MODEL RISK MANAGEMENT PROGRAM AND PLAN FOR AMMONIA REFRIGERATION

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Prepared by

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This document provides generic guidance on the Risk Management Program (RMP) for Ammonia Refrigeration Facilities on how EPA intends to exercise its discretion in implementing its regulations on Accidental Release Prevention: Risk Management Program Under the Clean Air Section 112(r)(7). The document does not substitute for EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA may change this guidance in the future, as appropriate.

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MODEL RISK MANAGEMENT PROGRAM AND PLAN FOR AMMONIA REFRIGERATION

1.0 INTRODUCTION

This guidance has been developed to help owners and operators of ammonia refrigeration facilities comply with the United States Environmental Protection Agency's (EPA) Risk Management Program (RMP) regulations, 40 CFR Part 68, and the Occupational Safety and Health Administration's (OSHA) Process Safety Management (PSM) Standard 29 CFR 1910.119 (both sets of regulations have a 10,000-pound threshold for anhydrous ammonia).

It is pertinent to begin by distinguishing between the Risk Management <u>Program</u> and the Risk Management <u>Plan</u>. The Plan is the information that the owner or operator will prepare and submit to a central point to be specified by EPA. This single submission will be deemed equivalent to a submission to the implementing agency, State and local planning and response agencies with jurisdiction for the area where the stationary source is located. The Program is the system that backs up the plan and ensures that the plant is being operated safely. This guidance is intended to explain the elements of the Program in such a way that owners or operators will understand what is needed to develop an adequate Program and will have all of the information needed to prepare a written Plan.

There are a large number of ammonia refrigeration facilities in the United States, which span a wide range of sophistication and knowledge about what it takes to operate safely. This guidance is primarily intended to help those owners or operators who may be looking for assistance on where to start in the development of an RMP and who may have few resources to devote to this objective. Although compliance with the RMP regulations is first and foremost a requirement of the law, a good RMP (particularly the Prevention Program) should also pay dividends in efficiency and profitability; that is, the resources devoted to developing the RMP ought to be more than recovered.

Although, as noted above, this guidance has been developed to help facilities get started on their programs, it is hoped that it will also prove useful to those facilities that already have excellent safety and prevention programs in place. However, the guidance is not meant to be prescriptive, and owners and operators will be free to develop their Programs in a different way if this fits better with their current management practices and procedures and available technical resources.

In summary, the guidance is intended to be in a simple form that is easy to use, while still covering all those elements that are necessary to comply with the regulations and to operate safely and efficiently.

This report is organized as follows:

Section 2 describes a simple way of performing the Hazard Assessment requirements of the regulations. It is intended to stand alone--that is, an owner or operator who reads and uses it will have completed a satisfactory Hazard Assessment. However, the development of Section 2 required consideration of a great deal of technical information on accidental releases of ammonia and how to handle their atmospheric dispersion. This information is extensively discussed in Appendices A, B and C.

Section 3 describes the Prevention Program and the Emergency Response Plan. There is an initial introduction that summarizes some of the history of prevention programs, and then goes on to discuss the applicability of the current guidance to the specific case of ammonia refrigeration facilities. Section 3 continues with a discussion of the requirement for a Management System, and then provides information and guidance on each of the elements of the Prevention Program. Section 3 concludes with a brief review of the elements of the Emergency Response Plan. Finally, Appendix D provides a brief review of past accidental releases of ammonia and their root causes from EPA's Accidental Release Information Program (ARIP) data base.

Please send comments to Dr. Lyse Helsing at EPA, (202) 260-6128, FAX (202) 260-0927 or e_mail helsing.lyse@epamail.epa.com. Technical questions about the Prevention Program and the emergency plan can be directed to Ray Brandes at (504) 761-4011, FAX (504) 769-9339, or e_mail RayBrandes@aol.com. Technical questions about the hazard assessment should be addressed to Dr. Geoff Kaiser at (703) 318-4626, FAX (703) 709-1042 or e_mailgeoffrey.d.kaiser@cpmx.saic.com.

2.0 HAZARD ASSESSMENT

The required elements of hazard assessment are as follows:

§68.25 Worst-case release scenario analysis
§68.28 Alternative release scenario analysis
§68.30 Defining offsite impacts - population
§68.33 Defining offsite impacts - environment
§68.36 Review and update
§68.39 Documentation
§68.42 Five-year accident history

The current chapter gives simple guidance on how to comply with each of the above requirements; it is intended to stand alone. Backup technical information is provided in Appendices A, B and C, including the reasons why the guidance has been developed in its current form.

2.1 <u>Worst-Case Release Scenario Analysis</u>

2.1.1 Mandatory Input

The following input is required by the Risk Management Program rule:

- a) The worst-case release quantity M(lb) shall be the greater of the following:
 - 1) For substances in a vessel, the greatest amount held in a vessel, taking into account administrative controls that limit the maximum quantity; or
 - 2) For substances in pipes, the greatest amount in a pipe, taking into account administrative controls that limit the maximum quantity.

Appendix A shows that, for ammonia refrigeration systems, a storage vessel or receiver is the place where the worst-case release quantity is expected to reside.

- b) Per §68.25(c)(1), because ammonia is a vapor at ambient temperature and is handled as a liquid under pressure in most parts of a refrigeration system, the quantity M is completely released over a period of 10 minutes. Appendix A explains why this is actually a reasonable assumption for worst-case release scenarios in ammonia refrigeration systems.
- c) Wind speed/atmospheric stability class: The owner or operator shall use a wind speed of 1.5 meters per second and F stability class. If the owner or operator can demonstrate that local meteorological data show a higher minimum windspeed or a less stable atmosphere at all times during the previous three years, these minimums may be used. For simplicity's

sake, the guidance below is restricted to a wind speed of 1.5 meters per second and F stability class.

d) The toxic endpoint for ammonia is 200 ppm (0.14 mg/L). This airborne concentration has been published by the American Industrial Hygiene Association (AIHA) and is the maximum airborne concentration below which it is believed that nearly all individuals can be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

2.1.2 Mass Released in the Worst-Case Release Scenario

Take the largest mass M(lb) of ammonia that is liquefied under pressure in any vessel in the ammonia refrigeration system. For many systems, this vessel will be the high pressure receiver with typical pressures in the range 100 to 200 psig. Other candidate vessels include: a) an outside vessel in which ammonia is stored as a liquid at ambient temperature (some, but not all, facilities have such a vessel); b) an intermediate receiver with typical pressures in the range 20 to 60 psig (typical of two-stage ammonia refrigeration systems); or c) a low-pressure receiver with pressures in the range 10-60 psig (typical of single-stage refrigeration systems).

The mass M should include any liquid ammonia in pipework connected to the vessel and in any other vessel that can discharge directly into pipework connected to the vessel. In addition, the maximum amount of ammonia that could be in the vessel at any one time, not just during normal operation, should be considered. For example, if the vessel is used to store some or all of the ammonia while the rest of the system is being serviced, then M should include the additional mass of ammonia that is in the vessel at such a time. However, if there are administrative controls that limit the amount of ammonia that is allowed in the vessel at any one time, this limit can also be taken into account when estimating M.

Appendix A gives more detail on the reasons for the above described way of estimating M.

2.1.3 Distance to the Toxic Endpoint

Take the mass M and go to Table 2-1. Find the entry in the "Mass Released" column that is closest to, but also higher than, M. Read off the corresponding distance from the urban or the rural column. This is the "distance to the endpoint" that must be submitted in the RMP information per §68.165(b)(10).

To decide whether the site is rural or urban, use the following guidance. If 50% of the landmass within a 1-mile radius can be described as indicated below, the area can be classified as urban:

Total Mass	Predicted Distance to	o Toxic Endpoint (ft)
Released (lb)	Rural	Urban
1•000	3•100	2•100
1•500	3•700	2•500
2•000	4•300	2•900
3•000	5•200	3•500
4•000	6•000	4•000
5•000	6•600	4•500
6•000	7•300	4•900
7•000	7•800	5•200
8•000	8•400	5•600
9•000	8•900	5•900
10•000	9•500	6•200
15•000	11•500	7•500
20•000	13•300	8•600
25•000	15•000	9•500
30•000	16•400	10•400
35•000	17•800	11•200
40•000	19•100	11•900
45•000	20•300	12•600
50•000	21•400	13•200
60•000	23•600	14•400
70•000	25•600	15•500
80•000	27•400	16•600
90•000	29•100	17•500

 Table 2-1

 Predicted Distance to Toxic Endpoints - Worst-Case Release Scenario

- a) Heavy industrial (large chemical, other manufacturing facilities, 3-5 story buildings, flat roofs, grass and trees extremely rare); or
- b) Light-to-moderate industrial (rail yards, truck depots, warehouses, industrial parks, minor fabrication, 1-3 story buildings, flat roofs, limited grass and trees); or
- c) Commercial (offices and apartments, hotels 10-story heights, flat roofs, limited grass or trees); or
- d) Compact residential (single and some multiple family dwellings closely spaced, 2-story or less, alleys, pitched or flat roofs, limited lawns and few old established trees, no driveways).

If none of the above apply, the site should be classified as rural.

Figure 2-1 represents Table 2-1 in graphical form. The basis for Figure 2-1 is extensively discussed in Appendices A and B.

2.1.4 Passive Mitigation

The guidance on Table 2-1 has been prepared with the assumption that <u>no</u> passive mitigation is available. At first sight, it might appear that this is a highly pessimistic assumption because, in many ammonia refrigeration systems, the worst-case mass M will come from a vessel that is indoors in an area such as a compressor room. However, it is not easy to show that a typical building that houses compressors and vessels will effectively contain and mitigate a release of ammonia if the worst-case scenario occurs inside. Appendix C shows that, for many building configurations, the sudden loss of the contents of a high-pressure receiver (for example) would generate pressures that could not be withstood by a typical cinder block or unreinforced concrete structure. Therefore, it may be difficult to prove that the worst-case scenario can be mitigated by structures. However, if the owner or operator can demonstrate for a specific facility that structures can contain and mitigate the worst-case release scenario, then he/she can take credit for such mitigations.

2.2 <u>Alternative Release Scenario</u>

The owner or operator must identify and analyze at lease one "alternative" release scenario.

2.2.1 Mandatory Inputs

- a) The alternative scenario should be more likely to occur than the worst-case scenario.
- b) <u>It should reach an endpoint offsite</u>, unless no such scenario exists (note that this requirement means that the release rate for the alternative scenario must be fairly large, or it will generally not propagate offsite).

