Layer of protection analysis for reactive chemical risk assessment

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ARTICLE INFO

ABSTRACT

Reactive chemical hazards have been a significant concern for the chemical process industries (CPI). Without sufficient control and mitigation of chemical reaction hazards, reactive incidents have led to severe consequences, such as release of flammable and toxic materials, fires and explosions, and threats to human lives, properties, and the environment. Consequence of reactive hazards can be well understood through calorimetric testing and computational techniques. However, risks of incidents caused by reactive chemicals have not been well addressed due partly to sparse failure frequency data. In this paper, the semi-quantitative layer of protection analysis (LOPA) approach is used to estimate reactive chemical risk, and the probabilities or frequencies of failure scenarios are addressed. Using LOPA, reactive risks can be evaluated with respect to predefined criteria, and the effectiveness of risk reduction measures can be assessed. The hydroxylamine (HA) production system is employed as a case study to demonstrate the application of LOPA to reactive chemical risk assessment.

1. Introduction

Out of control chemical reactivity has led to great losses in the chemical process industry. The U.S. Chemical Safety and Hazard Investigation Board (CSB) reported that reactive chemical incidents resulted in an average of five fatalities per year in the U.S. between 1980 and 2001 [1]. It is generally agreed that the risks of reactive chemicals must be evaluated so that risk-informed management of reactive chemicals can be more effectively implemented.

It is widely recognized that current legislative, regulatory, and policy framework for chemicals is inadequate. The CSB report [1] suggested that there are gaps in existing Occupational Safety and Health Administration (OSHA) and Environmental Protection Administration (EPA) regulations, because over 50% of the 167 incidents involved chemicals are not covered by current regulations. Also, National Fire Protection Association (NFPA) instability ratings were designed for emergency response and have significant limitations with respect to identification of reactive hazards and especially hazardous pressure increases.

However, some progress has been made in reactive chemical regulations. New Jersey's Toxic Catastrophe Prevention Act (TCPA) program [2] added reactive chemicals to the list of extraordinarily hazardous substances that trigger the TCPA risk management planning requirements. Instead of proposing a limited list of individual chemicals, the TCPA program covers chemicals that contain selected unstable functional groups. Also, the European Union (EU) proposed a new Registration, Evaluation, and Authorization of Chemicals Regulation (the REACH Regulation) [3], which aims to make manufacturers, importers, and suppliers of substances responsible for ensuring that the chemicals do not adversely affect human health and the environment.

Regulations and legislations can play an important role on the safe usage of chemicals, but it is the responsibility of the producers and users of the chemicals to evaluate and control the risks of chemicals. Reactive hazards and risks are not associated only with intrinsic properties of chemicals but also are greatly dependant on specific process conditions. Because almost any chemical can be significantly reactive under certain conditions, it is extremely challenging to regulate reactive chemicals. The intrinsic properties of many chemicals have been thoroughly analyzed using screening tools [4] and advanced experimental testing and quantum mechanical calculation methods [5,6]. The chemical properties determine the tendency of a chemical to cause upset incidents and affect the severity of the incidents, but a complete picture of chemical reactivity risk must include operation conditions. Chemical reactivity and operational risks must be combined to provide a realistic evaluation of reactive chemical risk in terms of both consequent severity and occurrence probability.

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2. Risk assessment

The risk of an adverse event is the combination of the probability or frequency of occurrence and the consequence severity. The probability is the chance of the event occurring in specified circumstances, and frequency is the rate of the event occurrence per unit time. The consequence severity is the degree of harm caused by the event. Of the numerous methods for risk assessment [7], some of them, such as the hazard and operability study (HAZOP) and the failure mode and effects analysis (FMEA) can be used to evaluate the risk of an installation and its process. But these methods by themselves are not sufficient to rank the contributions of specific system components to the total risk of a chemical facility. On the other hand, risk assessment methods such as quantitative risk assessment (QRA) or semi-quantitative methods such as layer of protection analysis (LOPA) can analyze risk levels associated with hazardous activities and provide information needed for risk-informed decision-making.

Fig. 1 represents a risk assessment process with three levels of activities, which are designated risk analysis, risk assessment, and risk management. Risk analysis is a purely technical process that involves hazard identification, frequency analysis, and consequence modeling. The risk assessment level introduces issues of risk acceptability, risk reduction decisions, and cost-benefit judgements. Risk management, which consists of actions to monitor, test, and control risk levels, is part of the safety management plan of the organization.

