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# RISK-INFORMING SAFETY REVIEWS FOR NON-REACTOR NUCLEAR FACILITIES

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## ABSTRACT

This paper describes a methodology used to model potential accidents in fuel cycle facilities that employ chemical processes to separate and purify nuclear materials. The methodology is illustrated with an example that uses event and fault trees to estimate the frequency of a specific energetic reaction that can occur in nuclear material processing facilities. The methodology used probabilistic risk assessment (PRA)-related tools as well as information about the chemical reaction characteristics, information on plant design and operational features, and generic data about component failure rates and human error rates. The accident frequency estimates for the specific reaction help to risk-inform the safety review process and assess compliance with regulatory requirements.

## 1 INTRODUCTION

U.S. Department of Energy (DOE) has recently been carrying out research on separation technologies related to closed fuel cycle architectures [1]. Part of this research is related to solvent extraction processes, e.g., PUREX or modified PUREX processes [2] used in fuel reprocessing plants to remove impurities from the feed that may consist of reactor spent fuel or other fissile material. The extraction operation generally employs an organic solvent, usually tributyl phosphate (TBP), diluted in an organic matrix, as an extractant along with concentrated nitric acid in various processes. In this process, one or more components that are present in the solution, e.g., uranium and/or plutonium as well as metal impurities, are transferred between two immiscible liquid phases, typically an organic phase and an acidic aqueous phase. One concern in the facilities that utilize this process is the occurrence of an explosive, runaway nitration oxidation reaction (NOR) that can occur when the organic solvent TBP, and its degradation products, comes in contact with concentrated nitric acid at elevated temperatures. Such events have occurred before, in the U.S. and other countries, in facilities that employ solvent extraction. These reactions occur continuously over a wide temperature range but the reaction rates and the heat and gases generated at lower temperatures below about 60 $^0$C are low and passive heat removal and normal venting are adequate. At higher temperatures (about 80 $^0$C and higher), facility-specific heat removal measures are needed along with actions to ensure that the amount of TBP that can enter heated acid-bearing vessels is limited. A recent report issued by the Defense Nuclear Facilities Safety Board (DNFSB) [3] summarizes the events that have occurred in the extraction operations at Savannah River and Hanford in the U.S. and the accident at the

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Tomsk plant in Russia and states that “maintaining a temperature of less than 130°C is generally accepted as a means to prevent” any explosive reactions.

### 1.1 Safety Strategy

Considering that the undesired reaction occurs if the organic solvent comes into contact with concentrated nitric acid at an elevated temperature, the safety strategy and approach for coping with the possibility of NORs is as follows:

1. Segregation of separate phase solvent (TBP) from acid bearing and heated process equipment such as evaporators; this is meant to ensure that a separate phase of TBP or TBP in excess of its solubility limit that could be entrained with the aqueous phase does not come into prolonged contact with highly concentrated nitric acid at elevated temperature. This strategy is usually implemented through process sampling and density monitoring and control, and may include a passive engineered system to allow for the separation of organic and aqueous phases based on their density difference. The equipment and procedures that would credited for this strategy may include sampling points and procedures, process density control loops and monitors, and a passive system to separate organic and aqueous phases.

2. Heat transfer strategy; this relies on passive convective and radiative heat transfer mechanisms to the surrounding environment. The strategy should demonstrate an adequate heat transfer to the room environment of heat that may be generated from all possible sources including the exothermic reactions such as the solvent nitric acid reaction (at relatively low temperatures). The temperature of the surrounding environment needs to be controlled to ensure adequate heat transfer during routine and pre-defined upset conditions. The equipment and procedures credited may 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 ensure that the proper diluent is used.

3. Evaporative cooling strategy; this provides for heat removal via evaporation of water in the aqueous phase in heated process vessels where some (limited) amount of TBP is expected to be present, and where the possibility of the exothermic nitration oxidation reaction exists. This strategy depends on the large latent heat of vaporization associated with the aqueous phase, and it also requires the fulfillment of certain criteria, such as maintaining a minimum aqueous to TBP ratio, a maximum TBP layer depth, a maximum process solution temperature and an open, vented system. The equipment and procedures credited for this strategy could be: process sampling and administrative flushing controls to limit the amount of TBP accumulation in undesired vessels or locations, level controls to maintain the minimum aqueous to TBP mass ratio, temperature controls to limit solution temperatures, and an offgas venting system of sufficient capacity to relieve pressure from any gases released in the reactions.