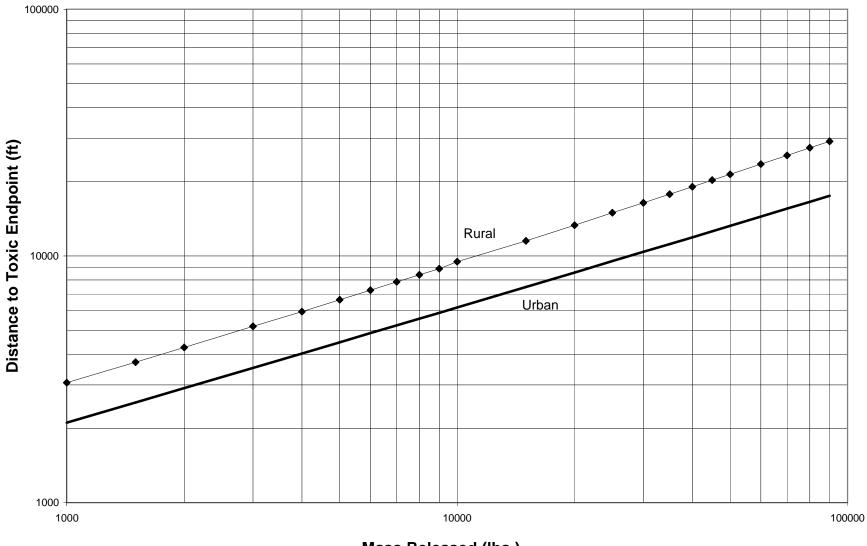


Figure 2-1 - Worst-Case Ammonia Release over 10 minutes Generic Guidance on Distance to Toxic Endpoint

Mass Released (lbs.)

c) The owner or operator should use "typical meteorological conditions for the stationary source". For the guidance presented below, an "average" weather condition of wind speed 3 m/s and D stability class has been chosen. The owner or operator is free to use different conditions if he/she can show that these other conditions are typical of a specific site.

2.2.2 Choice of the Alternative Scenario

As is shown in Appendix A, there is a great variety of potential alternative scenarios. Many, probably most, of these will not be large enough to exceed the toxic endpoint offsite.

For the purposes of the present guidance, a very simple definition of an alternative scenario has been chosen (a 1/4" effective diameter orifice leading to an airborne release, representative of a pump seal leak or a gasket rupture). For typical conditions in a high-pressure receiver, the corresponding rate of release is 100 lb/min (see Appendix A). In average weather conditions, namely a wind speed of 3 m/s and Stability Class D, the predicted distance to the toxic endpoint is 450 feet at an urban site and 1,000 feet at a rural site (also see Appendix A).

The owner or operator may simply quote the results for this "canned" scenario. For different choices of alternative scenarios, or if the distances quoted above do not extend offsite, see Appendix A.

2.3 <u>Presentation of Results</u>

Figure 2-2 is one suggested example of how the consequences of worst-case and alternative scenarios might be presented. It is a simplified map that shows the radius to which the vapor cloud might extend, given the worst-case release in worst-case weather conditions (the owner or operator should use a real map of the area surrounding the site). Organizations that have already begun to prepare Risk Management Programs and Plans have used this form of presentation (for example, in the Kanawha Valley or in Tampa Bay).

2.4 <u>Defining Offsite Impacts - Populations</u>

For each worst-case and alternative scenario, the owner or operator must estimate, to two significant digits, the population within a circle, with its center at the point of release and a radius determined by the distance to the endpoint calculated as described in Sections 2.1 and 2.2 above (i.e., the circles shown on Figure 2-2). The population must include the residential population. The presence of schools, hospitals, prisons, public recreational areas, arenas and major commercial and industrial developments, must be noted in the Risk Management Plan. The owner or operator may use the most recent Census data to estimate the population potentially affected. Cognizant local authorities can give information on schools, prisons, etc.

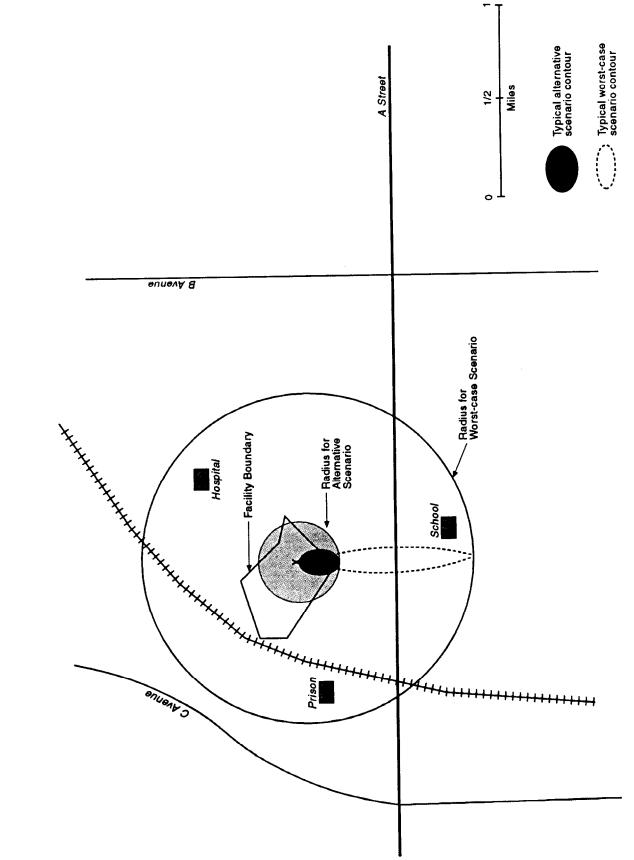


Figure 2-2. Simplified Presentation of Worst-Case and Alternative Scenarios on a Local Map

2.5 Defining Offsite Impacts - Environment

In the Risk Management Plan, the owner or operator must list environmental receptors within the circles shown on Figure 2-2. Environmental receptor means natural areas, such as national or state parks; forests or monuments; officially-designated wildlife sanctuaries, preserves, refuges, or areas; and Federal wilderness areas. The owner or operator may rely on information provided on local U.S. Geological Survey maps or on any data source containing U.S.G.S. data to identify environmental receptors. All that is required is to note the existence of these receptors.

2.6 <u>Documentation</u>

The owner or operator needs to maintain onsite the following records on the offsite consequence analyses:

- a) For the worst-case scenario, a description of the vessel or pipeline selected as worst-case, assumptions and parameters used and the rationale for selection; assumptions include use of any administrative controls and any passive mitigation that were assumed to limit the quantity that could be released. If the current guidance has been used, Section 2.1 can be referenced as the basis for the choice of the worst-case scenario.
- b) For alternative release scenarios, a description of the scenarios identified, assumptions and parameters used and the rationale for the selection of specific scenarios; assumptions include use of any administrative controls and any mitigation that were assumed to limit the quantity that could be released. Documentation includes the effect of the controls and mitigation on the release quantity and rate. Section 2-2 can be referenced here if the "canned" scenario is used.
- c) Documentation of estimated quantity released, release rate and duration of release.
- d) Methodology used to determine distance to endpoints (it will be sufficient to reference this guidance).
- e) Data used to identify potentially affected population and environmental receptors.

2.7 <u>Review and Update</u>

The owner or operator must review and update the offsite consequence analyses at least once every five years. If changes in processes, quantities stored or handled, or any other aspect of the stationary source might reasonably be expected to increase or decrease the worst-case distance to the endpoint by a factor of two or more, the owner or operator must complete a revised analysis within six months of the change and submit a revised Risk Management Plan.

2.8 Five-Year Accident History

The owner or operator must include in the five-year accident history all accidental releases of ammonia that resulted in deaths, injuries, or significant property damage on site, or known offsite deaths, injuries, evacuations, sheltering in place, property damage, or environmental damage. For each accidental release included, the owner or operator is expected report the following information in the Risk Management Plan:

- 1. Date, time and approximate duration of the release
- 2. Chemical(s) released
- 3. Estimated quantity released in pounds
- 4. Type of release event and its source
- 5. Weather conditions if known
- 6. Onsite impacts
- 7. Known offsite impacts
- 8. Initiating event and contributing factors if known
- 9. Whether offsite responders were notified if known, and
- 10. Operational or process changes that resulted from investigation of the release

Numerical estimates should be provided to two significant digits. The above information should be available from the reports of a good incident investigation procedure.

3.0 PREVENTION PROGRAM AND EMERGENCY RESPONSE PLAN

3.1 Introduction

In June, 1988, in preparation for determining the role of the Federal Government in reducing the likelihood and severity of chemical accidents, EPA prepared the SARA 305(b) report, *Review of Emergency Systems*. In this report, it was concluded that:

"Prevention of accidental releases requires a holistic approach that integrates technologies, procedures, and management practices".

The report went on to outline the elements of such a program. These were based on a compilation of industrial programs that had been shown to be successful in reducing both the likelihood and severity of chemical releases, fires and explosions. At the time, a review of practices revealed that no industry, nor any individual firm, practiced all of these elements. The compilation was of practices found throughout industry, bought into the EPA report as an overall program.

Both the OSHA regulation, 29 CFR 1910.119, and this EPA Part 68 - Accident Release Prevention Program, are founded on the program initially laid down in the SARA 305b report.

Thus, this prevention program is intended to assure that designs are reviewed so that new plant and equipment is in conformance to safe design principles. The remainder of the requirements assures that the operation, maintenance and control of hazards are well done. This will prevent inadvertent changes outside that safe design and operating envelope.

Readers will recognize that this prevention program is intended to provide for ongoing management of highly-hazardous substances. It in not a list of "once and done" actions. Rather, it provides a means for assuring safe operations throughout the life of the facility.

3.2 Applicability to Ammonia Refrigeration

A review of the ammonia releases from refrigeration plants found in the ARIP data base (see Appendix D) reveals that several of the individual elements of this rule would have been effective in preventing those releases. That is, the elements found useful in industry generally are fully applicable to ammonia refrigeration plants as a means of preventing accidents in its industry.

In that review, some elements were found to be especially applicable to accident prevention in the ammonia refrigeration industry. However, all elements are useful as part of the holistic approach to prevention. The detail involved in applying each element will vary between industries and between facilities in the same industry. This was foreseen in the performance orientation of this rule and in the OSHA regulation.

EPA recognizes that ammonia refrigeration plants are very different from complex chemical processing operations. Many of the operations in chemical processing are not found in refrigeration plants. There

are no chemical reactions. Moreover, ammonia refrigeration is a mature industry. While there are new developments leading to more efficient operations, the design principles are fully available. A complete understanding of the safe design and operating envelope is available to design and operating practitioners in the industry.

This guidance takes the differences between chemical plants and ammonia refrigeration plants into account. It is based on the operating characteristics of ammonia refrigeration facilities. The International Institute of Ammonia Refrigeration (IIAR) has been most helpful in the formulation of this guidance. EPA wishes to thank the IIAR for their practical and valuable insight and advice about the industry.