QRA is the most sophisticated technique to calculate the risks of incidents, estimate the uncertainties of the calculated risk levels, and provide metrics for cost-effective risk minimization [8]. In addition to quantifying the effects of data uncertainty, QRA uses models to estimate conditional probabilities of failure for components or layers of protection that are not mutually independent. For risk assessment related to reactive chemicals, statistical data from incidents are often insufficient and are related to specific circumstances. As a result, effective implementation of QRA methods, such as statistical inference, requires significant cost, time, and experience. Therefore, less costly qualitative and semi-quantitative risk assessment techniques can be used effectively to identify where a more quantitative analysis of the most critical components of a chemical system may be needed.

Layer of protection analysis [9–11], is a semi-quantitative approach to evaluate the risk of potential incidents and to provide guidance on the adequacy of independent protection layers (IPLs) to lower risk. A LOPA typically uses order of magnitude categories for initiating event frequencies and for the probabilities of failure of IPLs, which can mitigate the frequency or reduce the consequence of an incident [10]. For example, LOPA has been used successfully to evaluate the risks of ammonia nitrate [12]. This study concluded that the 'order of magnitude' risk assessment cannot yield the precise risk results of a QRA, but it can provide an evaluation of risks against predefined risk criteria. In addition, LOPA can focus risk reduction efforts on impact events with high severity and high probability.

LOPA often follows a qualitative risk analysis performed as part of a HAZOP to identify and characterize hazards. Because of its ease of use, LOPA has become a popular alternative to a QRA or a screening approach to QRA. Also, the accidental risk assessment methodology for industries (ARAMIS) methods sponsored by the European Commission involve a simplified risk assessment approach that employs LOPA to assess hazard barriers [13]. The overall ARAMIS approach, however, requires more effort than needed for LOPA alone in its consistent use of fault trees and event trees to calculate initiating event probabilities and to represent accumulated risk from multiple outcomes of each initiating event.

3. Hydroxylamine (HA) production facility

In this paper, a generic HA production facility is used as a case study to illustrate the application of LOPA for reactive risk assessment. Since 1999, HA has been involved in two tragic incidents that caused multiple fatalities and injuries [14,15]. The CSB incident report on the hydroxylamine production facility at Concept Sciences raised several issues including inadequate hazard evaluation and improper facility siting [16]. Thereafter, significant research of the thermal stability of HA/water solutions have shown that HA decomposition, which is catalyzed by metals, metal ions, acids, and bases, is highly exothermic with a large pressure build-up in a contained environment [17,18]. Also, theoretical studies have been conducted to understand the HA decomposition mechanism [19]. The accumulated information from experimental and theoretical research provides a substantial foundation for HA process risk assessments.

The CSB report on the Concept Science facility [16] provided a general description of a hydroxylamine production process. Fig. 2 shows a simplified process diagram for hydroxylamine produced as a 50-mass% aqueous solution. The process includes a reaction vessel, salt separation system, vacuum distillation system, and product purification through ion exchange cylinders.

A hydroxylamine production process includes the following:

1. Hydroxylamine sulfate and potassium hydroxide react to produce 30 mass% HA and potassium sulfate (in solid) aqueous slurry.

$$(NH_2OH)_2 \cdot H_2SO_4 + 2KOH \Rightarrow 2NH_2OH + K_2SO_4 + 2H_2O$$
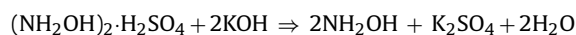
2. Separation of solid potassium sulfate from the produced slurry is conducted in a filtration unit. Following separation, 30 mass% HA is temporarily stored in a filtrate tank before feeding into a vacuum distillation system.
3. In the vacuum distillation system, 50 mass% HA is produced by separating HA from the dissolved potassium sulfate. As shown in Fig. 2, the vacuum system consists of a glass-heating column (a tube in a shell heat exchanger) with a remote water heater, a glass condenser column with a remote chiller, vacuum pump, and three tanks (charge tank, forerun tank, and final product tank). The distillation is performed in two phases:

   The first phase involves the circulation of HA aqueous solution between the charge tank and heating column heated by 50 °C water. Vapor from the heating column is condensed in the condenser column, and the distillate is directed into the forerun tank. When the concentration of HA reaches 10 mass% in the forerun tank, the distillate is directed to a final product tank until the HA concentration in the charge tank reaches a certain threshold. Then, the charge tank and column are cleaned using a 30-mass% HA solution, and the charge tank is taken out of service.

