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APPROACHES FOR PREVENTING AND MITIGATING ACCIDENTAL GASEOUS CHEMICAL RELEASES

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SUMMARY

This paper presents a review of approaches to prevent and mitigate accidental releases of toxic and flammable gases. The prevention options are related to: choosing safer processes and materials, preventing initiating events, preventing or minimizing releases, and preventing human exposures. The mitigation options include: secondary confinement, de-inventory, vapor barriers, and water sprays/monitors. Guidelines for the design and operation of effective post-release mitigation systems are also presented.

I. ACCIDENT PREVENTION AND MITIGATION OPTIONS

Accident prevention and mitigation in the process industries is based on the military concept of defense in depth,[1] if one line of defense fails, then others are available.

Engineering and administrative options to prevent and control accidental releases and reduce their consequences can be considered sequentially in five steps, each comprising an additional layer of protection:[2]

a) Inherently safer technologies, processes and materials.
b) Options to prevent accident initiating events (e.g., detection and monitoring systems, and procedures for safe operation).
c) Safety systems to prevent/minimize releases at the source (e.g., automatic shut-offs, flow restricting valves, cooling and containment systems).
d) Systems to mitigate, delay, or dilute releases to the environment: Passive systems (e.g., vapor barriers) and active systems (e.g., scrubbers and water curtains).
e) Options to prevent or minimize human exposures and their consequences (e.g., emergency preparedness and response plans, warnings, and evacuation plans).

A. Technology/Process/Material Selection

The most efficient strategy to reduce hazards is to choose technologies which do not require the use of large quantities of hazardous gases. This is especially important for new technologies where this approach can be implemented early in development, before large financial resources and efforts are committed to specific options. Such strategy can be implemented as: i) substitution (i.e., using safer or environmentally more benign materials), ii) use a safer, less mobile form of a hazardous material, and iii) reduce the quantity in storage and/or the temperature and pressure of a process. The relative risk of pressurized and refrigerated storage for ammonia, chlorine, butadiene, ethylene oxide and vinyl chloride have been examined by Marshall et al.[3] A general discussion on conflicts and decisions in the search for inherently safer process options can be found elsewhere.[4]

B. Prevent Initiating Events

Once specific materials and systems have been selected, strategies to prevent accident initiating events need to be evaluated and implemented. Administrative and engineering options should be considered (e.g., maintenance, inspection and testing, worker training, operating procedures, and safeguards against process deviations). The importance of the administrative options and procedures need to be emphasized. In the chemical industry many accidents have happened not because safety engineering systems were lacking, but because safe procedures and preventive strategies were not followed.

C. Prevent/Minimize Releases

The next step is to implement safety options to suppress a hazard when an accident initiating event occurs (e.g. early detection, flow restricting and isolation valves, cooling systems, double-containment, and adequate ventilation). Fail-safe equipment and

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valves, warning systems and safety controls can reduce and interrupt gas leakage. Flow restricting orifices has become a common option in pressurized cylinders with highly toxic gases and pyrophoric gases (e.g., AsH_3, PH_3, SiH_4). These orifices can reduce the flow out of an open cylinder valve by up to two orders of magnitude and provide, therefore, a superb passive flow reduction. Double containment, in the form of either double wall storage tanks or double co-axial distribution lines and raceways, is an important measure against leaks of toxic gases into occupational space. Finally, emergency evacuation (de-inventory) of fluid from leaking equipment can reduce and terminate leakage.

D. Control/Minimize Releases to the Environment

If an accident occurs and safety systems fail to contain a hazardous gas release, then engineering control systems will be relied on to reduce/minimize environmental releases. If the release is confined and can be diverted into the control equipment, chemical scrubbers and combustion chambers can be used. The highly transient character of accidental large gas releases demand special designs and configurations for these systems.[2] Unconfined releases of toxic hazardous gases present special challenges; their mitigation is discussed in sections 2 to 6 below.

E. Prevention/Minimization of Human Exposures

As a final defensive barrier, the prevention of human exposures is needed if a hazardous gas is released, in spite of previous strategies. This barrier includes remote location of gas storage, exclusion zones adjacent to plant boundaries, early warning systems, emergency preparedness, response, and evacuation plans to prevent exposures to the public. It is essential that such plans be regularly rehearsed and practiced under simulated emergency conditions to test the response of personnel, increase their base of experience, and evaluate the effectiveness of equipment. Quick response and medical preparedness is essential to reduce consequences if exposures do occur.

Although preventing industrial accidents through the choice of inherently safer technologies, processes, systems, and safety procedures is of the utmost importance, vapor and gas releases may happen, in spite of all precautions. Therefore, techniques to mitigate these hazards should be in place. These are discussed below.

