

## Unlock the Hidden Value of QRAs to Optimise Risk Management

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Quantitative Risk Analysis (QRA) is an extremely powerful tool to help one objectively assess the risk of complex processes. Most processes that use Highly Toxic Materials (HTMs) are complicated and pose hazards both to the employees on site and, in many cases, to the neighbouring offsite community. Understanding the risk associated with these HTM processes is often complicated due to the many risk mitigation systems that may be employed by the operator to control the hazards. Companies often conduct QRA studies to evaluate the potential risk exposures to their employees and neighbouring communities and, in some cases, to satisfy regulatory requirements. Regulatory bodies increasingly scrutinise QRA studies as part of their determination on the tolerability of risk posed by facilities processing HTMs.

The QRA studies provide an objective analysis of the consequences and likelihoods associated with potential accidental releases of the HTM in question. Properly conducted QRA studies account for existing mitigation systems and can provide insight into potential risk reduction benefits of enhancements to existing mitigation systems or installation of a new mitigation capability. While this is very helpful in providing data to leaders to make decisions, the follow-up engineering of the enhancements, as well as the design of new mitigation systems, is left to the engineering group who may not appreciate the value of the data that resides in the QRA study.

By using QRA data, one can optimise the use of mitigation equipment without sacrificing risk reduction benefits. Using the quantitative data can remove the guess work as to where detectors should be placed and to ensure that enough detectors are in the path of a potential cloud to ensure voting logic can be satisfied for automatic activation. This paper provides three case studies, taken from Hydrofluoric Acid (HF) Alkylation Unit QRA studies, which illustrate the value of using QRA data to optimise the design of mitigation systems as follows:

- Case Study One used consequence data to augment existing HF detection to provide a more robust coverage of the detector array.
- Case Study Two used scenario risk data to locate water mitigation equipment and detection equipment to optimise water usage for a site with severe water restrictions.
- Case Study Three used consequence and process data to segregate process areas to more effectively automate the activation of the Rapid Deinventory system.

QRA studies have considerable value embedded in the data and calculations performed. Unlock the value of this data by using it to design mitigation systems that deliver the desired risk reduction benefit, yet optimise the equipment to produce a cost-efficient system.

Keywords: Quantitative Risk Assessment, QRA, risk management, detection, prevention, mitigation

### Introduction

By definition, highly toxic materials (HTMs) pose a hazard to anyone who may be exposed. However, as many such materials are essential as feedstock, catalysts and for specialist uses within industrial processes, there is a need to manage these hazards in order to control the resulting risks to an acceptable level. Risk management actions fall into one of two categories; prevention or mitigation.

Prevention includes those actions taken to minimise the likelihood of an incident occurring, or in simple terms, those action that “keep it in the pipes”. Examples include design standards, material selection, operating procedures, operating limits, inspection, testing and preventative maintenance, and trips and interlocks.

Mitigation measures take effect once a release has occurred to reduce the consequence by limiting the amount of material released and reducing the exposure of the impacted population. Systems to detect a loss of containment and associated manual or automatic isolation and/or inventory transfer can limit the material available and effectively curtail a release. In some situations systems such as water curtains may also be effective in reducing the amount of material allowed to reach the exposed population. Any resulting exposure impact is also mitigated by prior actions to limit the population in the area and by providing safe havens and evacuation and emergency response plans.

Most industrial scale processes that use Highly Toxic Materials (HTMs) are complex and pose hazards both to the employees on site and, in many cases, to the neighbouring offsite community. Understanding the risk associated with these HTM processes is often complicated due to the many prevention and risk mitigation systems that may be employed by the operator to control the hazards. Clearly, a poor understanding of the risks may result in an increased likelihood of incidents. Conversely, in an organisation which believes itself to be safety conscious and risk averse, a poor understanding may also result in capital investment decisions, associated ongoing lifetime costs and potential operability impacts associated with unjustified and ineffective risk management systems.

Quantitative Risk Analysis (QRA) is an extremely powerful tool to help one objectively assess the risk of complex processes. The QRA studies provide an objective analysis of the consequences and likelihoods associated with potential accidental releases of the HTM in question. Properly conducted QRA studies estimate the likelihood of a potential release,

identify all of the actions of existing mitigation systems to determine the various outcomes and combine them with the associated frequencies to provide insight into the existing facility risk profile. The key steps in the QRA process can be summarised as follows:

- What are the potential failure scenarios?
- How likely is the failure?
- What are the conditional probabilities of successful activation of mitigation?
- What is the potential impact for each outcome?
- How does the risk profile compare to internal or external risk criteria?
- How effective are existing mitigation systems?