   In the second phase, the solution in the final product tank is further concentrated by distillation at a temperature of 60 °C. Water is removed from the solution until the HA concentration in the product tank reaches 50 mass%.
4. The distillate is purified through ion exchange cylinders, but this step is not considered in the process diagram.

The hydroxylamine production process requires many safety functions to prevent runaway reactions. The purpose of LOPA is to determine if there are sufficient layers of protection against credible upset scenarios.
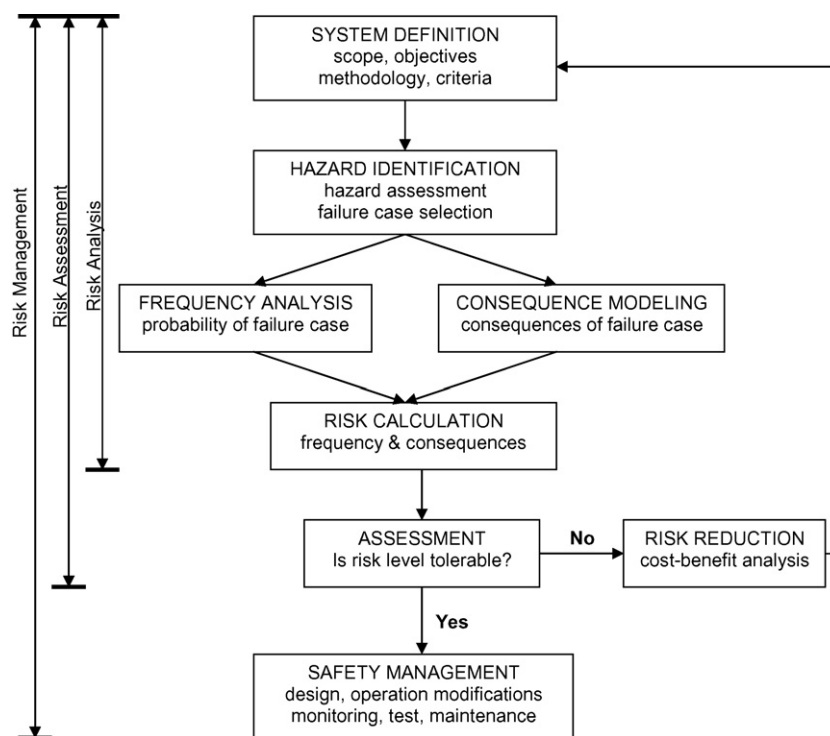
Fig. 1. Flow diagram for a risk assessment process.

4. Layer of protection analysis

LOPA is an analytical tool that builds on hazard identification and characterization information developed during a HAZOP [10]. LOPA involves a multi-disciplined team, similar to a HAZOP team including operators, process engineers, instrument/control engineers, and risk analysts. For reactive hazard evaluation, a reactive chemical specialist must be present in the team to provide input concerning reactivity. LOPA analyzes each credible cause-consequence pair. Initiating cause probability is estimated on an order of magnitude basis, whereas consequence severity is estimated qualitatively or calculated using software tools such as PHAST [20]. Each safeguard can reduce the frequency or severity of a potentially hazardous event.

For LOPA, only independent layers of protection (IPL) are employed. An IPL must also be effective in reducing risk and must be auditable [10]. Each layer should be analyzed or tested to determine its basic independence from the initiating event and from the other protection layers. A probability of failure on demand (PFD) is assigned to an IPL to account for its reliability to respond to system demand. The main objective of a LOPA layer of protection is to prevent a scenario from progressing to the specified upset scenario given the occurrence of the initiating event and regardless of the performance of other layers of protection.

