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A REVIEW OF ACCIDENTS, PREVENTION AND MITIGATION OPTIONS RELATED TO HAZARDOUS GASES

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BIOMEDICAL AND ENVIRONMENTAL
ASSESSMENT GROUP

ANALYTICAL SCIENCES DIVISION

DEPARTMENT OF APPLIED SCIENCE

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A REVIEW OF ACCIDENTS, PREVENTION AND MITIGATION OPTIONS IN THE CHEMICAL INDUSTRY

Vasilis M. Fthenakis

1. A Brief Review of Accidents involving Hazardous Gases

Statistics on industrial accidents are incomplete due to the lack of specific criteria on what constitutes a release or accident; at best, there are only estimates on the number of accidents over the course of this century. In this country, most major industrial accidents were related to explosions and fires of flammable materials, not to releases of chemicals into the environment. The risk that these type of releases present to the public were, however, exemplified by the 1984 tragedy in Bhopal, India. In this chapter focus is given to accidental releases of chemicals in stationary or "fixed" facilities. The Environmental Protection Agency (EPA) in a study of 6928 accidental releases of toxic chemicals revealed that accidents at stationary facilities accounted for 75 % of the total number of releases, and transportation accidents for the other 25 %. About 7 % of all reported accidents (468 cases) resulted in 138 deaths and 4,717 injuries ranging from temporary respiratory problems to critical injuries. In-plant accidents accounted for 65 % of the casualties (Montgomery, 1986). In the following, several accidents are briefly analyzed. Emphasis is placed on what went wrong, how the accident could have been prevented, what safety controls were in-place, and how effective were the controls and procedures.

The worst accident involving a chemical release happened on December 3, 1984, when methyl isocyanate (MIC) vapor leaked from a Union Carbide Corporation plant manufacturing pesticides in Bhopal, India (Bowonder, et al., 1985; Varma, 1987;

Hudson, 1986). The vapor spread over an area of five square miles, killed approximately 2500 people, and injured 200,000. The developments on that evening appear to be as follows: Water entered an MIC storage tank, probably when "a worker whose training did not meet the plant's original standards was ordered by a novice supervisor to wash out a pipe that had not been properly sealed", and triggered a violent chemical reaction. As the reaction of MIC with water greatly increased the temperature in the tank, the presence of an abnormally high level of chloroform at high temperature in the tank formed chloride ion, which rapidly corroded the stainless steel tank. The iron from the corrosion (or from earlier cross-contamination) catalyzed a trimerization of MIC and further increased temperature and pressure. The CO_2 evolved caused mixing of chemicals, which, with the rise in temperature, accelerated both reactions; finally, the build-up of pressure burst the rupture disk in the line to the safety valve. The valve was open for about two hours, during which most of the material in the tank, about 41 metric tons, was released to the environment as vapor. Based on the heats of reaction, a reaction involving 40 % of the MIC would have released enough heat to vaporize the remaining 60 %.

Abandonment of several safety procedures contributed to the initiating events. Although the issue still is debated, inadequate procedures for cleaning pipes may have caused a large amount of water to enter the tank, which started the initial reaction. Also, the presence of large amounts of chloroform helped produce the runaway reaction. The concentration of chloroform in the tank was about 32 times above the required concentration (probably due to cross-contamination via the MIC refining still), and the Bhopal plant staff did not monitor the tank for chloroform for 6 weeks before the accident, although daily monitoring was required.

There were five major safety systems at the plant, but they were not operational or did not function as expected. Specifically, these systems were:

i) A refrigeration system to keep the MIC cool, slow down a chemical reaction and decrease vaporization and pressure build-up. This system had been shut-off since June 1984 to save electricity.

ii) A spare tank for temporary storage of off-specification MIC for processing, which in the case of an emergency could be used to confine gas released from the other two tanks. It is not clear if this spare tank was empty or not, however, the operator(s) did not (in the confusion of the accident) open the valves connecting the tanks.