What other options should be considered? This data is increasingly used by management to support capital investment decisions. However in many cases the engineering of the enhancements or the design of new mitigation systems, is often left to the engineering group who may not appreciate the detail and the potential impact of design and engineering decisions. The data that resides in the QRA study can be extremely valuable when it comes to analysing the risk benefit of options and combinations of options, or even the use of alternate technology, as the design and engineering progresses.

### QRAs - A Word of Caution

The value of the data generated by a QRA is reliant on the quality of the input data, the accuracy of any models utilised in the analysis, and the robustness of the assumptions made. The often quoted statement by 20th century statistician George Box "essentially, all models are wrong, but some are useful", is particularly pertinent when applied to QRAs. Another useful analogy comes from Belgian surrealist painter René Magritte, and his painting "The Treachery of Images", shown below.



Figure 1. "The Treachery of Images" by René Magritte

When challenged over his caption "This is not a pipe", Magritte responded "No, it's just a representation, is it not? So if I had written on my picture 'This is a pipe', I'd have been lying!" Similarly, a QRA should never be considered a perfectly accurate picture of the risk. However, if the representation of risk in the QRA is based on sound principles and performed in a rigorous and consistent manner it can provide a justifiable and valuable baseline upon which to make risk management decisions, much as a quality of a market forecast might guide or mislead investment decisions.

### Hydrofluoric Acid and HFA Alkylation Units

The case studies that follow are all related to hydrofluoric acid alkylation units. This section gives a brief summary of HF and HF Alkylation units for context.

HF is a strong and highly corrosive acid with a strong, irritating odour. HF is toxic at low concentrations and is a contact-poison with the potential for deep, initially painless burns and ensuing tissue death. It may also cause systemic toxicity and eventual fatality by interfering with body's calcium metabolism.

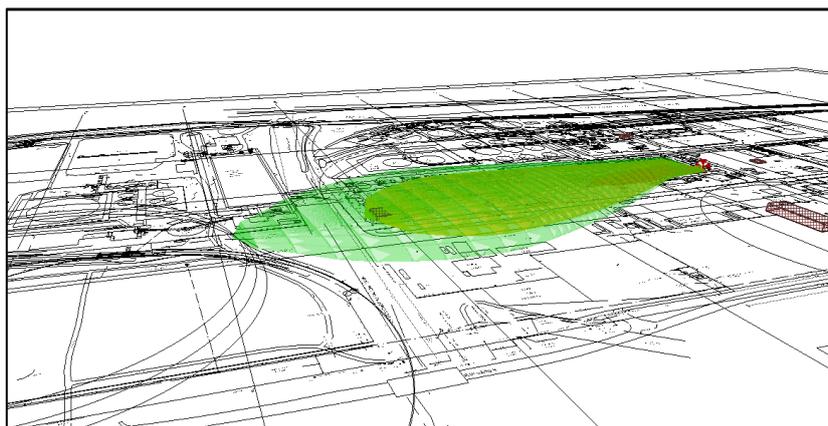
Many oil refineries operate Alkylation units which utilise HF at a catalyst, including four of the six refineries operating in the UK. The alkylation process produces a synthetic alkylate which is used as a blending stock for upgrading gasoline/petrol. HF is also widely used for glass etching, plastics production, electronic circuit cleaning and production and purification of radioactive materials.

The HF Alkylation unit on a refinery site usually represents the toxic hazard with the potential for the highest impact off the refinery site.