Assuming the layers are determined to be independent, the final mitigated event frequency, f_i^C, is calculated by multiplying the initiating cause frequency, f_i^I, by the PFDs of the individual IPLs, PFD_{ij}, as shown below [10]:

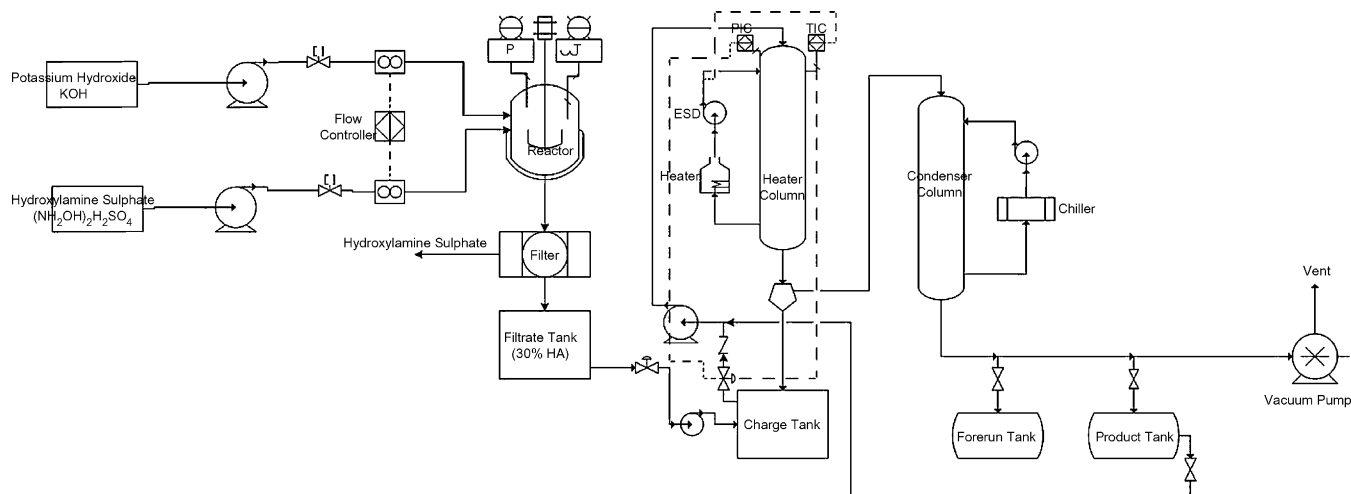$$f_i^C = f_i^I \times \prod_{j=1}^{j} PFD_{ij} \qquad (1)$$

Fig. 2. Process flow diagram of hydroxylamine production.

As each independent layer of protection is called upon to function, the scenario frequency f_i^C becomes progressively smaller by the factor of the PFD for that layer of protection.

PFD values for types of components and human actions are provided and discussed by various sources [8,10,21,22]. When used initially, generic failure data can be updated by plant and system specific data as they become available [8].

The mitigated event frequency f_i^C is compared with risk criteria to determine the risk levels. If the risk is unacceptable or intolerable, the inherent safer design approach to reduce hazard levels, or additional IPLs must be applied to reduce the risk to tolerable levels. Therefore the two main issues for a cost-effective LOPA approach are the risk reduction level for each layer of protection and the minimum number of layers required for acceptable system risk. Additional layers can cause unnecessary complexity and associated costs. Assuming a process hazard analysis or HAZOP has been formed to identify and characterize hazards, the overall LOPA procedure [10] is summarized below:

LOPA procedure

1. Select an incident scenario and cause.
2. Estimate the frequency of the initiating event for the scenario.
3. Identify each IPL and estimate the probability of failure on demand of each IPL from failure rate data and test information.
4. Calculate the mitigated frequency of consequence occurrence by combining the initiating event frequency and the IPL probabilities.
5. Estimate the risk of the scenario by combining the consequence frequency and consequence severity.
6. Evaluate the risk of the scenario based on tolerable risk criteria. Return to #3 if needed to lower the scenario frequency and risk to a tolerable level.
7. Continue to analyze all credible and significant scenarios or cause-consequence pairs.

4.1. Consequence

For hydroxylamine production processes, the most serious consequence is significant thermal decomposition resulting in runaway reaction, vessel rupture, and explosion, which is most likely to occur in the reactor or in the vacuum distillation system. In this paper, two cause-consequence pairs, vessel rupture in the HA reactor, Scenario #1, and vessel rupture in the HA distillation system, Scenario #2, are discussed to illustrate the LOPA process.

On a mass basis, the explosive energy of HA is equivalent to TNT [16]. From PHAST v.6.42 calculations, blast waves generated by 500 kg hydroxylamine can break windows within 250 m radius and damage non-reinforced concrete walls within 50 m radius [20]. Within and near a HA plant, a HA explosion has the potential of causing multiple fatalities and large property losses.

