Mitigation Options for Accidental Releases of Hazardous Gases

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ABSTRACT

The objective of this paper is to review and compare technologies available for mitigation of unconfined releases of toxic and flammable gases. These technologies include: secondary confinement, de-inventory, vapor barriers, foam spraying, and water sprays/monitors. Guidelines for the design and/or operation of effective post-release mitigation systems and case studies involving actual industrial mitigation systems are also presented.

1. ACCIDENT PREVENTION & MITIGATION OPTIONS

Accident prevention and mitigation in the process industries is based on the military concept of defense in depth (Kletz, 1993); 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 (Figure 1), each comprising an additional layer of protection (Fthenakis, 1993):


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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).

Figure 1 Prevention and Mitigation Options for Hazard
Management.

1.1 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

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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.

Choosing a substitute is not always easy. HF is such an example. The use of this chemical in large quantities in chemical and petroleum facilities is under attack from federal and local regulators as a potential public health and environmental hazard, because potential HF releases from alkylation units form a denser-than-air cloud which can cause public health hazards. Plans to ban HF use in refineries are based on the belief that there is a safe alternative to using HF in the alkylation units, namely, sulfuric acid (H₂SO₄), which has a higher boiling point than HF, and in case of a release would form primarily a liquid spill instead of a vapor cloud. The issue, however, is more complex than what the boiling point numbers may suggest. In sulfuric acid based units, 140 times more H₂SO₄ is needed for the same operation, producing 280 times more waste than in the case of HF. Consequently, H₂SO₄ presents greater transportation and environmental disposal hazards than HF. Also, large H₂SO₄ and H₂SO₄/hydrocarbon systems would be more susceptible to leaks than HF systems because of their bigger volume and the relatively greater amount of piping needed. Preliminary industry studies show that the mixture of H₂SO₄ and hydrocarbons (the form in which most of H₂SO₄ exists in refineries) when released may volatilize to a significant degree, thereby reducing the safety factor offered by the high boiling temperature of H₂SO₄. Vapor clouds can also be generated from leaks of either SO₂ or SO₃ in the acid regeneration unit, and from foaming in the sulfuric acid alkylation unit.
Other options to reduce HF related risks include lower operating pressure, temperature, and smaller inventory, to reduce the amount of airborne material during an accidental release. Also, instead of using pure anhydrous HF as the alkylation catalyst, mixtures of HF and other chemicals or acids have the potential of changing the physical properties in such a way that a lower percentage of the leaking material remains airborne and a substantial fraction can be collected as a liquid. Currently, some companies are working on this problem, but have not released any of the proprietary process information.

The relative risk of pressurized and refrigerated storage for ammonia, chlorine, butadiene, ethylene oxide and vinyl chloride have been examined by Marshall et al., 1994. A general discussion on conflicts and decisions in the search for inherently safer process options can be found elsewhere (Hendershot, 1994).

1.2 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).

1.3 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 valves, warning systems and safety controls can reduce and
interrupt gas leakage. The first step in minimizing a gas release is a prompt detection of the leak. Toxic-gas detectors should be installed at critical locations inside the plant to provide prompt warning. Several types of gas and vapor detectors are available for a wide range of chemicals (Atallah, 1993).

Flow restricting orifices has become a common option in pressurized cylinders with highly toxic gases and pyrophoric gases (e.g., AsH₃, PH₃, SiH₄). 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. Isolation valves can interrupt the flow but need to be activated "on-demand". These valves should be "fail-safe" (e.g., closing on loss of instrument air or electric power), and be operated from a safe, remote location (e.g., a control room having a reliable fresh-air supply). All control valves should be as close to storage as possible, for a potential valve leak to be handled by the same systems (e.g., water curtains) which are installed to ameliorate massive releases from storage. Check valves can be used to prevent back-flow from a larger container to avert a leak. To assure reliable operation, these check valves should be checked periodically. Operating push-buttons for actuating isolation valves and shutting off pumps should be located in the prevailing upwind direction, not far away from the equipment they control. A second emergency push-button should be located in the control room.

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.
1.4 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 (Fthenakis, 1993). Unconfined releases of toxic hazardous gases present special challenges; their mitigation is discussed in sections 2 to 6 below.

1.5 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.

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. Failure to follow safety procedures caused the release of dioxin in Seveso, Italy; the control systems were poorly maintained and not operative at the time of the tragic accident in Bhopal, India; and temporary unsafe
connections resulted in the accident at Flixborough, England.

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.

2. 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 walls, double piping, dikes, and total enclosures.

2.1 Double Piping

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.