In addition, the experience gained in applying process safety requirements to ammonia refrigeration plants in one state, Delaware, demonstrated the value of concentrating on specific elements of process safety. In particular, maintenance, or Mechanical Integrity, is vital. For that reason, this guidance puts that element first. Delaware's requirements come from their Extremely Hazardous Substances Regulation. This experience strongly parallels the results of the review of the ARIP data base, noted above. EPA wishes to thank the Delaware Department of Natural Resources and Environmental Control (DNREC) for their insight, assistance and advice. DNREC is responsible in Delaware for both enforcement and assisting in compliance.

This RMP rule and the OSHA PSM standard (29 CFR 1910.119) apply to ammonia refrigeration plants where the total quantity of ammonia is over 10,000 pounds. Because the PSM standard applies, ammonia refrigeration plants are considered to be Program 3 facilities, as provided in §68.10(d) of the rule. If the requirements of the OSHA regulation are met, the prevention provisions of the EPA RMP rule will also be essentially satisfied, because EPA has prepared the RMP rule so as to avoid duplication of effort in this regard by owners and operators. EPA however, has added that the owner or operator must be prepared to demonstrate that a management system is in place to assure continued fulfillment of prevention requirements. EPA also requires, beyond OSHA's requirements, an offsite consequence analysis, emergency response planning and registration of the facility.

3.3 Judgment of Facility Owners or Operators

The elements of process safety in both the EPA RMP rule and in the OSHA PSM standard express performance requirements. This allows for the individuality of each plant to be taken into account in determining the means of accomplishing that performance. Owners and operators must, therefore, determine exactly how they will accomplish it. They are expected to select the means that best suits both the effectiveness and efficiency with which the desired result is to be achieved at that plant.

Owners or operators, when taking the individuality of their plant into account, are free, indeed encouraged, to integrate their prevention program into routine business management. EPA is aware that, where this has been done, the burden of compliance is less than where compliance is considered an "add-on" to plant management. Many requirements of this rule are part of normal good operating practices; accomplishing them as an "add-on" can result in duplication of effort.

This guidance is, therefore, necessarily general in nature, with a few exceptions. EPA expects to find a wide variety in the means employed to meet the performance requirements. EPA regards the management system required by §68.15 as the source of the judgment needed as to how each element is to be accomplished. It is an integral part of the prevention program.

3.4 Management System

The RMP prevention program begins with a requirement for a Management system that assigns responsibility for implementation of the prevention program. This requirement for a Management System is intended to ensure that each element is fully and effectively carried out. The requirements are given in §68.15 of this rule. The elements of the prevention program are spelled out in Subpart D Program 3 Prevention Program, §68.65 through §68.87.

The elements of the prevention program are laid out to provide the actions needed in many different kinds of facilities that have hazardous materials subject to the rule. The application of each element will differ, depending on the industry and on the needs at individual facilities. For example, among ammonia refrigeration facilities, there are considerable differences between refrigerated warehouses and food processing plants. The age and design of individual facilities will have a large impact on the actions necessary to effectively carry out each element of the prevention program. For this reason, the Management System, in assigning responsibilities, must provide for the actions needed at each individual facility.

In evaluating whether their Management System has been implemented, owners or operators of covered sources will need to assess that the responsibilities have been fully and effectively assigned. Because the necessary actions differ amongst covered sources, what it is for which persons are made responsible must be spelled out. That is, the goals of accomplishment at the specific refrigeration facility against each element should be stated and understood by the person responsible for the outcome. As an example, a goal might be that *the operating procedures for the plant will be up to date and readily available to operators*.

Another measure that the responsibility has been effectively assigned is that there will be plans to carry out the goals. These plans will take into account the interrelationships between elements of the prevention program. For example, the plans might provide that *there will be updated and correct P&IDs before attempting to carry out a Process Hazard Analysis (PHA)*. Owners or operators should ensure that plans to execute the assigned responsibilities are prepared and understood.

- 1. In addition to this section, there are related elements to be considered when evaluating compliance with the Management System requirements:
- 2. §68.79 provides for an audit that each element is fully carried out. This measures whether the assignment of responsibility was effective, and provides a mechanism to institute corrective action to improve the Management System, if needed.

In assigning responsibilities for executing

- Process Hazard Analyses (§68.67)
- Accident/incident investigations (§69.81)
- Compliance Audits (§68.79)

The Management System must assign responsibility to track the resolution or completion of recommendations and findings from these elements.

Owners or operators should ensure that the audits do measure that the several elements of the Prevention Program have been effectively accomplished, and that the resolution tracking responsibility has resulted in completion of these requirements.

3.5 §68.175, Information Required

As owners or operators provide the required information pursuant to this section, they may want to consider the guidance given below. Careful attention to the suggested practices is essential to assuring that the execution of the process safety element will be consistent with good industrial practices.

3.5.1 §68.175(h), Maintenance (see §68.73)

Experience in Delaware, corroborated by a review of accidents in the ARIP data base (see Appendix D) indicates that this element is of principal importance in preventing ammonia releases from refrigeration plants. EPA believes that a sound and well-run inspection, test and preventive maintenance program is essential to preventing equipment failure that could result in a hazardous release.

Written procedures should include all equipment that should be inspected, tested, or maintained. Good engineering practices and manufacturer's recommendations or experience should determine the means of inspection, test, or preventive maintenance. In older plants, operating experience in that plant should be taken into account when determining the appropriate level of preventive test, calibrations, or maintenance. Owners or operators are expected to judge the adequacy of the list of equipment to be maintained, the methods employed and the frequency of the preventive maintenance.

The rule requires that owners or operators report the date of review of procedures, and the date inspections and tests were done. Owners or operators should ensure that these tests and inspections are being done, and that deficiencies are corrected if any are found.

In ammonia refrigeration plants, experience suggests that it is especially important for these to be done:

- Periodic walk-throughs to find unusual or increasing vibration, incipient leaks, or other indications of potential upsets or failures that could lead to a release. In older plants, or in food processing units where frequent changes are made, this might be done daily. On more modern plants, weekly walk-throughs are likely to be sufficient.
- Inspection of pressure vessels. There may be need to consider whether stress corrosion cracking (SCC) is of concern. Industry guidance should be consulted; IIAR's Bulletin 110 provides information regarding this issue. However, attention to ammonia water and oxygen content throughout the life of the refrigeration system may preclude the need for internal inspections for SCC.
- Periodic replacement, or preventive inspection and maintenance, of pressure relief valves. ASME, ANSI/ASRAE 15, state and local codes should be consulted for guidance. Industry guidance from the IIAR, their Bulletin 10, recommends a five-yearly replacement of these valves.
- Periodic inspection and calibration of those liquid level, temperature and pressure instruments, switches and shutdown devices that have safety implications. Owners or operators will need to judge which of these devices have safety implications and which do not, e.g., a liquid level shutdown on a compressor suction is vital to safe operations.
- Periodic inspection of major powered equipment, including compressors, pumps and large fans, bearings, couplings, shaft seals, mountings, etc., for vibration, or incipient mechanical failure. Where expertise is needed, owners or operators are expected to secure it. Either employees or, if necessary, contractors, skilled in refrigeration equipment maintenance, can provide this expertise.

Experience also shows the importance of pre-startup safety reviews following extensive maintenance activity. See the guidance in Section 3.5.7.

If the plant relies on employees for maintenance activities, owners or operators should ensure that these employees are trained to perform that work. If contractors perform the work, the owner or operator will be expected to know that the contractor is qualified to work on refrigeration equipment.

Spare parts should be proper for refrigeration service. Where pertinent, spares should be purchased from refrigeration equipment vendors to be sure that the right materials are used.

New equipment design is vital. Owners or operators answering this question affirmatively will be expected to have assured that new equipment meets appropriate design codes or standards, including ASME pressure vessel code, ANSI safety and performance standards, ASHRAE and IIAR standards, and local mechanical and fire codes for refrigeration equipment. While larger firms may have competent engineering employees to do this, smaller firms may need to rely on contractors to provide this assurance. If the latter applies, owners or operators are expected to select contractors who are familiar with these codes and standards.

3.5.2 §68.175(d), Process Safety Information (see §68.65)

Owners or operators are to supply the date this information was last revised. In doing so, the owner or operator should verify that all of the information needed to safely operate the ammonia refrigeration system is on hand and up to date. In general, it should comprise of:

- information about the hazards of ammonia and other hazardous, materials, e.g., chlorine for water treatment if any are present
- information about the design basis for the plant
- information about the equipment in the plant

This general list should be considered in light of the simpler design basis for refrigeration plants, when compared to complex chemical operations. For ammonia refrigeration plants generally, process safety information is likely to consist of:

- Material safety data sheets for ammonia and any other hazardous materials present
- A block flow diagram for the plant
- Piping and instrument drawings (P&IDs)
- A complete list of safety relief valves, showing their location, design basis and capacity, set point, date of installation, and the design of discharge piping systems. The result and date of the most recent inspection, test, maintenance, or replacement should also be available.
- A complete list of high- and low-level, and high- and low-pressure, shutdown or alarm devices, their set point and location, and result and date of the most recent calibration of each.
- Equipment manufacturer's operating instructions, including safe operating limits, for vessels, piping, rotating equipment, heat exchangers, valves, controls and other equipment in the plant.
- Equipment drawings and specifications. Care should be taken to assure that these reflect asbuilt installed equipment.

3.5.3 §68.175(e), Process Hazards Analyses (see §86.67)

Process Hazard Analyses (PHAs) provide for understanding potential hazardous events, the means by which they can occur and what actions are likely to prevent them. Many methods to do these analyses have been developed by the engineering profession. For ammonia refrigeration plants, the industry, through the IIAR, has taken a strong lead in developing a simple and readily used checklist.

In giving the completion date of the last PHA, the owner or operator should ensure that a proper procedure was used. It may be the IIAR checklist, another checklist, or any of the methods outlined in §86.67 of this rule. Care should be taken to ensure that offsite consequences are evaluated.

PHAs usually result in findings or recommendations for improvements to prevent potential releases. The management system (see above) includes that these findings or recommendations are promptly brought to resolution. Owners or operators, when giving the dates of implementation or recommendations, should verify that this resolution is being done.

3.5.4 §68.175(f), Operating Procedures (SOPs) (see §68.69)

Owners or operators are asked to state when their operating procedures were prepared or last revised and updated. Operating procedures provide the basis for proper and safe operation of an ammonia refrigeration plant. These procedures should show a clear path to the safe operation of the plant. The procedures should:

- Be based on relevant process safety information and may take operating experience into account. (Note that in refrigeration plants, the equipment manufacturer's recommended operating procedures are often satisfactorily used as plant operating procedures. If this is done, owners or operators should ensure that these procedures are kept up to date, consulting with the equipment manufacturers if necessary.)
- Be up to date, reflecting all changes to the plant
- Include safe operating limits for temperature and pressure
- Describe the consequences of operating outside these safe operating limits
- Include procedures to correct maloperation outside these safe operating limits and to bring the plant into a safe state
- Provide a description of safety systems and how they operate. This should include pressure and liquid level trips and alarms, and pressure relief valves with their discharge locations.
- Include procedures for:

Normal Operations

Startup. Experience indicates that, in ammonia refrigeration plants, startup procedures after maintenance activity should include an inspection to ensure that the maintenance is complete, that drain valves, etc., are in the proper position, and piping is fully connected.