4.2. Initiating causes

For each consequence, credible initiating causes are identified to perform a LOPA study of each cause-consequence pair. Risk calculations are then performed using the estimated probability and estimated severity of each consequence. An initiating cause for thermal decomposition in the HA reactor, Scenario #1, is a failure of the flow control system to cause excessive transfer of KOH into the reactor.

A previous study demonstrated that KOH catalyzes the thermal decomposition of HA and lowers the onset temperature of significant decomposition, T_0, significantly below the onset temperature measured without KOH [17]. As shown in Table 1, the HA decomposition rate and thermal energy generation can be significantly

Table 1
Calorimetric tests of HA decomposition [17]

HA (mass%)	KOH (mass%)	T_0 (°C[a])
50	0	139 ± 4
43	1.5	114 ± 4
43	12	86 ± 2
38	14	46 ± 2

[a] T_0 is the onset temperature of detected HA decomposition.

high at temperatures below 50 °C with onset temperature of 46 °C measured for HA concentration of 38 mass% and KOH concentration of 14 mass%. At ambient temperature, excessive KOH flow can cause sensible hydroxylamine decomposition at high rates even for HA concentrations much lower than the standard 50 mass% [17].

The frequency of a control system failure as an initiation event includes failure of any one or more control components such as sensor, transmitter, and actuator with a generic control failure frequency of 1 in 10 years or 10^{-1}/year [10].

An initiating event for thermal decomposition in the HA distillation system, Scenario #2, is failure of the operator to control HA concentration in the charge tank below 75 mass%. The stability of HA concentrations above 70 mass% is very sensitive to temperature and metal contaminants [18]. When hydroxylamine concentration is above 75 mass%, the process heat (50 °C) may initiate violent decomposition. A conservative frequency for this initiating event is 10^{-1}/year, assuming that the operators are appropriated alerted and are following clear procedures [10]. For Scenarios 1 and 2, a summary of the initiation events and independent layers of protection information is provided in Table 2.

4.3. IPLs

For Scenario #1, a first IPL is high temperature and pressure alarms displayed on the distributed control system to alert the operator to shut off the HA and KOH feed lines to the reactor. Once the feed is stopped, cooling water can quench the reaction at an early stage. The PFD of an operator to respond to a high temperature alarm within half of the maximum allowed time of 10 min is 1 failure in 10 demands or 10^{-1} [10].

A second IPL, a SIL 2 system will shut off the reactor heating, activate emergency cooling, and close the control valve and a separate block valve for each of the HA and KOH feed lines. For the SIL 2 system to perform as an independent protection layer with a PFD of 10^{-2}, the temperature sensor and the pressure transducer must be separate and independent of the temperature and pressure equipment used to alert the operator [10].

For Scenario #2, a first IPL is the operator is high temperature and pressure alarms to alert the operator to shut off the feed line to the distillation column. The PFD of an operator to respond to a high temperature alarm within half of the maximum allowed time of 10 min is 1 failure in 10 demands or 10^{-1} [10].

A second IPL is a SIL 2 shutdown system that is activated by an independent temperature sensor and an independent pressure transducer. For Scenario #2, the SIL 2 system will shut off the column heating, activate emergency cooling, and close the control valve and a separate block valve on the distillation column feed line.

4.4. Mitigated event probability

Using the initiating event frequency and the independent protection layer PFD values, the LOPA mitigated event frequency for

Table 2
Layer of protection analysis of two HA decomposition scenarios

#	Consequence & severity	Initiating cause & frequency	IPLs and PFD values	Mitigated event, f_i^C (year^{-1})	Meet criterion (10^{-5}/year)?	Recommendations
1	Significant thermal decomposition in the reactor to result in a process area explosion. Blast waves may cause fatalities and property losses.	Failure of flow control system causing excessive KOH feed into the reactor. The probability of occurrence is once in 10 years or 10^{-1}/year.	1. Alarm: high T and P alarms alert operator to shut off feeds and activate emergency cooling: PFD = 10^{-1}. 2. SIL 2: trip reactor heating, activate emergency cooling, close feed control and block valves on high T or high P: PFD = 10^{-2}.	10^{-4}	No	3. Add an emergency reactor quench system activated by high temperature or high pressure SIL 1: PFD is 1 in 10 demands = 10^{-1}. Mitigated event: $f_1^C = 10^{-5}$ year^{-1}
2	Significant thermal decomposition in the distillation column to result in a process area explosion. Blast waves may cause fatalities and property losses.	Operator fails to control HA concentration in distillation charge tank below 75%. The probability of occurrence is once in 10 years or 10^{-1}/year.	1. Alarm: high T and P alarms alert operator to shut off feeds and activate emergency cooling: PFD = 10^{-1}. 2. SIL 2: trip the hot water pump, activate emergency cooling, close control and block valves to shut off feed into distillation column on high T or high P: PFD = 10^{-2}.	10^{-4}	No	3. Add an emergency distillation column quench system activated by high temperature or high pressure SIL 1: PFD is 1 in 10 demands = 10^{-1} Mitigated event: $f_2^C = 10^{-5}$ year^{-1}

