

Characterization of Accidental Chemical Releases

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INTRODUCTION

The 1990 Clean Air Act Amendment (CAAA) section 112 (r) *Prevention of Accidental Releases* requires the United States Environmental Protection Agency (EPA) to establish measures for owners and operators of facilities processing or handling hazardous materials to prevent accidental releases of regulated substances and other extremely hazardous materials to the air. Additionally, it requires the consequences of releases to be minimized by focusing preventative measures on those chemicals that pose the greatest risk. Section 112(r) begins with a general duty clause requiring owners and operators to:

- Identify hazards that may result from releases
- Design and maintain a safe facility
- Minimize the consequences of releases when they occur.

Another provision of section 112(r) is the requirement to promulgate a list of at least 100 substances, including threshold quantities, that are known to cause, or may be reasonably anticipated to cause, injury or serious adverse effects to human to health or affect the environment when released to air. The list and threshold quantities would be used as a basis to determine which facilities would be required to comply with the accident prevention provisions. Other requirements were “reasonable regulations and appropriate guidance” to provide for the prevention and detection of accidental releases and for pre-planned responses to such releases.¹

The enabling legislation for 112(r) of the CAAA was published in October 1993 as proposed rule 40 CFR 68 Risk Management Programs for Chemical Accident Prevention. Due to numerous industry groups, states and other implementing agencies said that EPA had underestimated the cost of the proposal. In response, EPA trimmed back the proposed requirements in a separate notice in March 1995. In March 1996, the agency plans to issue a final rule that would require compliance within three years.²

When the rule is finalized, it will require affected facilities to establish Risk Management Programs (RMP). The RMP rule is designed to reduce the risk of accidental releases of acutely toxic, flammable, and explosive substances. The RMP is organized into three major categories:

1. Hazard Assessment
2. Accident Prevention Program
3. Emergency Response Program.

If a facility has on-site threshold quantities of any of the 77 acutely toxic, 63 flammable or Department of Transportation-classified explosive substances, an RMP will need to be developed.

The focus of this paper is to characterize various potentially hazardous scenarios that would require a hazard assessment. This paper will discuss the type of models that can be used to determine the consequences (off-site impact) due to the potential hazard scenario. The off-site impact study information will influence the RMP planning process.

HAZARD CHARACTERIZATION AND ASSESSMENT

One of the major differences between the present OSHA Process Safety Management (PSM) regulation and the proposed new EPA RMP regulation is the hazard assessment requirement. The OSHA regulations address incidents where the effects of consequences would be contained within the boundaries of the facility, whereas the EPA regulations are concerned with possible effects to life, property, and the environment outside the boundaries of the facility. Also, the RMP rule requires a quantitative analysis of potential consequences.

As the EPA's regulation is currently proposed, a hazard assessment will need to be conducted for each regulated substance as follows:

- Determine the worst-case scenario assuming that “all of the regulated substance in the process is instantaneously released and all mitigation systems fail to minimize the consequence of release.”
- Identify other more likely significant scenarios where the regulated substance is manufactured, processed, used, stored, loaded, or unloaded.
- Analyze the off-site consequences of the worst-case scenario and other more likely significant release scenarios for both the worst-case meteorological conditions (i.e., least turbulent atmospheric conditions, F stability and 1.5 m/s wind speed) and the meteorological conditions most often occurring at the facility. The analysis is to estimate the distance from the point of release where significant damage may occur to the surrounding population or environment. The extent of damage is evaluated by determining off-site exposure to the vapor cloud, pressure wave, or flying debris that may occur from the incident. In doing so, the analysis identifies the populations, sensitive ecosystems, migration route, vulnerable natural areas, and critical habitats for threatened or endangered species that might be affected.
- The hazard assessment is to be reviewed and updated at least once every five years or within 60 days of any changes to the process safety information.
- The facility is also to prepare and maintain a five-year history of all incidents involving regulated substances and processes. Reports on significant accidental releases are to include the date, time, substance, quantity, duration, concentration, and any off-site consequence such as fatalities, injuries, hospitalizations, medical treatments, evacuations, sheltering in-place, and off-site environmental impacts such as soil, groundwater, or drinking water contamination, fish kills, and vegetation damage.

RMP PLANNING GUIDES AND WORST-CASE SCENARIO DETERMINATION

The significance of EPA's worst-case scenario definition may not be fully appreciated until facilities begin performing process hazard analysis using these criteria. A few facilities have developed task forces in their cities to develop and define the “worst-case scenario” as part of their RMP planning guide.

The first step is to determine chemicals in the facility that are regulated under 40 CFR 68 *Chemical Accident Prevention Provisions*. The worst-case scenario definition for vessels and pipelines is identified in the following section.