Shutdown

Emergency operations for leaks or other foreseeable operating problems

Emergency shutdown, including when it is required

In ammonia service, attention to the quality of ammonia is important to preventing stress corrosion cracking of carbon steel. Operating procedures should provide that ammonia used to charge, or recharge, the system be of proper quality. The procedures should provide that operations are run in a way that maintains proper ammonia quality. Guidance on this issue is provided by the IIAR in their Bulletin 110. Testing of ammonia for water and oxygen is described in the IIAR Bulletin 108.

In addition to operating procedures, §68.69 calls for procedures for safe work practices. These generally address non-routine work, such as maintenance and construction, within an operating plant. The date these procedures were prepared or updated should also be reported. These safe work procedures are included:

- lockout/tagout
- confined space entry
- opening process equipment and piping
- control of access to the plant. This procedure is intended to ensure that plant management controls the activities and safety of workers other than those regularly assigned to work there.

Note that OSHA has described the requirements for lockout\tagout and confined space entry in separate standards that apply to any workplace. Also, note that a hot work procedure is called out separately in this rule.

3.5.5 §68.175(g), Training (see §68.71)

The rule's requirement for training is that each employee operating equipment in the plant shall have been trained to operate it safely and understands the training. Owners or operators should verify that this is the case. The training materials should be up to date; EPA requires that the date these were updated be specified.

Refresher training at least every three years is a requirement. Documentation should show that it has been done and when.

Verification of understanding of the training is an important aspect of the management of training. It may include observation of performance, written testing and/or oral testing. Training documentation should show how understanding was measured or verified.

3.5.6 §68.175(i), Management of Change (see §68.75)

When changes or expansions are done, it is necessary to assure that the change or expansion is at least as safe as the original design. Also, change can unexpectedly introduce new hazards. Owners or

operators should ensure that the provisions of §68.75 are met whenever equipment is changed and not replaced in kind. Also, the provisions apply whenever operating conditions are changed beyond the limits given in process flow diagrams or in equipment specifications.

In particular, care should be taken that changes are identified. Small additions or rerouting of ammonia piping are changes that are often overlooked. Small, inadvertent change as a consequence of maintenance is also often overlooked. If these small changes are made, it is expected that they will have been identified and their impact on safety addressed.

Equipment replacements, when not exactly the same as the older versions, are changes to be evaluated: releases have occurred when equipment has been replaced, especially when the new equipment was not designed for refrigeration service.

In considering the technical basis for the change and its impact on safety and health (see §68.75[b][1] and [2]), EPA anticipates that a Safety and Health review, process hazard analysis, or similar review, will be used. A person qualified by experience or training should conduct the review. If the review shows the need to improve the design for safety reasons, the improvement should be completed before startup.

3.5.7 §68.175(j), Pre-Startup Review (see §68.79)

The owner or operator should ensure that the requirements of §68.79 are being met if there are changes in the plant.

This requirement is intended to be a redundant follow-up to Management of Change, discussed in the previous section. It provides for an independent recheck that changes are in condition to be operated prior to startup. In complex chemical plants and refineries, it is a vital redundancy; in ammonia refrigeration plants, a simple review by a manager that the provisions of Management of Change are complete should be sufficient.

3.5.8 §68.175(k), Compliance Audits (see §68.79)

Compliance audits provide a means by which the management of a plant assures itself that employees are properly carrying out their duties for preventing accidental releases. This element of the Prevention Program is essentially a follow-up to the requirement for the Management System delineated in §68.15 of this rule.

A vital activity is that any deficiency found in an audit be corrected.

3.5.9 §68.175(l), Accident Investigation (see §68.81)

Events that either might or did cause an accidental or unexpected release of ammonia are to be investigated. The objective is to correct deficiencies in such a way as to prevent repetition. EPA

expects that corrective actions will be completed in a timely way. This is related to the Management System requirement (see above.)

3.5.10 §68.175(m), Employee Participation Plan (see §68.83)

This element of the Prevention Program requires that owners or operators consult with their workers about process safety. In particular, workers should participate in process hazards analyses and be consulted as to how the other elements of the Prevention Program are carried out. A written plan to do this is required. Owners or operators should ensure that their written plan is followed.

3.5.11 §68.175(n), Hotwork Permits (see §86.85)

Hot work is defined as spark or flame producing operations, such as welding, brazing, metal cutting and grinding, sandblasting, etc. A permit is required describing the hazards of the hot work to be done and the needed precautions to prevent fires. These permits should be used to communicate the hazards and precautions to the workers performing the hot work.

OSHA has described the necessary precautions in 29CFR 1910.52(a).

3.5.12 §68.175(o), Contractors (see §86.87)

Many ammonia refrigeration plants use mechanical and refrigeration contractors for construction, maintenance and repair and other work. Owners or operators should judge that these contractors are knowledgeable about ammonia refrigeration, understand the applicable codes and standards, and are capable of working safely in an ammonia refrigeration plant.

Refrigeration plant owners or operators often hire contractors for their expertise in maintenance or construction. However, it is expected that the owner or operator will ensure that the contractor understands the safety requirements of the plant, and ensure that contractors have trained their workers in them. Also, the rule requires that owners or operators will ensure that the field practices of the contractor's workers are in conformance to the safety requirements of the plant.

Related to both this contractor requirement and to Management of Change (see above), contractors often make additions and changes to plants. Owners or operators may call on the contractor to furnish safety information about the change or addition. Thus, a contractor's familiarity with the requirements of the RMP rule and ability to meet them can be important qualifications for their employment.

3.6 §68.180, Emergency Response Program

The emergency response program for ammonia refrigeration plants will be individually tailored to each plant and the emergency response services available in the community. §68.180(b) asks whether the plant has a plan and whether it is coordinated with the LEPC plan. In considering this question, owners or operators should consider these factors:

- Whether the details of the plan were worked out with local emergency responders through the Local Emergency Response Committee (LEPC)
- Whether the plan is based on the consequence assessment required by §68.165 of this rule
- Procedures for informing public and local authority about releases
- Site response procedures to protect workers and minimize the offsite consequences (note the requirements of 29 CFR 1910.38)
- Organization, responsibilities and training of responsible persons
- Internal alarms (note provisions of 29 CFR 1910.165)
- Evacuation, emergency response training and drills. Training should include hazardous materials training where pertinent (note provisions of 29 CFR 1910.120)
- Emergency valve closures and equipment shutdown; operator training in foreseeable emergencies
- Containment of releases
- Fixed fire protection equipment and its operation
- Protective gear; training in its use
- Coordination with local emergency responders
- Provisions for communication
- Shelter in place and/or offsite evacuation
- Drills and critiques
- Spill cleanup; Hazmat training if any (see 29 CFR 1910.120)

APPENDIX A

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APPENDIX A

GUIDANCE ON CHOICE AND MODELING OF WORST-CASE SCENARIO AND ALTERNATIVE SCENARIOS FOR AMMONIA REFRIGERATION FACILITIES

1.0 INTRODUCTION

1.1 Outline of Appendix

The purpose of this Appendix is to provide backup to the guidance in Chapter 3 on how to choose both "worst-case" scenarios and "more likely" or "alternative" scenarios, and how to perform the atmospheric dispersion modeling that is required by 40 CFR Part 68. The intention is to provide technical and scientific support for the key assumptions. In addition, earlier drafts of this guidance attracted certain questions, and the more important of those questions are provided with an answer.

Section 2 provides background in the form of a description of the various conditions under which ammonia exists in a typical refrigeration system. It also contains a qualitative discussion of how these conditions affect the predicted rate of release and other parameters that control the atmospheric dispersion analysis. Section 3 briefly reviews the atmospheric dispersion modeling for the worst-case release scenario. Section 4 discusses the choice and modeling of alternative release scenarios. Section 5 provides advice on where to go to obtain guidance if the owner or operator chooses to do his/her own modeling and not to use the material provided in this guidance.

Appendix B discusses how the atmospheric dispersion modeling was performed to support Sections 3 and 4. Appendix C contains a discussion of buildings and whether it is likely that, if the worst-case scenario takes place inside a typical compressor room, there will be effective containment and mitigation of the resulting ammonia vapor cloud (the conclusion is that this cannot be taken for granted). Finally, Appendix D is provided as additional guidance for owners or operators who wish to perform their own dispersion analysis.

1.2 <u>Assumptions</u>

There are certain assumptions in this Appendix that are mandated by the regulation:

- o In the worst-case release scenario, the duration of release is 10 minutes at a constant rate.
- o The toxic endpoint is the ERPG-2 of 200 ppm (0.14 mg/L) for an exposure time of one hour.
- o The consequences of the worst-case scenario should be modeled in atmospheric stability category F weather conditions with a windspeed of 1.5 m/s.

- The alternative scenario should be large enough to cause offsite effects above the toxic endpoint.
- o The consequences of the alternative scenario should be modeled in typical weather conditions.

2.0 BRIEF SUMMARY OF THE VARIOUS STATES IN WHICH AMMONIA EXISTS IN A TYPICAL REFRIGERATION FACILITY

A typical block diagram of a two-stage ammonia refrigeration facility is shown on Figure A-1. A similar diagram of a single-stage facility is shown on Figure A-2. It is pertinent to begin by discussing the state of the ammonia in various parts of the system because the potential rate of release through an accidentally-formed orifice and the subsequent atmospheric dispersion is strongly dependent upon this state.