### 1.2 Probabilistic Risk Assessment

A limited-scope probabilistic risk assessment (PRA) model can be used to evaluate the failure of some of the safety strategies due to internally initiated process deviations and assess their contribution to the facility risk posed by the nitration oxidation reaction (NOR). Such a model was recently used to study the risk posed by a NOR for a facility that would be based on a modified PUREX process. 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 such events as emulsification, and the formation of a third phase or a rag layer, leading, eventually, to a violation of the success criteria for evaporative cooling. The PRA can be considered a limited-scope risk assessment for several reasons:

1. The generic risks due to external hazards, such as seismic events or loss of offsite power events, including station blackout, were excluded from the analysis. These initiating events can potentially lead to other high consequence outcomes, similar to NORs, and would have greatly enlarged the scope of the study.

2. Failures of the heat transfer strategy were not considered in the analysis. This strategy applies to the adequacy of passive heat transfer to the room environment from process vessels containing solutions at lower temperatures (about 55 $^0$C and below) and depends for its success on the availability of room cooling, i.e., the proper operation of the facility's HVAC system. Consideration of the failures of the HVAC system, however, would have greatly enlarged the scope of the analysis.

3. A semi-empirical model for the TBP-nitrate reactions based on thermal decomposition alone, used to set the success criteria for the evaporative cooling safety strategy, was accepted as the basis for further evaluation of the phenomenon.

## 1.3 Qualitative Risk Assessment

A qualitative assessment of the factors that may contribute to the possibility of NOR in the various process units was first carried out to determine in which process units organics and nitric acid either contact each other during normal operation or have the potential to come into contact and where there is somewhat higher risk of a NOR occurring. Each of the process units was evaluated for the possibility of a NOR in terms of the equipment employed, the sequence of operations, and the conditions (temperature, pressure, etc.) under which the operations occur. Based on this assessment and taking into account the heat sources present, the heat balance and the potential for TBP transfer, several vessels in two process units were selected for more detailed evaluation. For each of the vessels selected, a qualitative safety review was performed followed by a quantitative risk assessment of NOR. The qualitative review is summarized first followed by a summary of the quantitative risk assessment.

Two of the vessels selected are evaporators: the first one is a natural recirculation thermosiphon type boiler which utilizes pressurized super heated water as a heating fluid. The first evaporator operates under vacuum. The normal process temperature is below 66 $^0$C and the normal super heated hot water temperature is 105 $^0$C. The hot water system temperature is equipped with controls to ensure a maximum temperature of 122 $^0$C is not violated. The mitigation strategy applied to the first evaporator is evaporative cooling. Two conditions are necessary for a viable NOR scenario to occur in this vessel: (1) a rising process temperature above 80 $^0$C; this can be due to an inability to maintain the hot water system temperature below 122 $^0$C or the occurrence of a heat exchanger tube rupture, and (2) failure of evaporative cooling to successfully mitigate the event. The success criteria for evaporative cooling involve maintenance of a minimum aqueous phase to TBP ratio, a maximum TBP layer depth, a maximum process solution temperature, and an open adequately vented system. The conditions under which these criteria could be violated include equipment failures (loss of temperature control, heat exchanger tube ruptures, venting system failure), human failures (operator failure to flush the system on schedule as required), and process failures (formation of emulsions, or a third phase or rag layer).