II. SECONDARY CONFINEMENT

Many installations handling toxic gases incorporate some form of double containment which provides for an outer barrier to hold the toxic gas if the inner containment fails. These double containment systems include: double piping, double walls, dikes, and total enclosures.[5]

Double containment, in the form of either coaxial distribution lines, raceways, and double-wall storage tanks, are an important measure against leaks of toxic gases into the occupational space. Double piping is used extensively in the semiconductor and photovoltaic industry where small diameter tubes carrying highly toxic gases are enclosed in larger pipes under nitrogen pressure, or are placed into air-purged raceways. Double-wall storage is practiced in many applications including atmospheric ammonia storage.

Dikes are used to provide a secondary containment outside a vessel that, in case of a spill, will hold the entire contents of the vessel in a pool. In designing a dike, in addition to accounting for the volume of the expected spill, one should consider the rate of filling, the surface area of the spill, and fire protection.[5]

Secondary enclosures for a plant handling gases and volatile toxic liquids can be effective in preventing their escape and reducing or eliminating their potential for harm.

III. EMERGENCY DE-INVENTORY

Transfer of fluids from leaking containers to emergency de-inventory vessels, reduces the duration and the rate of a leak by decreasing the pressure and/or the mass of a hazardous fluid in a leaking equipment. The lines connecting the vessels to be emptied with the recovery vessels have to be of a large diameter to facilitate a quick transfer. Furthermore, a fluid transport system based on pressure differential and gravity is more reliable for emergency operations than pumps or nitrogen pressurization.

Large capacity de-inventory systems are used in alkylation units and are capable of draining in a few minutes hundreds of thousands of pounds of acid from the acid settler system to a remote recovery vessel. Transfer of fluids from several segments of an alkylation unit to the recovery vessel(s) can be

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facilitated initially by differential pressure and gravity, and when pressure equalizes, by gravity only. Such a design basis has the advantages of being reliable as it is based on a passive transfer mechanism, and it provides total containment of both acid and hydrocarbons which do not need to be separated during transfer. Using more than one vessels for recovering the inventory has the advantages of: 1) Increased availability, since in case of an emergency if one vessel is out of service for maintenance, the other vessel will have the capacity to handle an acid-only de-inventory, and 2) potentially less expensive construction due to lower structural support requirements.

IV. VAPOR BARRIERS

Vapor barriers are vertical solid or permeable vapor barriers near the release point designed to dilute or delay a dense gas/vapor cloud. Vapor barriers are in the form of fences (e.g., single straight wall, a row of densely-placed trees), and of boxes (i.e., four-sided enclosures without a roof). The effectiveness of such barriers have been investigated in a series of wind-tunnel experiments[6]. These tests showed that fence barriers can dilute a dense gas by a factor of 2 to 9 in the near field (<500 m from the release), but the effect of this dilution becomes negligible after a distance of about 1 km. For vapor boxes, concentration reduction factors were in the range of 4 to 15 in the near-field, and 1 to 4 in the far field (~3 km). Therefore, vapor boxes had a sustained effect on dense gas concentration reduction, due to vapor retention in the box, whereas vapor fences had only a near field effect.[6]

Another type of barrier is the stagnation plate, designed and positioned so that it can cause liquid impingement of a high momentum, two-phase release and reduce, therefore the amount of vaporized material.[2] These barriers are currently under investigation for their effectiveness in HF releases.

V. WATER SPRAYS AND CANNONS

A. Removal of Water-Soluble Gases

The removal potential of water sprays to mitigate unconfined releases of water soluble gases (i.g, HF), has been investigated in large-scale experiments at the Department of Energy (DOE) Spill Test Facility, by Lawrence Livermore National Laboratory and Amoco Corporation unconfined (Goldfish tests)[7], and the Industry Cooperative Hydrogen Fluoride Mitigation / Assessment Program (ICHMAP (Hawk tests).[8] Both the Goldfish and the Hawk tests showed that when water is applied in a prudent way, it can absorb up to 95% of the released gas. Many companies have already installed HF mitigation systems comprising either fixed water sprays or monitors, and several of those have undergone actual testing. None of these systems have been used in actual emergencies involving HF, but portable water sprays have been found to be effective in actual emergency NH_3 releases.[9,10]

The Hawk tests represent the most comprehensive effort to evaluate a system capable of mitigating unconfined releases, and they are of a scale unprecedented in the evaluation of any other mitigation system in the chemical industry. Water sprays for scrubbing unconfined release of water-soluble gases have been studied theoretically, tested in field experiments and tried in actual emergencies. HGSPRAY, a verified mathematical model,[11] has been developed to quantify effectiveness of water sprays at specific installations, given specific release scenarios and weather conditions. HGSPRAY has the capacity to model chemical reactions in the liquid-phase and can be used to evaluate mitigation systems using caustic or oxidizing solutions for removal of various gases. The model has been used in aiding the design of several industrial HF mitigation systems.