iii) A chemical scrubber designed to treat with alkali solution the toxic gas and rendering it harmless. The scrubber was in a stand-by mode and required manual activation. The operator activated the scrubber, but the caustic solution pump was down, making it impossible to charge the scrubber with more caustic once the small amount of the solution in the equipment was used. In any case, the scrubber was underdesigned and could not handle such a massive release. It was designed to neutralize small leaks, about 1.5 kg/min at 35^{o}C, whereas during the accident, the leakage rate was about 200 times the specified capacity and about 6 to 10 times the temperature.

iv) A 30-m high flare tower, connected after the scrubber, intended to burn unneutralized toxic gases high in the air. However, the line connecting the flare tower with the scrubber was blanked off for repairs. The flare tower also was designed for relatively small releases.

v) A water curtain designed to spray water up to a height 12 to 15 meters in the air, forming a curtain around the vapor cloud and disperse or absorb it. Water reacts with MIC vapor to form, in the liquid-phase, dimethyl urea or trimethylbiuret, both comparatively harmless compounds. The water curtain was not activated until one hour after the release, and was inadequately designed for the height of release (the discharge of MIC reached a height of about 35 to 40 m).

The lack of adequate planning for emergency preparedness and response raised the death and injury toll, because people ran in panic often in the direction of the release, did not use simple protective measures against short-time exposure (e.g., wet towel on the face), and there were not sufficient means of evacuation. Lack of adequate medical supplies compounded the tragic accident.

The December 3, 1984, tragedy did not happened without earlier warnings. From December 1981 to October 1982, at least five incidents, some resulting in injuries, happened in the plant. In May 1982, a team of American experts from Union Carbide inspected the plant and were extremely critical of the operation. It is not clear whether or not the recommendations of the team were implemented.

Accidental leaks from Union Carbide plants also have occurred in the United States. EPA records 28 instances of MIC leaks from Union Carbide's plant in Institute, West Virginia, for the period January 1980 to December 1984. The tank that leaked was thought to be empty; the accident happened despite the new installation of a $5 million warning system.

In July 1976, in Seveso, Italy, an explosion at a plant producing 2,4,5-trichlorophenol (TCP), sent large quantities of dioxin into the atmosphere (Sambeth, 1983). The accident happened on a Saturday morning, a time coinciding with closing the plant for the weekend. Several procedures were not followed:

i) the operators left too much material in the batch when they distilled only about a third of the required quantity;

ii) instead of continuing to stir the mixture until completely cooled, the operators stopped the stirring after 15 minutes;

iii) they did not add water to cool the mixture down;

iv) instead of staying with the system until the temperature decreases to 50-60°C, the operators left early when the recorded temperature was 158 °C. An exothermic decomposition took place 6.5 hours later, and caused the rupture disk on the vessel to break, and an aerosol cloud containing dioxin to be released into the atmosphere.

Although all these safety procedures had been violated, it was not clear, for several years, how the exothermic decomposition occurred at these temperatures, because the critical temperature for this reaction is 230° C. A key discovery on the nature of the accident was made about four years later when investigations on the thermal stability of the mixtures used for producing trichlorophenol showed that some weak exothermic reactions were taking place at temperatures of about 180°C. The temperature was possibly raised to that level locally, at the upper layer of the liquid, due to residual superheated steam and the absence of stirring to uniformly distribute the heat in the mixture.

This accident happened in spite of several safeguards. The process (non-pressurized) and the solvent (ethylene glycol) used in the process, had been chosen as safer than other alternatives. The accident, however, was not connected with the process or the solvent. Superheated steam with a saturation temperature of only 188°C was used to prevent heating to the critical temperature of 230°C. Additional safety features were a large condenser for rapid cooling, a second condenser at the end of the vent line for trapping leaking vapors, and an inventory of 3,000 liters of water ready to quench the reaction mixture, if needed. Nevertheless, all these features required a human activation, and the operators were not there partly due to the lack of knowledge of the hazards presented. Thermal studies of the chemical reactions involved, under a wide range of conditions, especially those encountered during startup and shutdown, could have revealed the hazard. Strict compliance with the prescribed operating procedures should have prevented this accident from happening.