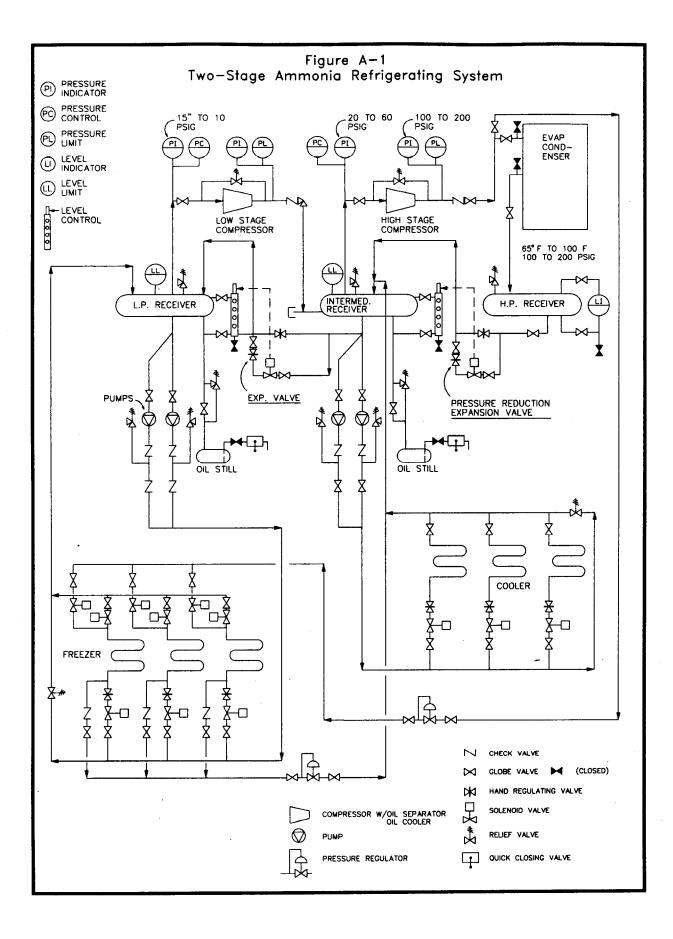
2.1 <u>Ammonia Liquefied Under Pressure</u>

2.1.1 Background

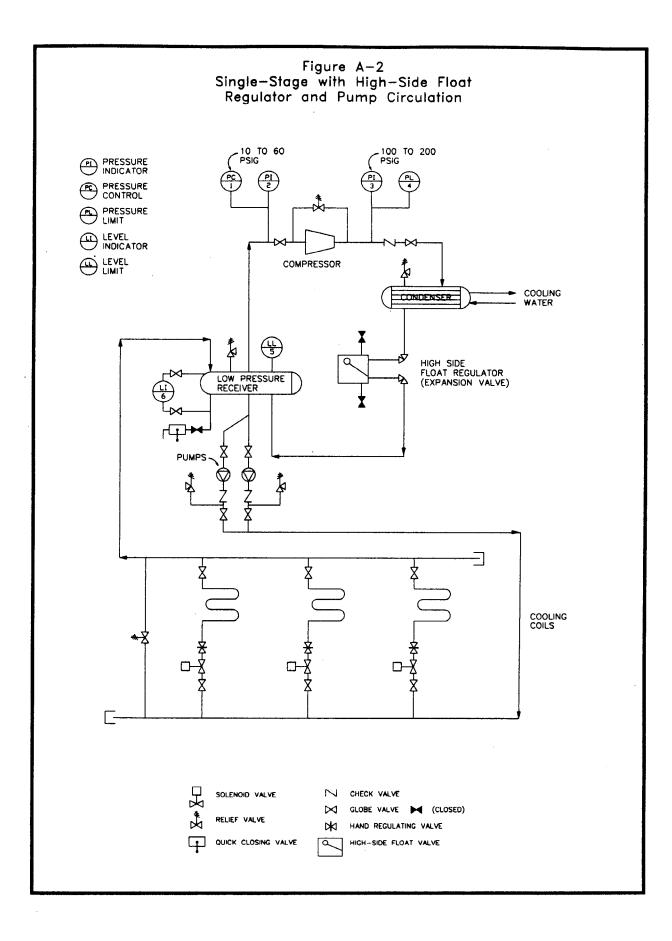
In many parts of a typical refrigeration system, there is ammonia liquefied under pressure. If the pressure and temperature are sufficiently high, and if there is a sudden release of liquid ammonia, it will all become and remain airborne as a mixture of ammonia vapor and very fine liquid droplets that do not fall to the ground. Experimental results clearly show that this is a real physical phenomenon (Goldwire, et. al., 1985; Kaiser, 1989). The droplets evaporate quickly as air is entrained. The evaporation process cools the air so that a cold mixture of air and ammonia vapor is formed. The mixture is denser than air, and a heavy vapor dispersion model is required to adequately predict airborne concentrations downwind of the point of release.

In earlier drafts of this guidance, a number of people raised questions about how much of the liquid ammonia actually becomes and remains airborne, as a function of the temperature of ammonia in the vessel, and what is the temperature that is sufficiently high to ensure that all of the ammonia remains airborne as the mixture of vapor and fine liquid droplets referred to above.

Figure A-3 shows the results of some experiments that were carried out on liquid chlorine and reported by Johnson (1991). Similar experiments were not performed for ammonia, but it is to be expected that ammonia results would look similar because, for example, chlorine and ammonia have similar density ratios of liquid to vapor and have similar atmospheric boiling points. Figure A-3 shows the percentage of liquid chlorine that falls to the ground as a function of superheat, which is the difference between the temperature of the chlorine initially in the vessel and its boiling point. Figure A-3 also shows for comparison the results of the Dow Model (Dow, 1993), which predicts that the fraction of airborne liquid droplets is five times the vapor flash fraction (the fraction of chlorine that immediately vaporizes as it is released to the atmosphere). Earlier drafts of this guidance were criticized for not using the Dow model, but, as can be seen, the Dow Model appears to be conservative (i.e., it predicts that too much ammonia falls back to the ground).



A-3



A-4

Figure A-3 also shows the results of a model (Ianello), known as the "RELEASE" model, that was used by Johnson (1991) to try to reproduce the experimental results. As can be seen, agreement is poor, possibly because the model neglects the evaporation from the airborne droplets as they fall towards the ground. Other models that take into account this evaporation lead to better agreement with experiments (e.g., Woodward and Papadourakis, 1991).

The principal conclusion, by analogy with the chlorine experimental results, is that, even at superheats of only 10° C (which would be a temperature of only about -23 °C for ammonia), only a small fraction of released liquid ammonia would fall to the ground. Therefore, at most, a small degree of conservation is introduced if it is assumed that, for superheats exceeding 10°C, all of the released ammonia remains airborne.

2.1.2 Applicability to Ammonia Refrigeration Facilities

In many refrigeration facilities, the ammonia travels from the discharge of the compressors through the evaporative condensers to the high-pressure receiver, which will be at typical conditions of 35°C (95°F) and 180 psig. Figure A-1 shows a range of typical pressures in the high-pressure receiver from 100-200 psig (approximately 8-15 atmospheres). Figure A-4 shows ammonia vapor pressure as a function of temperature. 8-15 atmospheres corresponds to ammonia temperatures of approximately 10-40°C, or superheats of about 40-70°C. These conditions are definitely such as to ensure that all of any liquid ammonia release will become and remain airborne.

Some (but by no means all) refrigeration facilities have an ammonia storage vessel (not shown on Figure A-1) in addition to the high-pressure receiver. This vessel will, in all likelihood, be outside, and its pressure will fluctuate with the external temperature. However, at an ambient temperature of (say) 25°C, the superheat would be about 60°C so that the characteristics of any release from such a vessel are expected to be similar to those of a release from the high-pressure receiver. If the capacity of the outside storage vessel exceeds that of the high-pressure receiver, a release from this vessel should be considered as a candidate for the worst case.

Some refrigeration facilities (such as that shown on Figure A-2) may not have a high-pressure receiver. In such facilities, ammonia at pressures as high as 180 psig is confined to pipework, and there may be a low-pressure receiver with a typical pressure in the range 10-60 psig (~ 2-5 atmospheres), also containing ammonia liquefied under pressure. From Figure A-4, the corresponding temperatures are -20-0°C, or superheats of 10-30°C. Referring to the discussion of Figure A-3 in Section 2.1 of this Appendix, it is only slightly conservative to assume that all of the ammonia released from such a vessel becomes airborne. Note that two-stage systems have an intermediate receiver, which has a range of operating pressures similar to those for low-pressure receivers in a single-stage system.

2.2 <u>Ammonia at Subatmospheric Pressures</u>

In some facilities (e.g., food processing plants), even colder ammonia may be needed (when, for example, very rapid freezing of food is necessary). Figure A-3 shows a low-pressure receiver

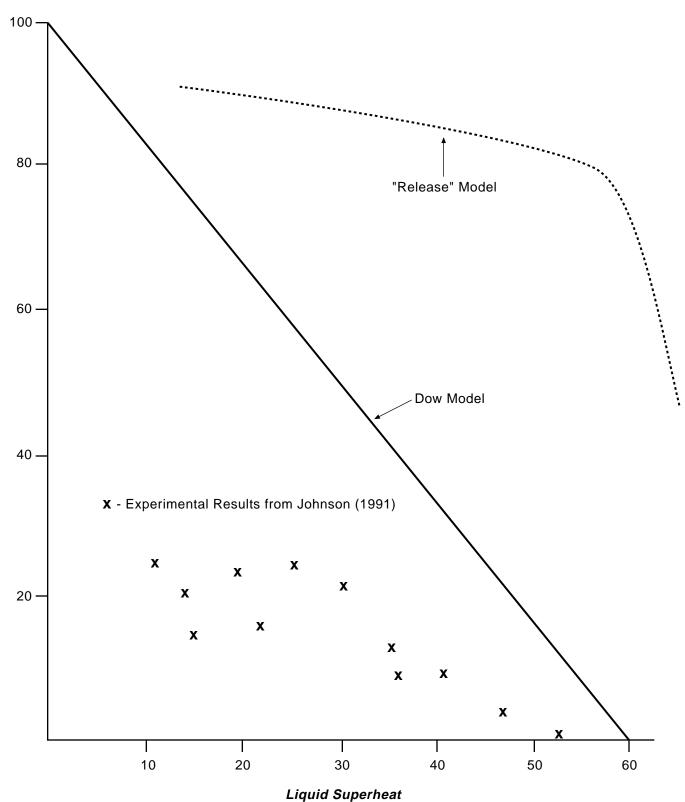


Figure A-3. Fraction of Liquid Chlorine Falling to the Ground as a Function of Superheat

(Liquid Superheat is Temperature Above the Chlorine Atmospheric Boiling Point of -34.6°C)

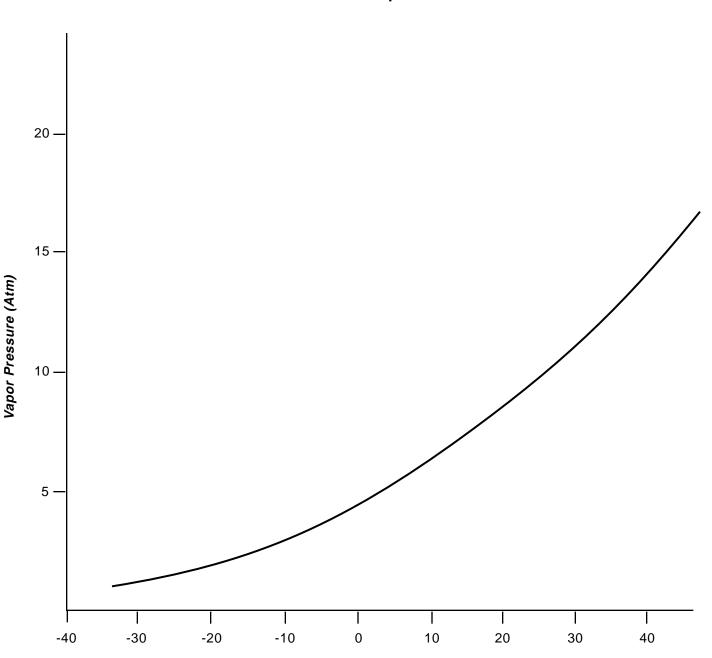


Figure A-4. Vapor Pressure of Ammonia as a Function of Temperature

Temperature (° C)

with subatmospheric pressures as low as 15 inches of water, which corresponds to a temperature well below the atmospheric boiling point. If released, the ammonia will spill onto the ground and, over an average period of 10 minutes or more, will evaporate at a much lower rate than a release from a worst-case rupture in such a vessel as the high-pressure receiver. In addition, these low temperature vessels are generally inside buildings, and it is likely that this would further reduce the effective rate of release to the atmosphere external to the refrigeration plant.

