failure of the operator to recognize the level alarm and take proper action.

The PRA model for ROE in the evaporator in the oxalic mother-liquor (KCD) unit is based on assessing the various pathways by which organics are transferred to this vessel. Two scenarios with their respective event trees are modeled: in the first one, the initiating event is solvent transfer by mechanical entrainment; and in the second one by a severe process malfunction leading to the transfer of a large amount of solvent. Both event trees consider the following events in sequence: The success of the wash column in breaking up and separating the entrained organics; the slab settler's effectiveness in preventing the transfer of any separate phase organics in excess of their solubility limit; and sampling for organics in the KCA batch tanks. The second scenario has another top event, sampling in drip trays, where samples of leakage are analyzed for their organic content before transfer to the KCD unit. Slab settler failures involve failures of the density controls, which were modeled by fault trees, operational failures that were taken from a supporting document on the slab settler's operation, density monitor failures, analyzed by fault trees, and loss of the integrity of the settler's baffle, estimated from data on corrosion rate. The other top events, except failures in the wash column, were modeled by fault tree methods. Three ROE sequences resulted, and in all, the dominant contributors include operational failures of the slab settler, failure of the diluent wash column, and failure of the air lift to stop the transfer of process solution to the KCD unit.

7. CONCLUSION

The red oil phenomenon is complex; the reaction takes place over a range of temperatures and several factors affect the exothermic reaction rate. The fact that ROEs occurred at a gross rate of about 0.1 per year over the last several decades in facilities employing processes similar to those proposed for MFFF suggests that the design of such facilities must incorporate sufficient measures to deal with this potentially explosive event. The design proposed for the MFFF appears to have incorporated the lessons learned from previous red oil events by including multiple safety strategies in different temperature regimes to deal with the risk of ROEs. Each strategy is implemented through a set of IROFS. The IROFS consist of a combination of active engineered systems or controls, passive engineered controls, enhanced administrative controls (human action combined with a physical device as an alarm to alert the operator), and administrative controls (required or prohibited operator actions). Each process or system also encompasses items and features of defense-in-depth. The application of industry codes and standards instills confidence in the reliability of the equipment selected as IROFS, along with the project's quality assurance program that is stated to be implemented in compliance with the requirements of 10 CFR 50 Appendix B. Within the qualitative definitions of event likelihood set out in 10 CFR 70 and the NRC's Standard Review Plan for the MFFF, an ROE can be considered to be highly unlikely at the proposed MFFF.

The results of the quantitative assessments show that the point estimate frequencies of a ROE in various process units are low. These low values reflect the robustness and defense-in-depth character of the multiple strategies employed in the facility to avert them. However, the quantitative estimates must be considered preliminary for several reasons. The failure rate database for equipment failures and human reliability in fuel cycle facilities, such as the proposed MFFF, is very sparse and uncertain, especially for equipment that may be exposed to harsh chemical environments. Moreover, the PRA carried out was a limited scope one for the several reasons discussed earlier.

The analysis performed here of ROEs using PRA techniques can be considered as risk-informing the qualitative analyses and the ISA process to help NRC's staff focus attention on areas of higher risk significance for ROEs. In particular, the identification of dominant contributors in the various sequences with ROEs as outcomes does direct attention on the crucial safety systems that the staff may choose to consider in reviewing the design. Hence, the proposed risk analysis methods can be considered as risk-informing the license review of fuel cycle facilities.