On January 4, 1986, also on a weekend, at a Kerr-McGee nuclear plant in Gore, Oklahoma, a release of about 29,000 pounds of uranium hexafluoride resulted in the death of a plant worker and 32 injuries. In violation of plant procedures, the worker heated an overfilled cylinder of uranium hexafluoride, the cask ruptured and the chemical escaped, sending 100 people to the hospital and killing the worker. Heating the vessels to reduce the mass was not an unusual event at this plant (Diamond, 1986).

Accidents involving uranium hexafluoride, under circumstances similar to the Kerr-McGee accident, also have occurred in the past. Among these accidents is a release of 17,800 pounds of liquid uranium hexafluoride from a ruptured cylinder that was being heated at a government uranium plant in Peducah, Ky, in 1960, injuring 21 men. In 1966, one worker was hospitalized when 3844 pounds escaped from a cylinder after a valve was improperly turned at a government uranium processing plant in Fernald, Ohio. Two similar accidents happened at the Portmouth, Ohio plant in 1978 and 1983, correspondingly.

In November 1987, 66 people were seriously injured and 3000 residents fled their homes in Texas City, Texas, when hydrofluoric acid (HF) leaked from a storage tank at the Marathon Petroleum Company refinery (Assoc. Press, 1987). The leak occurred when falling equipment sheared off a pipe connected with the storage tank. The acid vaporized and dispersed downwind. For several hours after the release, workers sprayed water over the vapor cloud to reduce its spreading, while they were pumping the leaking acid into tank cars.

In June 1988, a release of chlorine gas in a chlorine plant in Springfeld, Massachusetts, caused the evacuation of 25,000 people (Assoc. Press, 1988). A fire started when rain blew in a window in the plant and reacted with chlorine tablets in a hopper. The heat from the reaction started a blaze at this old facility; water from sprinklers in the building started a second fire later. To reduce the emission of vapor, firefighters sprayed huge quantities of water over the building. Sodium sulfate and boric acid were mixed with the water to neutralize the vapor.

Several times, emergency response to an accident was based on incomplete information, resulting in injury or damage to the environment that would not have happened otherwise. One such accident happened in 1980, in the Boston and Main Railroad switching yard in Somerville, Massachusetts, and involved the release of about 13,000 gal of phosphorous trichloride. Firefighters used water, first to try to prevent the chemical from entering into the sewer system, and later to try to suppress its vaporization. Using water resulted in the creation of clouds of toxic vapors; about 23,000 people were evacuated and 418 were treated in the hospital. A similar accident occurred in December 1985 on a ramp of the Capital Beltway, Washington, DC, when a truck carrying 4000 gal of ferric chloride overturned. The tank ruptured and toxic fumes were released. In this case, a more dangerous situation was averted because water was not used.

Another incident of this type was a spill of chemicals into the Rhine River, which happened when water was used to fight a fire at a Sandoz warehouse holding 1,200 tons of agricultural chemicals.

There have been a few recent accidents involving hydrogen fluoride. In October 1987 Marathon Oil refinery, Texas City, 30,000 lbs of HF were released; 800 people were treated for breathing disorders and skin problems. In November of same year, there was an explosion and fire in Mobil Oil alkylation unit in Torrance refinery, outside Los Angeles.

In most of these accidents a common pattern of failure can be observed: i) A large number of accidents are recurring since companies are reluctant to change "ways of doing things". ii) Most gas leaks occurred in storage tanks; tanks sometimes were overfilled. ii) Safety and control systems, although existing, were nonworking; (unavailability of safety systems is known to be a significant safety concern industrywide). iii) Lack of procedures or, more importantly, failure to stick with procedures. iv) many of these accidents happened in the weekend when the senior operators are not usually on-site.

2. MITIGATION, ADMINISTRATIVE, AND ENGINEERING OPTIONS

The information on engineering and administrative options to prevent and control accidental releases will be considered sequentially in five steps, each comprising a more advanced (in time) protection level:

a) Inherently safer processes and materials.

b) Options to prevent accidental initiating events (e.g., detection and monitoring systems, and procedures for safe operation).

c) Safety systems (e.g., automatic shut-offs, flow restricting valves, cooling systems and containment systems).

d) Options for control/mitigation

Passive systems (e.g., vapor barriers)

Active systems (e.g., scrubbers and water curtains).

e) Emergency preparedness and response plans, and procedures to prevent or reduce human exposures.