2.2 Dikes

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. Considering the liquid volume alone is sufficient for pipe failure and small cracks; however, in case of a catastrophic vessel failure, a massive spill may overtop a sloping dike and splash over a vertical wall. Surface area of a spill should be minimized for fluids that are highly toxic and have a significant vapor pressure at ambient conditions, such as acrylonitrile or chlorine (Englund, 1993). In these cases, deep dikes or some other design that minimizes surface area need be considered. Finally, the diked areas must not be allowed to fill with water, snow, or ice.

A dike should also provide some fire protection. Dikes around storage and process equipment should be designed in a way that will not allow flammable, combustible or corrosive liquids to accumulate around the bottom of tanks or equipment. The dike should direct potential spills away from the tank or equipment, and provide a fire wall to shield the equipment from the flames if a fire occurs. This consideration applies not only to flammable fluids but to corrosive ones as well. If, for example, bromine is spilled in a non-drained dike area containing bromine storage tanks, the automatic dump valve on the tanks may rapidly become corroded, making it impossible to transfer contents to another storage vessel (Englund, 1993).

2.3 Total Enclosures

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. In the design of such enclosures, one must consider the total amount of gas or vapor that can be released in the enclosure, the peak rate at which vapor can be formed, and the mechanism of release and vaporization under any possible circumstances (e.g., jet
discharge, spray evaporation, rain out, and pool formation/evaporation). Release and vaporization rates under worst conditions should be used to determine the capacity of a scrubbing or incineration system required for the treatment of the trapped in the enclosure toxic gas/vapor, and the maximum rate of pumping this gas into the pollution control equipment.

In case flammable materials are handled in a plant, total containment must take into account the possibility of a vapor explosion in addition to the release of toxic materials. In many cases, total containment can be accomplished by designing the process equipment to withstand the maximum pressure that can be expected from runaway reactions or explosions. An interesting example, where both a toxic and a flammable vapor are handled with a secondary containment, is a phosgene plant described by Englund (1993). This plant handles phosgene which is highly toxic but not flammable, and chlorobenzene which can form an explosive mixture with air. The plant's design evolved through different stages, from an open plant to a totally contained one. The open-air plant design provides for relief of a potential explosion, but it does not ameliorate the health risks from phosgene releases. An open-air plant with water curtain, can minimize explosion damage and also reduce the concentration of a phosgene release. When a combined water and ammonia curtain is used, the effectiveness of phosgene removal increases. The water and water/ammonia curtains, however, may be damaged in case of an explosion. A closed plant, provides for the containment of small leaks which can be transported by the ventilation system into a scrubber or incinerator for removal, but it does nothing to minimize the consequences of an explosion or the occupational health risk from exposure to phosgene. The next design entailed double-wall construction for the most critical parts of the plant, or enclosing them in a pressure vessel (pot-in-pot)
Such a design reduces the risk due to explosion damage, when the outside wall or vessel can withstand the overpressure of an explosion, while also containing toxic leaks. Phosgene releases from other parts of the plant, however, are not controlled. Another considered option was subsurface containment, where the most hazardous parts of the plant are placed in a hole in the ground, and hazardous releases are collected and incinerated. This structure is explosion resistant, but underground construction is expensive and there is a potential for subsurface contamination of soil and water. The final design is enclosure of the most hazardous parts of the plant in a very large pressure vessel. All vapor releases are contained and they are vented in an incinerator for treatment (Figure 2b). The structure can withstand a deflagration caused by a release of flammable vapors inside the structure. Entry into the large vessel is controlled and personnel entering must wear air packs. A facility using this technology has been built at the Dow Chemical Company Plant in Stade, Germany.

Figure 2. (a) Double wall construction; (b) Plant inside large pressure vessel.
3. EMERGENCY DE-INVENTORY

Transfer of fluids from leaking containers reduces the duration and the rate of a leak. De-inventory systems can reduce the leak rate by decreasing the pressure and/or the mass of a hazardous fluid in a leaking equipment. The pressure can be reduced by vapor release to an emergency disposal system, and the mass can be reduced by transferring the liquid to a disposal or recovery system. The later process has to be quick in order to be effective in an emergency situation. The lines connecting the vessels to be emptied with the recovery vessels have to be of a large diameter to facilitate such 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. In the non-emergency operation of transferring the material from a recovery vessel back to the storage vessel, nitrogen pressurization can be used.

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. This can be done by using bottom fitted valves, large diameter (e.g., 16 inch or 24 inch) connecting lines, and remote acid recovery vessel(s) at a lower elevation than the settler. Recovery vessel(s) are sized to contain both acid and hydrocarbons from the acid settler at the highest operating level, and the normal volume of acid from an acid storage drum. Of course reinforced pipe supports, piping laterals and long radius fittings are required to handle severe fluid hammer due to the initial slug flow in the transfer pipeline. Transfer of fluids from several segments of an alkylation unit to the recovery vessel(s) can be 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. The de-inventory of the acid can be very quick (e.g., 5 minutes or less); however, longer times are needed for the transfer of hydrocarbons to the recovery storage, because the vapor pressure in the settler is almost down to atmospheric when HF has been evacuated, and the quantity of hydrocarbons is much greater than that of HF. 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.