### Case Study 1 – Detector Coverage

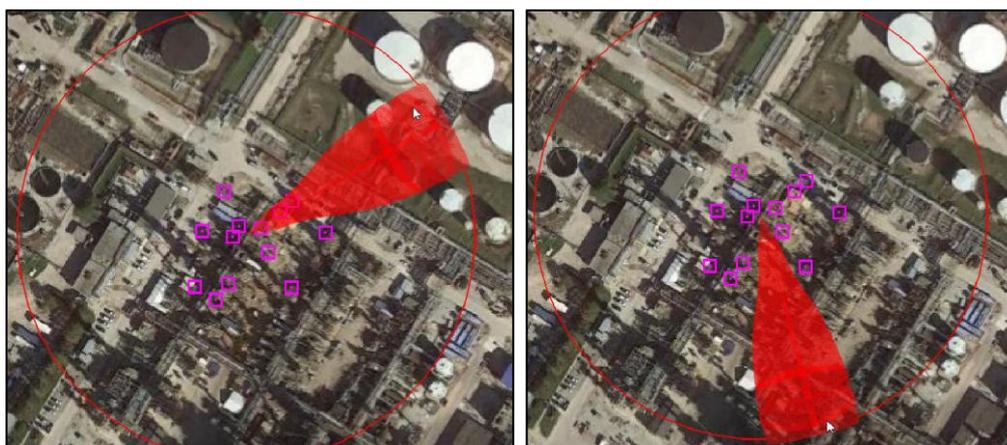
Analysis of the detection system is a key part of the HF QRA as early reliable detection is critical for effective mitigation. If the release is not detected any manual or automated mitigation systems will not be initiated.

Prior to analysing the adequacy of the detection system it was necessary to develop a comprehensive set of potential release scenarios that could challenge the detection system. Firstly the process information was scrutinised to identify those sections of the HF Alky unit where the HF concentration was above the threshold of concern. Process conditions including composition, HF concentration, temperature and pressure, and potential release locations were then reviewed to develop a list of representative release cases, typically numbering 20-30. These release case were then input into a 3D model of the site. For each scenario the discharge and dispersion was modelled for a selection of release sizes, representative weather categories and for all wind directions. With the combinations of all these permutations, well over a thousand calculated scenarios resulted. An example of a plume from one such release is shown in Figure 2.



**Figure 2. Example of Toxic Plume arising from HF Release**

The existing detection system was reviewed to determine the location, operation and reliability of the detectors and whether they were used for alarm only, alarm and activation, or alarm and activation based on voting. Many units have a combination of HF and hydrocarbon detectors. The composition of the material released dictated whether additional credit could be taken for the hydrocarbon alarms. The data was added to the 3D model and a consequence based analysis performed to determine if the scenario would be detected and by how many detectors. For illustration purposes, Figures 3 and 4 shows a series of snapshots from an output for the plume generated by one specific scenario. Figure 3 illustrates directions where good coverage is achieved and no coverage is achieved.



**Figure 3. Examples of Good (left) and Zero (right) Detector Coverage**

It is important to note that a number of gaps in coverage were only identified through use of a 3D model as the plume from some of the elevated release cases would have been too high to have been detected by some of the lower level detectors, which would not be visible in 2D alone. Figure 4 illustrates that the detector appearing to be covered by the plume in the 2D view is actually underneath the plume when viewed from the side (circled).



Figure 4. Example of Detector Coverage in 2D and 3D

Secondary risk based analysis was then performed to determine the detection probability for each scenario based on detector reliability and any voting logic present. A selection of results is shown in the ‘before’ column of Table 1. The coverage gaps and areas of low probability of detection were reviewed and additional detectors added to improve the likelihood of detection. The ‘after’ column in Table 1 below shows the effectiveness of this 3D, scenario specific, risk based analysis in improving the detection probability.