Figure 1 shows a hierarchy of such options for hazard management.

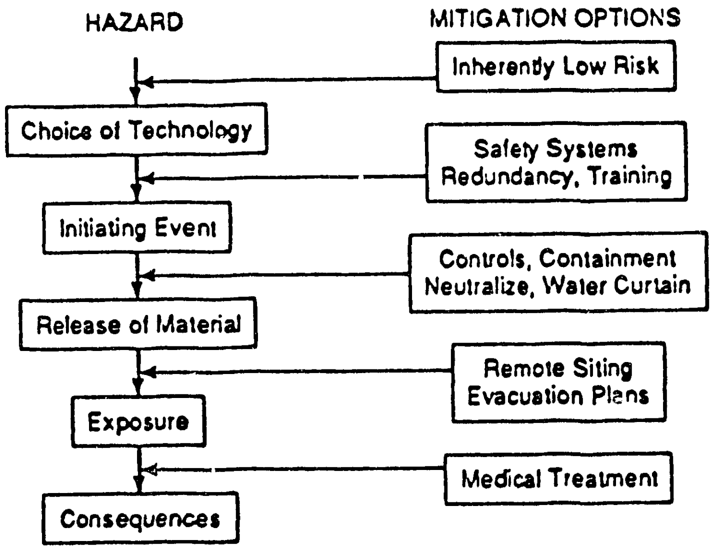

Fig. 1. A hierarchial approach for managing toxic gas releases.

2.1 Technology/System Selection

The most efficient strategy to reduce hazards is to choose technologies which do not require the use of large quantities of hazardous gases. For new technologies (e.g., photovoltaics), this approach can be implemented early in development, before large financial resources and efforts are committed to specific options.

Examples of inherently safer choices of material in photovoltaic manufacturing are: (i) silicon or zinc instead of cadmium (a probable carcinogenic material) based technologies; (ii) trimethylarsenic instead of arsine in manufacturing gallium arsenide photovoltaics (trimethylarsenic although poisonous is liquid and far less toxic than the highly toxic arsine gas; however, its potential for carcinogenicity still exists); (iii) zinc phosphide (a solid) instead of phosphine (a highly toxic gas) in manufacturing zinc phosphide devices.

The choice of a substitute for HF is not an easy one. 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. The South Coast Air Quality Management District (AQMD) has decided to ban large-scale use of HF in the Los Angeles basin by the year 1994 (Rule 1410). At the Federal level, an amendment of the Clean Air Act will ban the large-scale of HF by the year 1999. A factor in these decisions is the belief that there is a safe alternative to HF to use as catalyst in the alkylation units, namely, sulfuric acid; However, 140 times more sulfuric acid is needed for the same operation, producing 280 times more waste than in the case of HF. Consequently, transportation and environmental hazards may increase. Also, large H_2SO_4 and H_2SO_4/hydrocarbon storage systems would be more susceptible to leaks than HF storage systems because of their bigger volume and the relatively greater amount of piping needed (refrigeration system is required for the former). Preliminary studies in the industry show that the mixture of H_2SO_4 and hydrocarbons (the form in which most of H_2SO_4 exists in refineries) when released may volatilize to a significant degree, thereby reducing the safety factor offered by the low boiling temperature of H_2SO_4.

2.2 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., remote storage, maintenance, inspection and testing, quality control and worker training, guidelines for system integrity, operating procedures, and safeguards against process deviations.

It is preferable to store all compressed gas cylinders away from personnel working areas, ideally outside the building in open, well ventilated areas. If stored indoors, toxic gas cylinders should always stored in controlled, well-purged enclosures and always securely racked.

2.3 Prevent/Minimize Releases

The next step is to implement safety options to suppress a hazard when an accident initiating event occurs (e.g. flow restricting valves, cooling systems, double-containment with detectors and alarms, and adequate ventilation).