4. 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 by Petersen (1993) in a series of wind-tunnel experiments funded by the Industry Cooperative HF Mitigation-Assessment program (ICHMAP). These experiments 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.
The following general guidelines for vapor box design have been derived from the above fluid modeling tests: 1) The box to be lower than the surrounding structures; 2) the box volume to be approximately 2 times larger than the volume of the expected release; 3) the box width and length not to exceed 3 to 5 times the box height; 4) box effectiveness can be increased by installing porous screens upwind of the box; and 5) vapor boxes are more effective when the release points they contain are not higher than 3 times the height of upwind obstructions (Petersen, 1993).

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 (Fthenakis, 1993). These barriers are currently under investigation for their effectiveness in HF releases.

5. FOAM SPRAYING

Water-based foams have been used by the fire service to control and extinguish flammable liquid fire for over 50 years; foam blanketing of spills, cuts off the oxygen supply necessary for combustion, and also suppress the release of vapor from the liquid surface.

Originally developed for fire control, foam agents and equipment are now available specifically for spill control. Such foams can be used to a broad range of chemicals, including liquefied gases and water-reactive liquids. The long-time use of foam by the fire service for fire control has provided a firm base in foam technology. Some modifications and different guidelines are, however, necessary to apply the technology to spill control. For the most part these are still in the evolution stage, but the transition is progressing. Foam blanketing has been
found to be effective in suppressing vaporization from spills (400-700 lbs) of liquid chlorine, sulfur dioxide, monomethylamine, phosphorous trichloride and oxychloride, hydrogen fluoride and bromine; suppression effectiveness ranged from 60% to 95% depending on the specific chemical and foam (DiMaio and Norman, 1990). Also, Norman and Swihart (1991) give details of a design for NH₃ vapor suppression, which they estimate to be more than 80% effective.

Aqueous foam covers are easy to use and rapidly deployable. Alternate mechanisms, solid covers, oil layers, sorbents, gellants and solidification (freezing) all have significant problems that are associated mostly with cleanup and disposal, but also with cost and deployment. On the other hand, foams are not the perfect answer to vapor hazard control. Their capabilities are limited. Vapor from spilled chemicals can penetrate through the foam and escape to the atmosphere. Wind can affect spread and persistence of the foam, and some form of containment is usually needed. Where non-water-soluble gases are generated by hydrolysis, foam efficiency will be compromised by their movement through the foam. It is also noted that flammable mixtures can be developed within foam bubbles when a foam covers flammable liquids.

In the application of foam to a spill surface, certain general guidelines should be observed (Hill, 1993):

1. Cover the spill surface as rapidly as possible. Effective vapor mitigation will not begin until 100% of the spill surface is covered. With liquefied gases and water-reactive chemicals, the vapor hazard will actually be exaggerated until a full cover is achieved.
2. Use the highest foam expansion applicable to the specific spill situation, to minimize the water spill caused by the collapsed foam; disposal of waste water is a major cost of any spill treatment. In addition, excess water may cause overflow of containment and spread of an uncontained spill. The need for a low-water addition rate is obvious with the reactive chemicals.

3. Maintain a full foam cover at all times, otherwise it is like having no cover at all. 10% voids in the foam cover can cause vaporization rates equal to 90% of the uncovered vapor release rate.

4. Before applying foam, be sure that the cover can be maintained for the full duration of the incident. Failure to have sufficient foam or a foam chemistry that is not compatible with the spilled chemical, can result in a vapor hazard greater than that of the uncovered spill.

5. Do not apply foam to unignited spills of flammable liquefied gases whose gas density at ambient temperatures is greater than that of air at the same temperature. The vapor cloud may not be contained, since it could become buoyant by heating, rise, and later cool and collapse to the ground.