Vessels

The following methodology is recommended for vessels worst-case scenario definition and determination of impact

- Determine the largest mass of each chemical identified.
- Assume that the vessel contents are released over a 10 minute period. The release rate is assumed to be constant. All active mitigation systems (ones that require someone or something to happen) are assumed to fail. Examples of active mitigation systems are emergency isolation valves and water curtains. Assume that the vessel is at its normal maximum inventory.
- Determine passive mitigation systems that will impact the release of raw materials or their boil off rate. Dikes and sewers are examples of passive mitigation systems. Items such as dike drain valves are normally closed. If the facility has an effective mitigation program, they are assumed to be closed.

When water in the dike has a significant impact on boil off, the following assumptions are made. Assume that the dikes are dry if the facility has an administrative program to keep dikes water free. Assume that the dike contains a normal water volume if the facility does not have an administrative procedure to keep the dikes water free.

- Calculate the vapor release rate due to flashing from the leak and from boil off from the liquid pool of the chemical. Calculate the vapor release for a 10 minute period. Calculate the pool release rate until the liquid boil off rate is complete.

Pipelines

The following methodology is recommended for defining the pipeline worst-case scenario definition and determination of impact:

- Determine the pipeline failure that would give the largest release rate of each chemical identified. Do not take into account pipelines that are not on your facility's property and pipelines which are on your property but not under your control (using Department of Transportation definitions).
- Assume that the pipeline release continues for 10 minutes. All valves remain in their normal position for the ten minute period of time. Assume that all mechanical shutdown systems such as check valves and excess flow valves fail.
- Assume that all active mitigation systems fail. Assume that all passive mitigation systems work as designed.
- Calculate the vapor release rate for the pipeline failure. The release rate should be based upon flashing resulting from the leak and from pool boil off. For lines that pass over areas where the liquid boil up rate can be impacted by such items as presence of water, then the point of break should be at the point that gives you the largest vapor release.

Determine the worst-case release for each chemical by comparing the release rate from the largest vessel and the worst case pipeline failure. Normally, the highest release rate is the worst-case scenario for this chemical. Perform modeling using worst-case meteorology, defined in RMP drafts as F stability and 1.5 m/s wind speed. However, if the potential off-site impact is significantly different for the two cases, it may be necessary to model both events to determine which has the worst off-site impact.

MORE LIKELY CASE SCENARIOS

Industry groups have attempted to establish more likely case scenarios that would depict a realistic picture because often, the worst-case scenarios are remote possibilities. Also, the worst-case scenario increases the cost of complying with additional regulations and, in many cases, may result in unwarranted concern by the surrounding general public. A general outline of the more likely case scenario is outlined.

- Identify the pipeline that would have the largest mass flow rate of each chemical identified
- Assume that the vessel contents are released through a hole in the largest liquid-filled line below the normal liquid level over a 10 minute period. If the line is two inches in diameter or less, then assume a complete break with release from only one side (generally the “upstream” side) of the piping. If the pipe is greater than two inches in diameter, assume it develops a two inch hole in it. Assume that the vessel is at its normal maximum inventory.
- Passive mitigation systems are assumed to work properly. Active mitigation systems are assumed to work after a 10 minute “discovery time”. Determine the effect of any mitigation system that will impact the release of materials or their boil off rate.
- Calculate the vapor release rate due to flashing from the leak and boil up from any liquid pooling of the chemical for 10 minutes.
- Consider other potentially smaller releases of the same chemical that might have greater off-site impact because of their location. For example, a small leak at a fenceline may be more hazardous than a larger leak well inside the property. It may be important to model both scenarios to determine which has the greater off-site impact.

EVALUATING PASSIVE MITIGATION SYSTEMS DURING LIQUID SPILL

An example of the effect of passive mitigation systems (dikes) usage in controlling ammonia spills is illustrated. The various parameters that play a role in the off-site impact are analyzed.

A chemical company stores ammonia in its sub-cooled liquid form and wants to evaluate the off-site impact to choose a particular type of dike design. Three dike designs are evaluated for the storage of ammonia at its boiling point (-28°F) in a tank. The three dikes used in the analysis have areas of 25,094 ft², 29,430 ft², and 72,172 ft², respectively. The first two dike designs are concentric circles to the tank, whereas the third includes a square wall enveloping half of the concentric dike wall. The amount of ammonia being stored in the tank is 30,000 tons.

Since this is a sub-cooled liquid spill into a dike and not a pressurized liquid release, the rate of release is taken to be the evaporation rate (rate of volatilization). The following equation is used to calculate the rate of release to air for liquids in pounds per minute (lb/min):³

$$QR = \frac{(0.162) (MW) (K) (A) (VP)}{R (T1 + 273)}$$

where

- QR = Rate of release to air (lb/min)
- MW = Molecular weight (g/g-mole)
- K = Gas phase mass transfer coefficient (cm/s)
- A = Surface area of spilled material
- VP = Vapor pressure of material at temperature T1 (mm Hg)
- R = Universal gas constant (82.05 atm cm³/g-mole K)
- T1 = Temperature at which the chemical is stored (°C).