Releases can be prevented or reduced with fail-safe equipment and valves, adequate warning systems and controls to 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 materials. Some detectors are based on a chemical reaction within a sensor cell; others sense an obstruction at certain characteristic wavelengths along a beam. It is very important for the detectors be placed where the maximum signal is expected. For example, a detector for a toxic gas that is heavier than air should be placed near the floor or the ground. A detector at a higher level will not produce a prompt signal because the gas may stay close to the ground for a considerable time. Monitors should be set at levels no greater than one-half the concentration level considered dangerous. If major leakage is detected, the process should be designed so that the flow of fluid to the leak point can be stopped immediately. An emergency pushbutton should be provided which can interrupt the flow at the source via shut-off valves. Detector and alarm systems should be checked at every emergency drill. All personnel should be trained in what the various signals mean. All systems should have a back-up power supply (e.g., batteries), so that a power failure does not cause alarm malfunction. Emissions should be also monitored on all pollution control equipment to insure its proper performance. Ventilation exhausts should be periodically inspected for gas emissions, and scrubbers monitored for residual emissions.

Excess-flow valves and flow-limiting valves can increase the margin of safety by cutting-off the flow, and reducing the maximum flow through the valve, correspondingly. Flow-restricting valves currently are used for highly toxic gases (e.g., AsH_3, PH_3) in the semiconductor and photovoltaics industry. For a cylinder on 2000 psig pressure, the initial flow out of a wide open cylinder valve (e.g., opening of 0.25" diameter) will be approximately 2500 lpm; a 16 kg cylinder will be emptied in about one minute. A flow restricting valve with an orifice of 0.006" reduces the flow out of this cylinder to about 30 lpm which can much more easily controlled.

Isolation valves should be operated from a safe, remote location (e.g., a control room having a reliable fresh-air supply). Isolation valves generally should be "fail-safe" (e.g., closing on loss of instrument air or electric power). These and the other 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 also 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 pushbuttons 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 pushbutton 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. Adequate ventilation also ameliorates the potential of dangerous exposures of workers to hazardous gases. A well designed ventilation system can protect employees from small leaks indoors. The system must be designed so that the hazardous gas is not directed past the workers. Thus, the system should provide air circulation to draw in hazardous emissions and direct their flow away from the workers' breathing zone. The system should draw in fresh air, not air from another section of the plant. Cooling systems (e.g., sprinklers in gas cabinets and raceways) must be used suppress fire/explosion hazards if there is a leak or an abnormal increase of temperature in the gas system.

2.4 Control/Minimize External Release

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. Such systems are effective in controlling routine emissions of toxic gases, but their application in accidental large gas releases is not straightforward. The highly transient character of such releases demand special designs and configurations.

Fthenakis et al. (1988) suggested two scrubbing options for controlling accidental releases of H_2Se and H_2S: A conventional on-line packed tower scrubber and a stand-by confinement and subsequent scrubbing system.

As a general guideline, systems designed to control massive transient releases should meet the following criteria:

(i) They should be mechanically simple with a minimum number of moving parts and connections;

(ii) they should operate under a wide range of conditions, given the uncertainty of release conditions; and

(iii) they should assume fail-safe operation to the highest degree possible, through passive functioning and redundancy of components.

2.5 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. Evacuation planning requires the formulation of plans and liaison with outside authorities, including emergency service personnel, appointment of key personnel and defining their duties, setting up emergency control centers, development of site action plans including fire-fighting procedures and rescue systems, and plant shut-down procedures.

2.6 Reduce Consequences

Prevention of consequences forms the final defensive barrier. Medical facilities close by that can accommodate victims of the worst accident, can reduce the consequences of personnel exposure to hazardous gases. Plant managers should provide local health agencies and hospitals with information about the materials which could be released offsite. These groups should work together, well in advance of any incident, to identify the appropriate medical treatments required to mitigate exposures to the public. Subsequently, appropriate medical personnel (e.g., fire department paramedics, and hospital emergency room staff) should be trained to respond to such incidents; specialized medical equipment and antidotes may be required. Experience has shown that in real emergencies, there is often much confusion. Hence, 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. Lack of such planning and rehearsals can increase the risk to health.

The importance of the administrative options and procedures should 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 UF_6 at Kerr-McGee, Oklahoma; 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. Remember what Johann von Goethe said once, "everything has been thought of before, but the problem is to think of it again".

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