Besides blanketing, foams have been tested for scrubbing a vapor contaminant which is contained and diverted into a foam generator (Brown and Brugger, 1993). Small scale experiments indicate that this is a viable method for the capture and neutralization of large volumes of released toxic vapors. Additional research and development work is needed, however, to assess the effectiveness of this option in actual emergencies.
6. WATER SPRAYS AND CANNONS

6.1 Removal of Water-Soluble Gases

The removal potential of water sprays to mitigate unconfined releases of water soluble gases, has been investigated in large-scale experiments. In 1986, Lawrence Livermore National Laboratory and Amoco Corporation conducted large scale unconfined release tests on mitigation of hydrofluoric acid releases at the Department of Energy (DOE) Spill Test Facility (Goldfish tests -Blewitt et al, 1987). In 1988, the Industry Cooperative Hydrogen Fluoride Mitigation / Assessment Program (ICHMAP), a consortium of 20 chemical and petroleum companies conducted a series of 87 field tests in a large chamber at the Nevada test site (Hawk tests -Schatz 1993). 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 NH₃ releases (Pallen, 1989; Idaho State Journal, 1985). The effectiveness of water spraying in scrubbing accidentally released ammonia vapors has also been shown in numerous workshops where fire-men were trained to respond to ammonia vapor releases by applying water fog downwind of the release to absorb it (Greiner, 1993).

Perhaps, these tests and emergency responses did not explore the effectiveness of water sprays under the worst (maximum flow rate) conditions which may be encountered in a large industrial facility, nor they exhausted all the human factor issues associated with such an emergency. Nevertheless, they included releases
under actual storage conditions, realistic release scenarios and typical or worst weather conditions. These 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 (Fthenakis, 1993b), 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, two of which are described by this author in another paper of this volume.

6.2 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; a description of these studies can be found elsewhere (Fthenakis, 1993).

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 (Moodie, 1985). 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 (Fthenakis, 1993).
6.3 Water Curtains or Water Monitors?

A spray curtain typically is designed as a sectional, peripheral curtain around the high-acid concentration part of the alkylation unit. Spray curtains are used when there is space for the curtain at the perimeter of the unit to be protected, and operator's interaction with an accidental HF release is to be kept to a minimum. The simplest way to deal with a gaseous leak is to turn on the entire peripheral water spray curtain surrounding the alkylation unit. Thereafter it can be decided which sections of the spray can be turned off because they are upwind from the release. This approach, however, requires large amounts of water. Another way is to evaluate the wind direction first, and then turn on a U-shaped section downwind from the leak.

The Hawk tests indicated that water monitors, when properly located and operated, can achieve HF mitigation efficiencies almost as high as those obtained by water spray curtains at the same water rate. Monitors for HF mitigation have the advantage that they can alternatively be used as fire monitors. The reverse is true if the monitors are elevated to at least the level of an HF leak. Monitors are more flexible as to the size and location of an HF leak. In most cases an HF mitigation system using monitors is cheaper than a dedicated water spray curtain of the same capacity. A major drawback in the operation of monitor system is the complexity of the manipulation of multiple, remotely controlled monitors. While curtains can be operated with a single on-off control, monitors must be individually controlled to achieve optimal mitigation efficiency.

First, an operator has to identify which monitors are downwind from the release point, assisted by overhead camera(s) near the unit. Then the selection of the properly located downwind monitors can be
determined from a board-mounted plot plan. Each of these monitors might have a joystick on a control room console with which to set horizontal direction and vertical discharge angle. A second control permits adjustment of the water spray angle. All three variables of the monitors have to be adjusted in such a way that the HF cloud is contained and recirculated for maximum efficiency. Changes in wind speed and direction, as well as increases or decreases in HF release rate, require readjustment of the system. Operation of a system of six to eight monitors can be a challenge, especially since little opportunity exists to gain experience with the system, unless a comprehensive training program with simulated releases is implemented (Schatz, 1993).

6.4 Dry-Powder Sprays

Application of large amounts of water to an HF leak is an effective means of mitigation. In cold climates water sprays might not work at all, unless substantial heating down to the last nozzle is provided. At low temperatures, water drops crystallize and the interaction with an HF cloud is detrimentally reduced. Also, supplying, handling, and disposing of these large water volumes can be a challenge.

Mitigating HF releases may also be accomplished by use of other materials instead of water. Dry powders, such as metal carbonates, oxides, or hydroxides have the intrinsic advantage of large adsorption capacity (i.e., low weight to HF ratio). For instance, stoichiometrically, 1 kg of titanium dioxide can react with 1 kg of HF. Recent laboratory studies showed that, with low multiples of stoichiometric ratio, small, contained HF releases can be adsorbed with very high efficiency (Schatz and Fthenakis, 1994). Powder systems have the additional advantage of short response time, since they use high-pressure gas rather than water for dispersion. Several of these dry
powders are commercially used for fire fighting. However, no dry powder system has been designed yet to be large enough to handle powder rates of several tons per minute, the size required for a substantial HF leak.

7. 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.
8. 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.

Aqueous foam covers are easy to use, rapidly deployable, and have minimal cleanup problems. However their applicability is limited to suppress vaporization of liquid spills; their application to scrubbing vapors has not fully tested yet.

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.
Hybrid systems have the potential of increased reliability and effectiveness but they have not been investigated yet.

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