Table 1. Potential Probability of Detection Improvements Resulting from Analysis

Before		After	
Source Name	Detection Probability	Source Name	Detection Probability
10M4UN	54.70%	10M4UN	100.0%
10S4UN	62.44%	10S4UN	100.0%
11L4UN	58.42%	11L4UN	100.0%
12L4UN	60.88%	12L4UN	100.0%
13L4UN	85.06%	13L4UN	100.0%
13M4UN	76.71%	13M4UN	100.0%
14L4UN	74.64%	14L4UN	100.0%
14M4UN	50.44%	14M4UN	100.0%
15L4UN	54.19%	15L4UN	97.3%
17L4UN	64.28%	17L4UN	100.0%
18L4UN	26.27%	18L4UN	89.0%
18M4UN	17.73%	18M4UN	93.4%
18S4UN	26.27%	18S4UN	89.0%
1L4UN	68.00%	1L4UN	100.0%
1M4UN	62.23%	1M4UN	100.0%
154UN	72.82%	154UN	100.0%
2L4UN	65.63%	2L4UN	100.0%
2M4UN	65.63%	2M4UN	100.0%
254UN	76.54%	254UN	100.0%
3M4UN	65.63%	3M4UN	100.0%
3S4UN	76.54%	3S4UN	100.0%
4M4UN	75.93%	4M4UN	100.0%
4S4UN	71.14%	4S4UN	100.0%
5M4UN	75.50%	5M4UN	100.0%
5S4UN	75.50%	5S4UN	100.0%
6M4UN	92.92%	6M4UN	100.0%
6S4UN	92.92%	6S4UN	100.0%
7M4UN	58.98%	7M4UN	100.0%
7S4UN	58.98%	7S4UN	100.0%
8L4UN	62.23%	8L4UN	100.0%
8M4UN	65.63%	8M4UN	100.0%
8S4UN	76.54%	8S4UN	100.0%
9M4UN	65.61%	9M4UN	100.0%
<b>Total</b>	<b>64.76%</b>	<b>Total</b>	<b>99.08%</b>

The output from this analysis was used to inform a discussion on the use of different detector technology to improve coverage, use of multiple manufacturers to improve reliability, and refinements to the voting logic associated with activation of automatic mitigation equipment.

Part of the response when a suspected HF release is detected is usually for an operator to verify the release is genuine before any manual mitigation is initiated, and also to give the opportunity to abort certain types of automatic mitigation if the detection is spurious. Good video surveillance reduces the need for an operator to go out into the field to perform this verification. The video surveillance available to the operator was also reviewed and recommendations for improvement made in the following areas:

- Use of multiple camera and screens
- Use of elevated cameras to get a ‘bird’s eye’ view
- Benefits of fixed cameras or ‘home’ position reset on adjustable cameras
- Use of record and real-time playback capability

Implementation of the improvements arising from this study will give an increased detection reliability that will improve the reliability of the manual activation of mitigation systems. Furthermore, the improved understanding and level of confidence in the detection system also mean that options for the reliable automatic activation of mitigation systems are much more feasible.

### Case Study 2 – Water Mitigation of HF Releases

There are two basic approaches that have proven to be effective in the water mitigation of HF releases. These are:

- Allowing the HF cloud to disperse and then come into contact with the water mitigation (curtain or water wall). By permitting some dispersion, the HF is less concentrated and has lower momentum allowing for better contact between the water and HF in the cloud.
- Applying the water directly onto the release point in order to engulf the release and absorb the HF at the source of the release. This generally poses challenges in accurately directing the water onto the release point.

The three types of water applications that have proven effective in the absorption of HF aerosol releases are briefly described below.

#### Water Wall Mitigation

This method utilises the disperse and contact approach and involves an array of monitors with hydraulically balanced water nozzles set to produce a fog which create a wall of water, as shown in Figure 5. This type of system is often located along the perimeter of the HF Alkylation unit to achieve the spacing required for effective absorption and to maximise the scenarios it can effectively mitigate. Activation of the water wall can be automated, normally based on a voting logic involving multiple detectors, or manually initiated once a release has been confirmed.



Figure 5. Water Wall Mitigation in Operation

#### Water Curtain Mitigation

The water curtain disperse and contact approach is usually applied to high risk parts of the unit such as high inventory vessels and HF pumps, rather than the unit as a whole. Using strategically located monitors and/or rows of fog nozzles the area is encircled with a high flow, small drop size wall of water. A higher flow rate is required compared to the water wall approach as any HF release will only have had limited opportunity to disperse and thus be at a higher concentration and momentum before contacting the water mitigation. Water curtain systems can be activated automatically based on detector(s) or manually. Some systems allow segments of the curtain to be activated depending on the location of the release in order to reduce water usage. Figure 6 shows a water curtain system employing numerous fog nozzles surrounding a high inventory HF Settler prior to and during activation.



**Figure 6. Water Curtain Mitigation Prior to and during Activation**

### **Aim and Shoot Mitigation**

As the name implies, the aim and shoot method of water mitigation adopts the approach of direct application at the point of release. Typically, two, three or four water monitors with a cone shaped spray pattern are directed at the release point. Although this approach is effective in knocking out the HF it requires the water to be accurately applied. The monitors used for this duty can be fixed, remotely operated, manually operated or a combination of the three. Fixed monitors are usually pre-aimed at likely sources of release, remotely operated monitors often with a 'home' position based on likely release point, and manually operated monitors are usually located on the edge of the unit. Figure 7 shows an aim and shoot system utilising remotely operated monitors in operation.