Another vessel selected for evaluation is a collection tank for concentrates drawn off from the evaporator. The tank is cooled by a cooling water loop, and is maintained in a well-mixed condition by an air sparger to prevent the formation of any hot spots within the tank, which operates normally at a temperature around 40 $^0$C. If the temperature reaches a set point of 80 °C, steam jets will be shut off, and the solution volume is verified and maintained at a level to ensure that the evaporative cooling would be successful. The safety strategy for the concentrates collection tank is also evaporative cooling. A six monthly flushing of the tank contents is performed to ensure that any accumulation of TBP is limited to an amount that is within the criteria for successful evaporative cooling. Semi-annual flushing ensures that the amount of TBP is limited in the tank. Two conditions are necessary for a NOR scenario to occur: (1) a rising tank temperature above 80 $^0$C due to failure or degradation of the tank cooling/mixing system and (2) failure of evaporative cooling. An assessment of the conditions under which the success criteria for evaporative cooling in the tank could be violated include equipment failures of the tank cooler and/or sparger, human failures (flush tank contents every six months), and venting system failures.

The second evaporator selected for more detailed evaluation is also a natural circulation thermo-siphon evaporator which concentrates liquors supplied from a feeding tank. The evaporator includes a boiler used for evaporation of the feed solution and reflux from a rectification column. It has a tubular heat exchanger. The heating fluid (steam) occupies the shell side and the mother liquor to be evaporated circulates in the tubes. The conditions for a NOR is this vessel readily exist only if sufficient TBP is present. Hence, TBP prevention is the main safety strategy applied to this evaporator. The amount of TBP that enters the evaporator from the feeding tank is controlled below its solution detection limit. This small amount of TBP will be fully and safely reacted in the aggressive environment that exists in this evaporator. The study conservatively assumed that the undesired reaction could occur if the soluble TBP amount is not controlled or if a separated phase of TBP is transferred to the evaporator. These could happen either through a slow accumulation of mechanically entrained droplets that could eventually create a separate phase of TBP or a severe process malfunction leading to a transfer of a relatively large amount of solvent from other process units. Both ways of TBP transfer involve the circumvention of multiple barriers, including the passive organic-aqueous phase separation unit and process sampling controls that ensure that the amount of soluble TBP passing through the unit downstream to the evaporator remains sufficiently low. Operational failures in the units that could circumvent the barriers and allow TBP transfer to the evaporator were analyzed in the study.

### 1.4 Quantitative Risk Assessment

Quantitative evaluation, using accident sequence delineation presented in the form of event trees and fault trees, was carried out to gain further insights into possible combinations of failures that could lead to NOR in the process vessels selected after the qualitative assessment. Quantification was carried out using the SAPHIRE code [4] to obtain the point frequency of a NOR and a 5th percentile and 95th percentile frequency to show the range of uncertainty.

The NOR scenario in the first evaporator is modeled under two conditions of TBP accumulation: (1) normal accumulation of TBP, which refers to an accumulation of a small amount by mechanical entrainment with the aqueous phase, and (2) upset accumulation of TBP, which can occur due to a severe process malfunction such as formation of an emulsion that can transfer large quantities of solvent. Under the first condition, high solution temperature and failure of the evaporative cooling strategy is necessary for a NOR to occur. The initiating event for this scenario is the increase in solution temperature if the evaporative cooling strategy fails. This initiating event can happen due to a loss of temperature control or a heat exchanger tube rupture. The former is modeled via a standard fault tree model and the latter via generic data. The next top event in the event tree models the different ways by which the various success criteria for evaporative cooling, viz., maintaining the aqueous to TBP mass ratio and the TBP layer thickness, can be violated. The first can happen due to operator failure to flush the vessel at the end of a six month period, which is conservatively assumed to cause an unavailability of evaporative cooling for six months until the next flushing action is required. This failure is modeled via a fault tree based on human error probability to carry out an action. The failure probability for the second criterion, maintaining TBP level, is estimated through standard fault tree methodology. The last top event in the tree represents the success of venting to ensure that the solution temperature is maintained below the azeotropic limit for the nitric acid/water solution. Venting is provided by a two-train system consisting of fans and HEPA filters with an additional fan as standby. Failure of venting is modeled via a fault tree to evaluate the venting failure probability. There are two NOR sequences for this scenario; in the first the level control is successful but venting fails, while in the second, the amount of TBP accumulated is sufficient to violate the criteria for evaporative cooling. The dominant cutset in the first sequence is common cause failure of plugging of two sets of HEPA filters. In the second sequence, the dominant cutset is the failure of the operator to carry out the six-month flush out of the vessel. Under the second condition, multiple failures of the barriers that prevent TBP transfer from upstream process units to the evaporator have to occur. The failure probabilities for these were assigned based on very limited data. Further barriers to the transfer of organics to the evaporator are provided by sampling and density controls. Failure of these controls was modeled via standard fault tree modeling. The initiating event for this scenario is again a loss of temperature control or a heat exchanger tube rupture that leads to 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 dominant cutsets in one sequence are the ineffectiveness of density controls, common cause failure of the density transmitter, failure of sampling analysis, failure of diluent wash column, and malfunction of the pulse extraction column. In the other sequence, the dominant cutsets are ineffectiveness of density controls, fraction of the time sampling failed between successive sampling intervals, failure of diluent wash column, and malfunction of the pulse extraction column.