B. Dilution of Flammable Vapors

Investigators in England and the United States have extensively tested water sprays for their potential to dilute a released gas by inducing air flow. In the field-tests, dilution ratios (ratios of gas concentrations with and without the water sprays operating) were in the range of 2 to 5 measured 10 to 20 m downwind of the spray.[12] This dilution provided a worthwhile local enhancement of the rate of dispersion of heavy gas releases, which may be sufficient to reduce the concentration of a flammable vapor below its low flammability limit, but the effect of this local dilution is quite insignificant in reducing health hazards from highly toxic gases.[2]

VII. COMBINATION OF TECHNIQUES

Hybrid systems, combining features from different approaches, have not been investigated at this time. An exception is dikes which are often used with other techniques (e.g., foam blanketing). However, some of the previously described techniques can, in principle, be used together to enhance mitigation effectiveness. For example, vapor barriers may be combined with water sprays into a hybrid mitigation system with the advantages of passive operation and high effectiveness. However, potential accumulation of explosive hydrocarbon vapor cloud within the barrier is a concern, as well as reduced accessibility to the unit. Vapor barriers allowing ventilation by fans or wind, with louvers or drop curtain-type walls, may answer these problems. A hybrid system with a barrier (stagnation plate) near a potential HF jet release, can, if appropriately designed reduce the amount of airborne material and, therefore, assist the performance of a water spray system. De-inventory systems can also assist the performance of water sprays or monitors, since they reduce the release flow rate and its duration, and make removal by spraying easier.

Of course, combining prevention and mitigation options has a great value. For example, in-situ manufacturing of highly toxic gases to avoid the transportation risk, has resulted in smaller plants which are more amenable to secondary containment. Reduced quantities in storage, storage isolation and segregation reduces the magnitude of the inherent risk of a facility, while easing the task of a mitigation system.

CONCLUSIONS

Preventing and minimizing accidental releases of hazardous gases through the choice of inherently safer technologies, processes, materials and safety procedures is of the utmost importance. However, vapor and gas releases may happen in spite of all precautions, and techniques should be in place to mitigate such releases. Such techniques include but are not limited to secondary confinement, de-inventory, vapor barriers, foam spraying, and water sprays/monitors.

Dikes are necessary in any situation involving a liquid spill. Vapor barriers should be considered only as a near field option to assist a partial and local dilution of a gaseous release. They have, however, the advantage of increased reliability that their passive operation provides.

De-inventory systems can reduce the magnitude and the duration of a release and in combination with water spray systems provide an enhanced means of control.

Water sprays are probably the most tested unconfined gas/vapor mitigation systems in the industry today. Their effectiveness in dispersing gaseous releases is low (similar to that of vapor barriers), but their effectiveness in absorbing water-soluble gases has been shown to be high. In a typical refinery they can have a dual function, remove a water-soluble vapor cloud, and dilute a flammable vapor cloud.

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REFERENCES

1. Kletz T., Accident Prevention: Lessons Learned, in Fthenakis, 1993, above.
2. Fthenakis V.M., Prevention and Control of Accidental Releases of Hazardous Gases, Van Nostrand Reinhold, 1993.
3. Marshall J., et al., The Relative Risk of Pressurized and Refrigerated Storage for Six Chemicals, Paper presented at the 1994 AIChE Summer National Meeting, Aug. 14-17, 1994, Denver, CO.
4. Hendershot D. C., Conflicts and Decisions in the Search for Inherently Safer Process Options, Plant/Operations Progress 414(1): 52-56, 1995.
5. Englund S.M., Process and Design Options for Inherently Safer Plants, in Fthenakis, 1993, above.
6. Petersen R.L., Vapor Barriers, in Fthenakis, 1993, above.
7. Blewitt D.N., J.F. Yohn, R.P. Koopman, T.C. Brown, and W.J. Hague, Effectiveness of water sprays on mitigating anhydrous hydrofluoric acid releases. Proceedings of the Intl. Conf. on Vapor Cloud Modeling, pp. 155-71, Nov. 2-4, 1987, published by the Amer. Inst. of Chem. Engineers.
8. Schatz K.W., Mitigation of HF Aerosol Clouds with Water Sprays, in Fthenakis, 1993, above.
9. Pallen J.J., Lessons learned form an anhydrous ammonia release incident., resented at the AIChE 1989 Annual Meeting; Ammonia Safety Symposium, November 6 1989.
10. Idaho State Journal, October 20, 1985, p. 2 - Section A.
11. Fthenakis V.M., HGSPRAY: A complete model of spraying unconfined gaseous releases, J. Loss Prevention, 6(5), 327-331, 1993b.
12. Moodie K., The Use of Water Sprays to disperse spills of Heavy gases, Plant/Operations Progress 4(4): 234-41, 1985.