The gas phase mass transfer coefficient (K) is estimated based on a reference compound as follows:

$$K = K_{\text{ref}} \left(\frac{MW_{\text{ref}}}{MW} \right)^{1/3}$$

Using water as the reference compound:

$$K_{\text{ref}} = K_{\text{water}} = 0.25(u)^{0.78}$$

where

u = wind speed (m/s)

Combining equations for QR and K yields the following equation:

$$QR = \frac{(0.106) (u)^{0.78} (MW)^{2/3} (A) (VP)}{R (T1 + 273)}$$

Therefore, evaporation rate is a function of the wind speed, area of spill, temperature of storage, and vapor pressure at temperature of release (storage). The U.S. EPA's SCREEN3 model is used to model the source as an area source. DEGADIS cannot be used because this case is not a pressurized vessel rupture that results in the release of a dense gas. The evaporation rate and worst-case downwind concentration are both functions of wind speed. Higher wind speed will give a higher evaporation but probably a lower downwind concentration.

Therefore, the wind speed was varied from 1m/s to 5m/s to determine the flux of ammonia released from the area source. The flux is calculated as the evaporation rate divided by the surface area of the spill (QR/A) and issued as input into the SCREEN3 model. Since SCREEN3 provides one-hour averages, the resulting

concentrations represent the impact after one hour of release. An Immediately Dangerous to Life and Health (IDLH) value of 500 ppm for ammonia is plotted for each case.

It was observed from the footprint plots that the wind speed of 5m/s caused the IDLH isopleth to occur closest to the area source. This means that for the same pool size, the concentration falls off faster with increasing wind speeds. Also, for the same pool size, the maximum concentration occurs for the 1m/s windspeed than for the 5m/s case. It was also observed that for the same wind speed, the largest pool size produced the largest concentration downwind. Table 1 illustrates the results of this sub-cooled ammonia spill.

From this, it can be concluded that the downwind impact is a strong function of the surface area of the spill rather than the quantity of spill in the dike.

EVALUATING PRESSURIZED TANK RUPTURE

Some facilities store ammonia in its anhydrous form in a pressurized tank. One possible release scenario is a catastrophic failure in an orifice at the bottom of the pressurized tank.⁴ The mass flux is calculated as in all liquid flow, with any flashing occurring in the discharge jet region. The Bernoulli equation is used for calculating the mass flux of liquid from a hole in a pressurized tank as follows:

$$QR = C_D A r_1 \left(2 \frac{\Delta p}{r_1} + 2gH \right)^{1/2}$$

where

- QR = rate of release (kg/s)
- C_D = discharge coefficient (0.6)
- A = area of nozzle
- ρ_1 = density of liquid in tank
- Δp = $p_{\text{tank}} - p_{\text{atm}}$
- H = height of liquid in tank.

It can be observed that in this case, the release rate is a function of the liquid density, height of liquid in the tank, area of nozzle, and pressure difference between the tank and the outside. Ammonia liquid from such a release exists as an aerosol that is carried downwind in a jet and does not “rain out” on the surface.

Wind speed was varied from 1 m/s to 5 m/s. The model was run in an isothermal mode and a density profile was approximated. The results of the downwind concentration of ammonia due to the pressurized vessel rupture is provided in Table 2. The downwind concentration in the case of the dense gas ammonia dispersion shows a high initial concentration and a sharp decrease in concentration with distance downwind. The other industrial concern of storing ammonia in its anhydrous form inside an industrial facility is having to go through PSM requirements under the OSHA regulations.⁵

CONCLUSIONS

EPA's 112(r) rule has forced industry to evaluate offsite impact of materials processed and handled at the facility. Accurately characterizing an accidental chemical release is one of the most important steps in determining offsite impact. Since the new EPA regulations will increase the formal documentation and recordkeeping requirements beyond those of older OSHA regulations, industry should look to ways to integrate the OSHA and RMP requirements into a single management system. This should ease the burden of compliance with the regulations and ensure that the proper documentation is available in the event of an audit.

Industry groups in several towns have come together to define a worst-case scenario and realized that this is more often than not, unreal and can cause unwarranted concern to the surrounding general public. Working through real life examples such as the storage of ammonia can provide a facility tools to make a decision on its mode of handling hazardous materials. Evaluating more likely scenarios can be accomplished only when process and environmental engineers and scientists work together as a team.

REFERENCES

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Table 1. Results of the accidental release modeling of sub-cooled ammonia.

Case No.	Spill Area (ft ²)	Downwind distance (m)	Concentration (ppm) at wind speed		
			1 m/s	3 m/s	5 m/s
1	25,094	1	10,208	9,027	17,215
		1,000	4,238	3,654	1,376
		5,000	465	406	121
2	29,430	1	10,862	9,895	18,191
		1,000	4,508	3,977	1,454
		5,000	495	445	128
3	72,172	1	15,406	13,610	25,973
		1,000	6,396	5,509	2,076
		5,000	702	613	182

Table 2. Results of the release of anhydrous ammonia due to a pressurized tank rupture.

Downwind distance (m)	Concentration (ppm) at wind speed		
	1 m/s	3 m/s	5 m/s
1	5,959,129	5,959,129	5,959,129
1000	623	588	569
5000	--	--	130