The PRA model for NOR in the concentrate collection tank assumes: (1) failure to provide cooling flow to the tank heat exchanger could result in tank heat up and initiation of evaporative cooling (HVAC system failures that could also lead to tank heat up were not modeled as it was assumed that facility response to HVAC failure would be shutdown of the unit), (2) failure of spray mixing inside the tank could create hot spots leading eventually to initiation of evaporative cooling, and (3) if there was an increased amount of TBP in the tank due to inadvertent transfer, then loss of cooling or mixing would lead to NOR as the criteria for evaporative cooling would have been violated. The initiating event is the loss of cooling or mixing; its frequency was estimated from fault tree evaluations of the systems involved. The next top event is “no transfer of separate organics”, which was estimated using the models developed earlier for the evaporator, due to the common pathways for transport of separate phase TBP to the process vessels in the unit, including the evaporator and the concentrates tank. The next top event labeled “level control or No excessive TBP” addresses the operator actions needed to provide aqueous make up to maintain the criteria for success of evaporative cooling on the appropriate branches under conditions (1) and (2) above. The last top event in the tree, “venting”, represents the success of venting to maintain the solution temperature at a safe level to prevent a NOR. There are four NOR sequences. Two of them involve the transfer of large amounts of TBP to the tank due to 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 evaporator accident scenario and the dominant cutsets are also similar. The dominant cutset in the venting failure sequence is common cause failure of plugging of 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 NOR in the second evaporator is based on the evaluation of the various pathways by which organics can be transferred to this evaporator. Two scenarios with their respective event trees are modeled; in the first scenario, the initiating event is solvent transfer by mechanical entrainment, in the second by a severe process malfunction leading to the transfer of a relatively large amount of solvent. Both event trees consider the failures and successes of various barriers to the transfer of TBP, including success of wash columns to break up and separate the entrained organics, the effectiveness of passive systems in preventing transfer of any separate phase organics in excess of their solubility limit, and failures of sampling for organics in batch tanks. These failures were modeled by a combination of fault trees and corrosion rate data for failure of a baffle in the passive system. Three NOR sequences resulted from the analysis. The dominant cutsets in all of them include operational failures of the passive, failure of diluent wash columns and failure of an air lift to stop process solution transfer to the unit where the evaporator is located.

## 2 CONCLUSION

The example analyzed in this paper has shown that PRA methods and tools can be applied to model accident sequences in fuel cycle facilities that chemically process nuclear materials and to identify major vulnerabilities that may arise from combinations of equipment failures and human errors to cause undesired outcomes. However, while the results of the quantitative assessments show that the point estimate frequencies of the nitration-oxidation reaction in various process units are low, in the range of about 1E-5 per year, they must be considered preliminary for several reasons. The failure rate database for equipment failures and human reliability in fuel cycle facilities, especially for equipment that may be exposed to harsh chemical environments, is very sparse and uncertain. Moreover, the PRA carried out was a limited-scope one for several reasons as stated above. However, the analysis performed using PRA techniques can be considered as risk-informing the qualitative analyses. In particular, the identification of dominant cutsets in the various sequences helps to focus attention on the more important systems that impact the safety of the design with regard to reducing the frequency of nitration oxidation reactions.

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