**Figure 7. Aim and Shoot Water Mitigation System in Operation**

### **Water Mitigation System Options**

There are many other factors affecting the selection of the appropriate water mitigation system(s) and their effectiveness. Water supply, delivery and disposal are key considerations. For example, constraints on water supply can limit the overall volume of water available; header and delivery system design and capability can limit the individual and total volumetric delivery rate; capacity of the drainage system to retain the runoff to allow subsequent neutralisation.

### **Utilising the QRA Data**

The case study relates to a site with severe water restrictions. A baseline QRA model for the HF Alkylation unit was first developed, as described previously. The design and operation of the existing water mitigation systems was reviewed and then confirmed by physical inspection to validate the positioning, nozzle fitting and operation. The effectiveness of the systems was then determined in quantitative terms taking account of ability of the system to mitigate the release, the likely decontamination factor achieved, the likelihood of successful manual or automatic activation, activation delays due to pump start-up, and probability of equipment failure. This information was combined with the relevant scenario data to determine the risk reduction achieved by the existing systems and configuration on a scenario by scenario basis.

The results were presented and discussed with the site personnel and potential improvement options and combinations of options identified. The options identified included:

- Removal and/or reduction in use of high water usage systems with low mitigation effectiveness as the primary means of mitigation
- Segmentation of water wall systems around unit to allow targeted activation
- Improvements to water curtain system around critical pumps
- Improvements to detector coverage to aid in selection of water mitigation equipment and pre-aiming to release area
- Changes to detector voting logic to reduce spurious activation of water mitigation systems

A preferred set of options was selected and sensitivity studies performed using the baseline QRA to quantify the risk reduction achieved. Again this was performed on a scenario basis which allowed the dominant risk contributing scenarios and most effective mitigation effects to be clearly identified. Implementation of the findings would result in an incident management strategy for HF releases that provided more timely and effective mitigation and that was able to be sustained for longer due to the lower water usage.

### Case Study 3 – Rapid Acid De-inventory System

Within the HF Alkylation unit the largest HF inventory is held in the HF Settler. Many Alkylation units around the world include a means of rapidly dumping the Settler HF acid inventory to another vessel in the event of a release to minimise the material that can be released, commonly referred to as a RADS (Rapid Acid De-inventory System) or RATS (Rapid Acid Transfer System). Limiting the inventory available effectively limits the duration and therefore the impact of the release. The RADS can be manually or detector activated. Some automated systems incorporate a time delay to allow operations personnel the chance to visually identify the release location and to give an opportunity to abort activation. Activation might be aborted by the operator if the detection alarm is considered spurious or the operations personnel realise that the release is coming from another part of the unit that would be unaffected by activating the acid dump.

In the case considered the existing dump sequence did not include isolation of feeds and other connected equipment. Strategically located isolation valves were included in the design to:

- Segregate equipment from the HF inventory removed to the dump vessel
- Isolate the regeneration section
- Isolate the hydrocarbon feed
- Isolate the acid circulation pumps and other HF pumps

In addition to the baseline scenario modelled in the QRA an additional series of scenarios was defined to model the impact of the successful activation of the RADS. These scenarios modelled the consequences associated specifically with the continued feed and circulation through the settler. Further calculations were then performed to determine the changes to the consequences with the actuation of certain combinations of isolation valves. The resulting data allowed the facility to identify the critical valves that should be automatically isolated upon detection and then allow operators to manually activate the RADS sequence to achieve target risk reduction.

### Conclusions

A properly conducted QRA study that accounts for existing mitigation systems provides a valuable representation of the risk posed by a facility handling highly toxic materials. This is just the beginning of the potential value that can be unlocked and goes beyond any immediate need to satisfy corporate policies or regulatory requirements. This paper shows that the data and calculations performed as part of a QRA study can be utilised to help in selection of potential mitigation enhancements to achieve quantifiable risk reduction benefits. Furthermore, the QRA data can also be used to produce a cost-efficient mitigation system by helping to define the design parameters of the selected mitigation systems.