2.3 <u>Ammonia Gas</u>

Finally, there is ammonia gas (vapor) in the system under a range of temperatures and pressures. If there is a rupture in the vapor space of the high-pressure receiver (say), there will be a buoyant ammonia jet (i.e., the ammonia vapor is less dense than air). However, for a given hole size and a given pressure, the rate of release of ammonia gas is very much less than that of liquid ammonia, so that it is unlikely that a vapor release would be the worst-case.

2.4 <u>Buildings</u>

In many refrigeration facilities, the high-pressure receiver and other vessels will be indoors (e.g., in the compressor room). It is pertinent to ask what effect the building will have if there is a sudden release of the contents of the high-pressure receiver inside it. It might be assumed that mixing in the air in the building and subsequent relatively slow leakage through cracks or through the ventilation system will considerably mitigate the consequences of the release. However, there are several reasons why this assumption should be carefully investigated:

- 1. In many cases, pipework connected to the liquid space of the-high pressure receiver leads outside so that, if there is a severe leak in this pipework, the contents of the vessel will discharge through it and bypass the building.
- 2. In many cases, a compressor room has doors or windows on external walls of the refrigeration facility. In the worst case, it cannot be assumed that these are closed.
- 3. Sensitivity studies have been performed that show that, in the event of a sudden release of several tons of ammonia into a compressor room, the pressure in the room could easily rise to well in excess of 1 psig. A typical cinder block or unreinforced concrete structure will not withstand this pressure, and any windows will certainly be broken. (Note that cinder block buildings will withstand shock or blast waves that generate overpressures of 2-3 psi [FEMA, 1989]. However, the duration of the excess pressure will be much greater than for a shock wave in the case of the ammonia expansion considered here, so it is prudent to somewhat reduce the expected pressure that the building will withstand.) After the initial pressure rise, the released ammonia will mix with the air in the room. The resulting air/ammonia mixture can be very cold and cause subatmospheric pressures that would again damage the building. The foregoing observations are dependent on the amount of ammonia released and on the size of the room. However, they are true for typical ratios of room volume to released

ammonia mass. Similar results have been shown to be true for chlorine (Brighton, 1989). This issue is discussed further in Appendix C.

- 4. In modern systems, compressor rooms are sometimes designed with panels that blow out at overpressures of about 1 psi, to protect against explosive overpressures.
- 5. Notwithstanding the foregoing, the owner or operator can perform his/her own analyses if he/she can show that the building will indeed withstand the worst-case release.

3.0 MODELING THE WORST-CASE RELEASE SCENARIO

Section 2.1 of the main body of this guidance gives advice on how to choose the mass M that is released in the worst-case scenario and to estimate the distance to the toxic endpoint. That advice is consistent with the discussion in Section 2 of this Appendix.

It is pertinent to discuss the rule's requirement that all of the ammonia should be modeled as becoming and remaining airborne over a period of 10 minutes. Sections 2.1 and 2.2 of this Appendix show that the assumption that all of the ammonia becomes and remains airborne is a reasonable one for a worst-case scenario. To understand whether a release duration of 10 minutes is reasonable, consider Bernoulli's formula (CCPS, 1989) for predicting the rate of release Q(kg/s) of liquid from a vessel:

$$Q = c \rho_L A (2p_g / \rho_L + 2gh)^{0.5}$$
(3-1)

where:

с	=	a constant (typical value 0.6)
$\rho_{\rm L}$	=	the density of the liquid in the vessel (639 kg/m ^{3} for ammonia)
А	=	the area of the orifice $(m^2 - for example, the area of a hole of$
		diameter 1" is $5.16 \times 10^{-4} \text{ m}^2$)
p_{g}	=	the gauge pressure in the vessel (Pa - for example, 180 psig = 1.2×10^6 Pa)
g	=	the acceleration due to gravity (9.82 m/s^2)
h	=	the static head (m - negligible when the vapor pressure is as high as
		180 psig)

Note that this is the formula for the release of a pure liquid and would apply to a breach in the wall of a vessel or to the rupture of a very short pipe. For long pipes, there is a pressure drop between the vessel and the orifice that leads to flashing in the pipe and a reduce rate of release (Fauske, 1985; Fauske and Epstein, 1987).

The rate of release from a ruptured pipe from a high-pressure receiver as a pressure of 180 psig is predicted to be $\sim 12 \text{ kg/s} \sim 1600 \text{ lb/min}$ out of a 1" hole. Therefore, a typical mass M of 20,000 lb would be expelled in about 12 minutes. For a 2" hole, the duration of release would be 3 minutes. For an intermediate-pressure receiver at 30 psig, the predicted rates of release would be

 \sim 660 lb/min (1" orifice) or 2650 lb/min (2" hole), with corresponding durations of release for 20,000 lb of ammonia of 30 minutes and 7 minutes, respectively. Thus, as a "typical" release duration, 10 minutes is not unreasonable.

4.0 ALTERNATIVE RELEASE SCENARIOS

It is possible to envisage a whole host of alternative scenarios. Some of those identified from a review of past incidents in refrigeration facilities (see Appendix D) include:

- plant upsets leading to the lifting of relief valves
- leaks in rotating seals
- pipeline failures
- a blocked-in, liquid-full pipeline rupturing as it heats up
- failures during ammonia delivery, such as a hose leak

The rule suggests that the following scenarios should be considered:

- 1. Transfer hose releases due to splits or sudden hose uncoupling;
- 2. Process piping releases from failures at flanges, joints, welds, valves and valve seas, and drains or bleeds;
- 3. Process vessel or pump releases due to cracks, seal failure, or drain, bleed, or plug failure
- 4. Vessel overfilling and spill, or overpressurization and venting through relief valves or rupture disks; and
- 5. Shipping container mishandling and breakage or puncturing leading to a spill

In addition, active and passive mitigation systems may be considered, provided that they can be shown to withstand the cause of the release.

It is apparent that there is a great variety of more likely scenarios. However, the EPA requires that only one such scenario be identified and modeled. Many scenarios are effectively equivalent to a small orifice of diameter 1/4 - 1/2" (e.g., a gasket rupture or a pump seal leak). Therefore, one more likely scenario could be the release of ammonia at high-pressure receiver conditions through a 1/4" orifice. A typical rate of release would then be 0.75 kg/sec (100 lb/min) according to Bernoulli's formula (see Equation 3-1).

The scenario needs to be modeled in typical weather conditions. For many sites, Atmospheric Stability Category D with a moderate windspeed (e.g., 3 m/s) is close to average. Figure A-5 shows the predicted distance to the toxic endpoint as a function of release rate in these "average" weather conditions. For the 100 lb/min scenario, the distance to the toxic endpoint is ~ 1,000' on a rural site and ~ 450' on an urban site. If an owner or operator wishes to consider an orifice of a different size or a different pressure in the vessel, Equation (3-1) can be used to calculate the rate of release; Q is kg/s. Q can then be converted to lb/min by multiplying it first by 2.2 (kg \neg minutes). The distance to the toxic endpoint can then be estimated from Figure A-5 or from

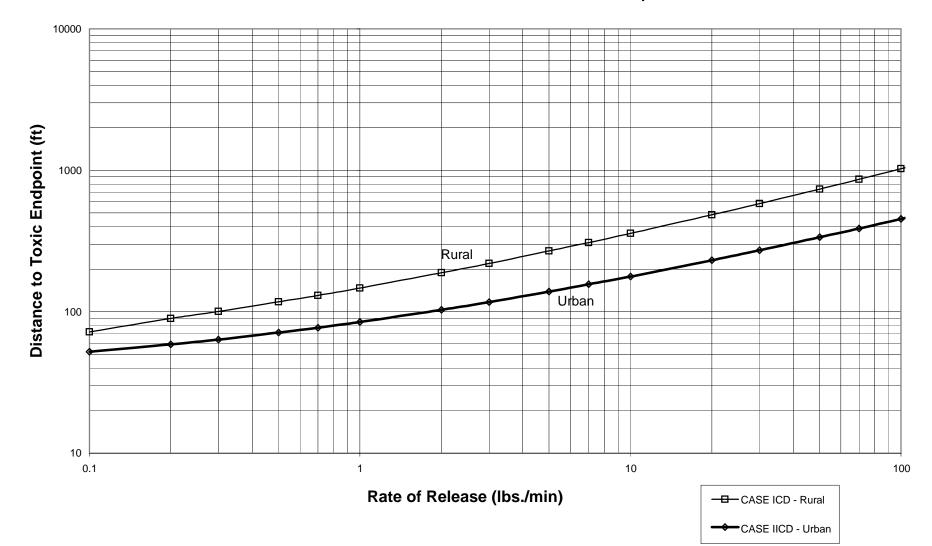


Figure A-5 - Alternative Release in Typical Weather Conditions Generic Guidance on Distance to Toxic Endpoint

Table A-1, which is a tabulation of Figure A-5. These results could simply be quoted in the Risk Management Plan.

Notwithstanding the foregoing, the owner or operator can identify his/her own alternative scenario(s). However, remember that the regulation requires that releases that are large enough to have the potential to exceed the toxic endpoint offsite shall be considered.

5.0 GENERAL GUIDANCE ON MODELING

If the owner or operator decides to perform his/her own modeling, there are two major items that are not trivial. These are:

- a. Correct characterization of the source term (e.g., rate of release, temperature, density, momentum, aerosol content, etc.)
- b. Choice of a suitable dispersion model

Unfortunately, it is not possible to cover in detail all of the issues that need to be addressed, although there are sources of useful advice. The quadrennial conferences on vapor cloud dispersion modeling that are organized by the Center for Chemical Process Safety (CCPS) are a good source of information on the latest developments in source term and dispersion modeling (CCPS, 1987, 1991, 1995). There are also CCPS Guidebooks: "Guidelines for Use of Vapor Cloud Dispersion Models" (about to be issued in a revised version); "Workbook of Test Cases for Vapor Cloud Dispersion Models"; and "Guidelines for Chemical Process Quantitative Risk Analysis".