Scenario #1 and for Scenario #2 is calculated from Eq. (1):

$$f_i^C = f_i^I \times \prod_{j=1}^{2} PFD_{ij} = (10^{-1} \text{ year}^{-1})(10^{-1})(10^{-2}) = 10^{-4} \text{ year}^{-1},$$

$$i = 1, 2 \tag{2}$$

4.5. Risk criteria

Risk criteria must be established before a LOPA is conducted. Most companies have their own risk criteria to judge the results of risk analysis. For each of Scenarios #1 and #2, a consequence frequency criterion of 10^{-5}/year is adopted here based on a Category 4 explosion to impact onsite workers (using a consequence severity scale from Category 1, lowest, to Category 5, highest) [10].

4.6. Recommendations

In Table 2, the mitigated event frequencies for Scenarios #1 and #2 are listed as 10^{-4}/year, which for the scenario of a 500-kg HA explosion does not meet an assumed criterion of 10^{-5}/year for a Category 4 consequence severity [10]. Therefore, an additional third independent protection layer, a SIL 1 quench system initiated by high temperature or pressure in the reactor for Scenario #1 and a SIL 1 quench system initiated by high temperature or high pressure in the distillation column for Scenario #2 is recommended to control a runaway reaction. To be independent from the other IPL, the temperature and pressure transducers in the reactor and distillation column must be separate and independent from the other pressure transducers used for the other protection layers. The third protection layer PDF, which is based mainly on availability of quench water, is 10^{-1} [10].

Using the initiating event frequency and the 3 independent protection layer PFD values, the revised LOPA mitigated event fre-

quency for Scenario #1 and for Scenario #2 is calculated from Eq. (1):

$$f_i^C = f_i^I \times \prod_{j=1}^{3} PFD_{ij} = (10^{-1} \text{ year}^{-1})(10^{-1})(10^{-2})(10^{-1})$$

$$= 10^{-5} \text{ year}^{-1}, \quad i = 1, 2 \tag{3}$$

Following these recommendations, a quench system for the reactor and for the distillation column reduces the mitigated event frequencies for Scenario #1 and Scenario #2 from 10^{-4}/year to 10^{-5}/year, which meets the assumed frequency criterion and the acceptable risk criterion for a Category 4 consequence severity [10].

These LOPA results are in overall agreement with a previous QRA study of a hydroxylamine production facility [23], where the frequencies of hydroxylamine runaway decomposition calculated using fault tree analysis in the reactor and in the distillation column were 3.2×10^{-6}/year and 9.5×10^{-6}/year, respectively [23]. With only critical events and components considered, the LOPA results were consistent with the fault tree results to within an order of magnitude and required much less effort.

5. Conclusions

Reactive chemical hazard evaluations have focused on consequence modeling, but risk analysis involving both outcome frequency and consequence severity is required for cost-effective risk management. In this paper, the simplified semi-quantitative risk analysis model LOPA was used to evaluate a highly reactive process and illustrate the benefit of risk assessment to follow a HAZOP hazard analysis. The risk assessment case study discussed here is based on generic hydroxylamine production information from a CSB incident report and knowledge of hydroxylamine chemistry based partly on research at the Mary Kay O'Connor Process Safety Center. Our results indicate that LOPA for cause-consequence

pairs takes much less effort than a more detailed QRA using fault tree and event tree analysis, but LOPA can provide satisfactory results especially for an initial risk assessment. For an inherently hazardous activity such as hydroxylamine production, a structured LOPA analysis using protection layers that are determined to be mutually independent and also independent of the initiating event is required to ensure tolerable risk levels. Dependence on human factors is minimized by implementation of automatic response equipment, such as automatic temperature control, safety instrument systems, emergency cooling, emergency quench, and interlocks.

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