The EPA has also published useful guidance. There is one document that looks carefully at the definition of source terms (USEPA, 1993). There is another that describes the EPA's own screening model for accidental releases of accidental chemicals TSCREEN (USEPA, 1992). The EPA has also performed an evaluation of dense gas dispersion models (USEPA, 1991). Another review of available models has been given by Hanna, et. al. (1991).

Release Rate	Predicted Distance to	Toxic Endpoint (ft.)
(lb/min)	Rural	Urban
0.1	70	50
0.2	90	60
0.3	100	65
0.5	120	70
0.7	130	80
1.0	150	85
2.0	190	100
3.0	220	120
5.0	270	140
7.0	310	160
10.0	360	180
20.0	490	230
30.0	580	270
50.0	740	340
70.0	850	400
100.0	1•020	450
150.0	1•260	540
200.0	1•970	940
300.0	2•450	1•160
500.0	3•240	1•510

Table A-1 Alternative Release in Typical Weather Conditions

17

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INTRODUCTION

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APPENDIX B

BACKGROUND INFORMATION AND DISCUSSION PAPER DEVELOPMENT OF GUIDANCE ON ATMOSPHERIC DISPERSION MODELING FOR ANHYDROUS AMMONIA REFRIGERATION FACILITIES

1.0 INTRODUCTION

Sensitivity studies were performed for developing guidance on atmospheric dispersion modeling for anhydrous refrigeration ammonia facilities, such as that given on Figure 2-1.

A plausible worst-case release for many facilities was assumed to be the accidental release of the liquid contents of a high-pressure receiver, or of pipework connected to the liquid space of the high-pressure receiver, or of a similar vessel such as an ambient temperature storage vessel. Further, it was assumed that the release takes place over 10 minutes per the requirements of §68.22 of the rule. For this scenario, SAIC's SACRUNCH model has been used. It was decided to use SACRUNCH because it does a reasonable job of making predictions that are in agreement with experimental data (e.g., the large-scale ammonia experiments known as "Desert Tortoise") and can easily be used to perform the required sensitivity studies. Further information on SACRUNCH and associated models is available upon request (SAIC, 1994). The fact that SACRUNCH was used is in no way intended to imply that EPA endorses or favors it. On the contrary, the guidance provided on, for example, Figure 2-1 and Table 2-1 of the main body of this report, can be used without reference to any atmospheric dispersion model.

However, note that the results of SACRUNCH and associated computer models have been accepted in a number of regulatory applications. These include acceptance by some Administering Agencies in California in the context of that State's Risk Management and Prevention Program. In addition, the New Jersey Department of Environmental Protection has accepted the models as suitable for use in satisfying the requirements of the New Jersey Toxic Catastrophe Prevention Act.

Distances to the 200 ppm (the ERPG-2¹) toxic endpoint for various conditions were calculated, again as required by §68.22. The results are discussed below and are illustrated with figures. The text in the legends lists the assumption for each curve. Table B-1 gives the description of each sensitivity study.

ERPGs are defined by the American Industrial ^{Hygiene Association.} ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

CASE	DESCRIPTION
I	Continuous, flashing rural release, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
ICD	Continuous, rural release over 1 hour, constant toxic endpoint, D Stability, 4 m/s windspeed, no deposition
IP	Instantaneous, flashing rural release, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
п	Continuous, flashing urban release, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
ПСD	Continuous, flashing urban release over 1 hour, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
ПР	Instantaneous, flashing urban release, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
ш	Continuous, flashing rural release, constant toxic endpoint, F Stability, 1 m/s windspeed, deposition
ШР	Instantaneous, flashing rural, release, constant toxic endpoint, F Stability, 1 m/s windspeed, deposition
IV	Continuous, flashing rural release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, no deposition
IVP	Instantaneous, flashing rural release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, no deposition
v	Continuous, flashing rural release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, deposition
VP	Instantaneous, flashing rural release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, deposition
VI	Continuous, flashing urban release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, No deposition
VIP	Instantaneous, flashing urban release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, no deposition
	Continuous, initially passive rural release, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
vш	Continuous, initially passive rural release, constant toxic endpoint, F Stability, 1 m/s windspeed, deposition
IX	Continuous, initially passive rural release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, deposition
x	Continuous, initially passive urban release, constant toxic endpoint, F Stability, 1 m/s windspeed, no deposition
XI	Continuous, initially passive urban release, time-varying toxic endpoint, F Stability, 1 m/s windspeed, no deposition

2.0 RESULTS AND SENSITIVITY STUDIES - WORST-CASE RELEASE

Figure B-1 shows the results of modeling a flashing liquid ammonia release over 10 minutes in the Category Class F Stability with a wind speed of 1.5 meter/second and an ambient temperature of 25°C (77°F). The distance to the 200 ppm toxic endpoint is plotted for different release masses.

Figure B-1 shows curves for both urban and rural areas. Note that, in SACRUNCH, in the far field, the urban and rural models asymptotically become identical to the Gaussian models in the

es, unless otherwise stated. Release duration is 10 minut

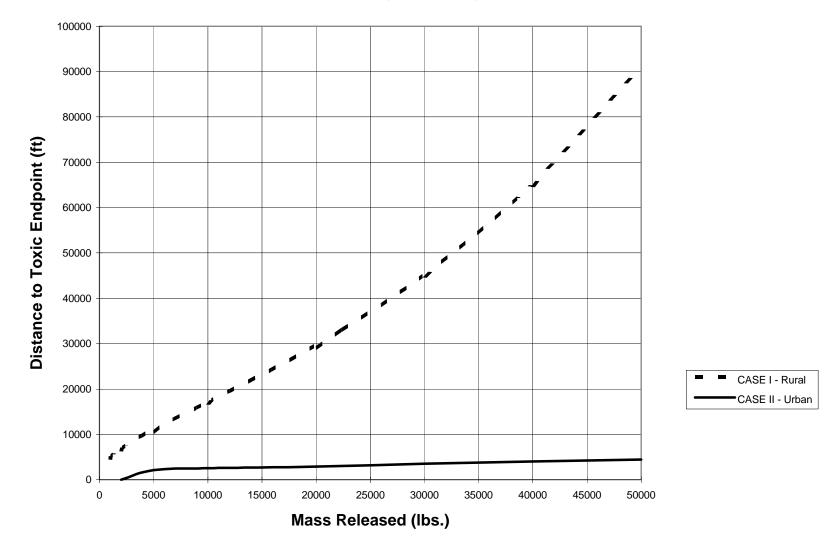


Figure B-1 - Worst-Case Ammonia Release over 10 minutes, Constant Toxic Endpoint, No Deposition

Green Book (USEPA, 1987). In an urban area, where there is additional turbulence due to buildings and heat sources, the rate of dilution of the cloud is higher than in a rural one. Thus, a given release in an urban area results in lower concentrations than in a rural area. The differences in the concentrations at a given distance downwind can be quite dramatic and span a range of an order of magnitude, as Figure B-1 demonstrates. Figure B-1 has been prepared because it is a potential candidate for use in the generic RMP as guidance for finding distances of toxic endpoints for worst-case scenarios. However, the rural case on Figure B-1 is potentially too conservative to use, as is explained in the following.

Sensitivity studies were performed by perturbing factors, such as dry deposition³ and a ^{time-}varying toxic endpoint⁴. The results are shown on Figure B-2. For convenience in comparing, the results on Figure B-1 are superimposed on Figure B-2. The assumption of deposition and/or time varying concentration in a *rural* area produces results that are similar to the results assuming an *urban* area (i.e., distances within a factor of two). Since it is quite likely that deposition will occur and that a time-varying toxic endpoint is realistic, the rural case assumption is likely too conservative for most situations.

On Figures B-1 and B-2, an assumption was made that the cloud is initially dense, as is expected for ammonia that is released as a liquid from vessels in which it is stored under pressure (Kaiser,1989: see Appendix A). Figure B-3 shows the sensitivity to the assumptions of the same factors, but for an initially passive cloud. The pattern observed on Figures B-1 and B-2, that a rural area

Constant concentration versus time-dependent concentration exposure profile - The hazard level for a given chemical is sometimes given as a constant exposure value with no regard to the duration of exposure. For instance, a 200 ppm constant endpoint value has been adopted by EPA for ammonia for the purposes of the RMP. A constant time-independent exposure value is easy to use to estimate the vulnerability zone. However, this approach may be too simplistic because it is erroneous to believe that a constant exposure concentration will have the same effect on exposed individuals regardless of exposure duration. In other words, if the exposure time is reduced (in a puff, for instance), then the concentration endpoint ought to be appropriately scaled up so as to produce the same health response. Needless to say, constant exposure values can be highly conservative, as they give no credit for short exposure duration. The discussion herein elaborates on this issue by assuming Haber's law for time-varying concentration (modified by a factor of two for short durations; details can be supplied upon request). Haber's law states that a given health effect is caused by a constant dose (USEPA, 1987).

Deposition - Deposition refers to the process by which material is removed from the cloud at the ground by means of chemical reactions, gravitational settling, etc. Deposition is often expressed in terms of an empirical deposition velocity (Hanna and Hosker, 1980). 10^{-2} meters/second is within the range that is usually accepted for reactive vapors and is the value that has been used in the present work for illustrative purposes.

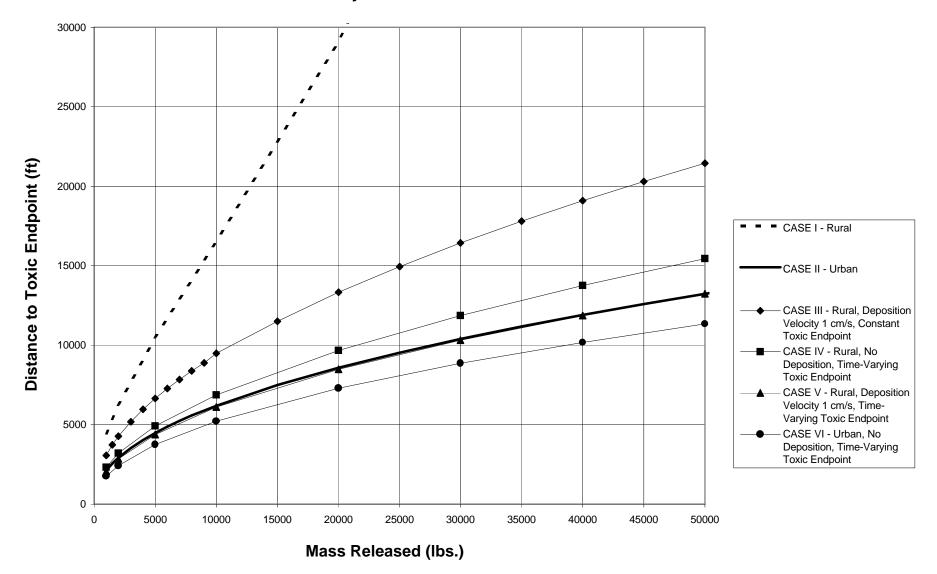


Figure B-2 - Worst-Case Ammonia Release over 10 minutes Sensitivity Studies

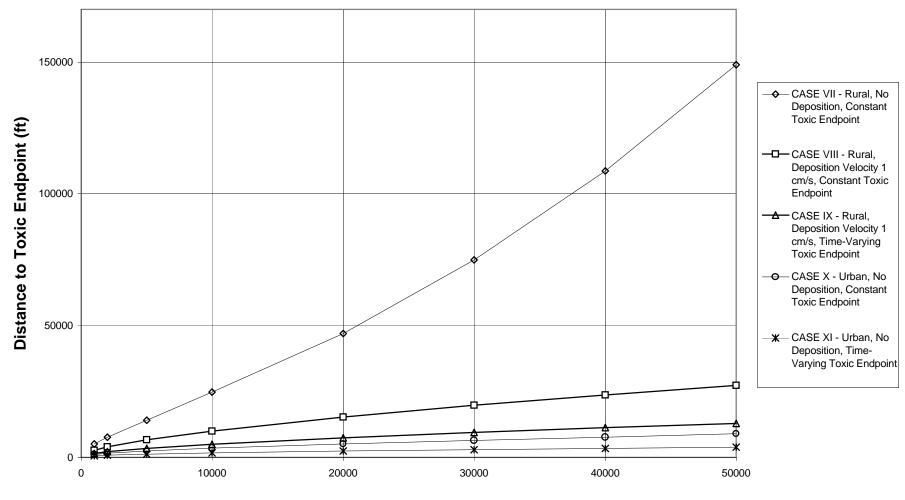


Figure B-3 - Worst-Case Ammonia Release over 10 minutes, Initially Passive Case, Sensitivity Studies

assumption with no dry deposition and constant concentration is far too conservative, is evident in this case also.

Figures B-1, B-2 and B-3 show results of continuous releases. Figure B-4, on the other hand, shows results for an instantaneous puff release. Figures B-1 and B-2 were for continuous releases of 10 minutes duration because that is what is required by the regulations. However, a puff release could be equally plausible as a worst-case release, and, in any event, a release of 10 minutes duration will evolve into a puff in the far field. Figure B-4 also makes it evident that the rural continuous model case, without any mitigating assumptions such as deposition, may be far too conservative. SAIC's SADENZ model was used for modeling instantaneous releases.

Figure B-5 gives a comparison between the continuous and instantaneous release cases for urban and rural areas. Figure B-5 confirms two points: (1) the rural case is the most conservative, and (2) the rural continuous release case is more conservative than the rural instantaneous "puff" case. The reason for the latter observation is that the puff is allowed to elongate along the wind direction in SADENZ, whereas the continuous release model is treated as a fixed-length "slug".

The overall conclusion is that, for worst-case release modeling, "unmitigated" rural modeling is far too conservative. With reasonable assumptions, the rural plots collapse until they are not too far away from urban ones. Figure B-6 has been chosen for the generic guidance (Case II and Case III from Figure B-2). It is identical to Figure 2-1 in Section 2 of the main body of this report. These cases envelope the sensitivity studies on Figure B-1 through B-5. Note that, in choosing the cases that are presented on Figure B-6, the use of judgment was required (i.e., that it is reasonable to choose guidance that envelopes reasonable sensitivity studies). Given the uncertainties in source term and atmospheric dispersion modeling, there is no means of arriving at a unique choice for the guidance. The above extensive discussion is intended to demonstrate that care and thought has been given to the preparation of Figure B-6.

3.0 ALTERNATIVE RELEASES

Smaller orifices in pipework or vessels are more likely. In such scenarios, the *rate* of release is important rather than the total *mass* released.

The "more likely" scenarios should also be modeled in "average" weather conditions. As an example, Figure B-7 shows the distance to the 200 ppm level as a function of release rate in Category D stability class and a wind speed of 3 meters/second. If deposition were included, it would not be a significant factor because in Category D, the predicted ground-level concentration is smaller than that in Category F, thus, deposition in Category D is smaller. Figure B-7 is identical to Figure A-4 in Appendix A.

4.0 CONCLUSIONS

The main observation from the above sensitivity studies is that the rural area assumption for the worst-case release is likely too conservative. An understanding of the modeling assumptions with regard to (1) rural versus urban dispersion, (2) deposition, (3) constant versus time-dependent

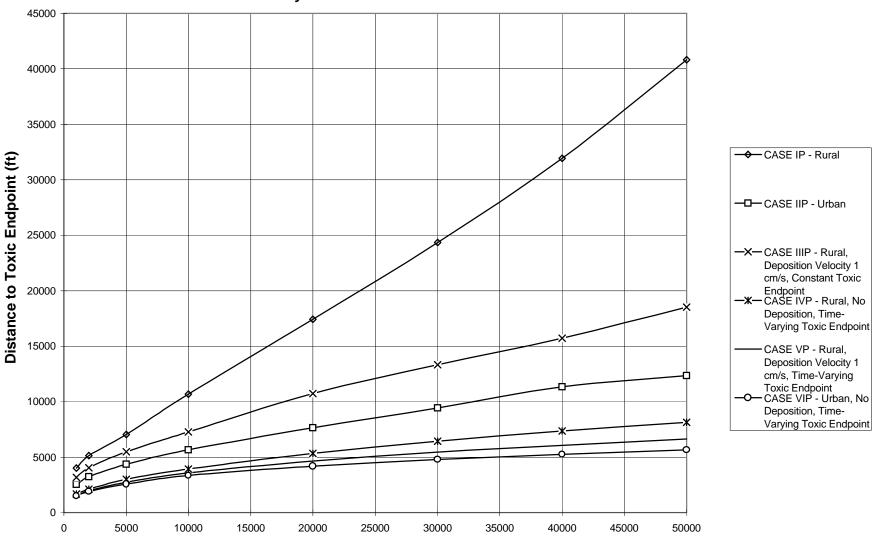


Figure B-4 - Worst-Case Instantaneous Ammonia Release Sensitivity Studies

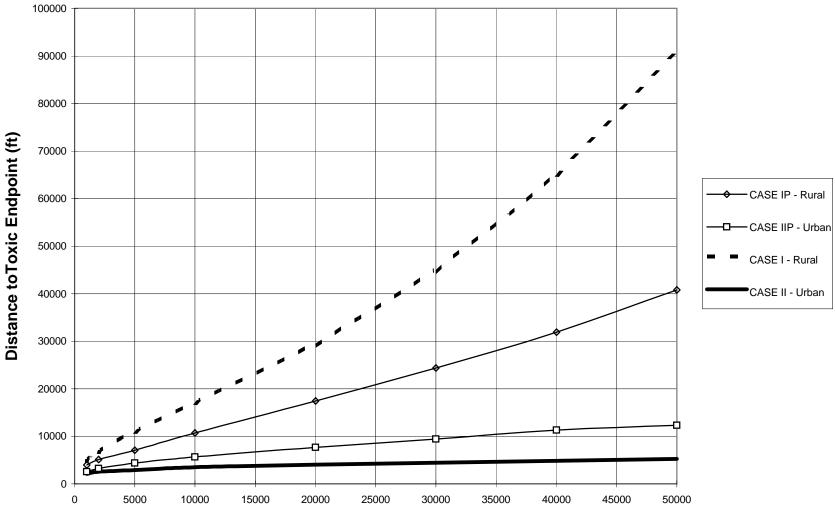


Figure B-5 - Worst-Case Ammonia Release Comparison of Instantaneous and 10-minute Cases

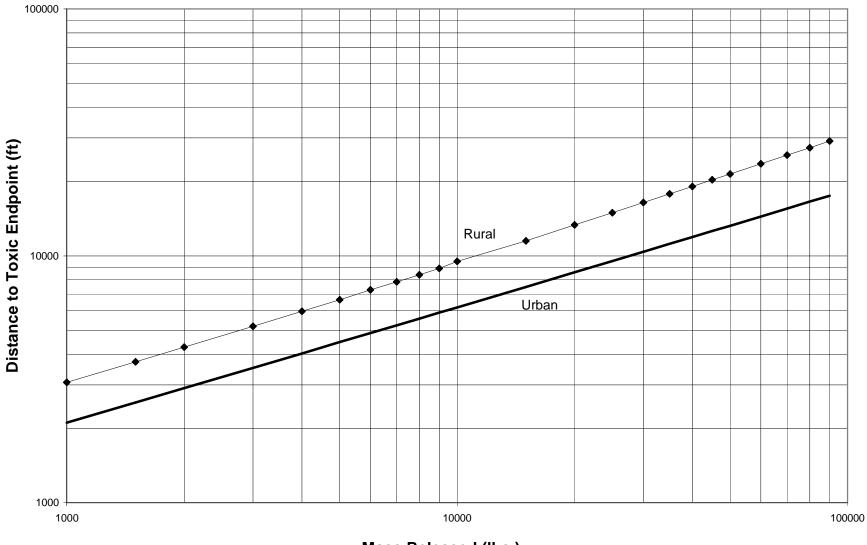


Figure B-6 - Worst-Case Ammonia Release over 10 minutes Generic Guidance on Distance to Toxic Endpoint

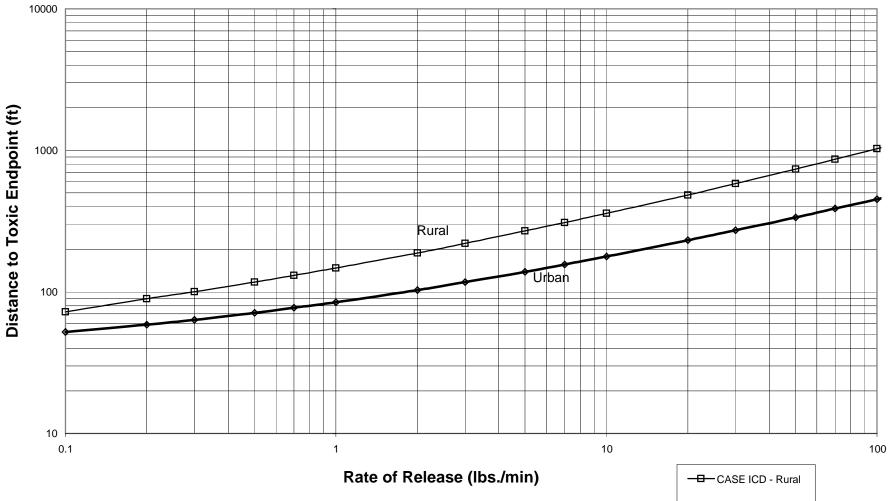


Figure B-7 - Alternative Release in Typical Weather Conditions Generic Guidance on Distance to Toxic Endpoint

CASE IICD - Urban

toxic endpoint, and (4) continuous vs. puff releases, is necessary for realistic modeling. There are other conservatisms that have been neglected, e.g., mixing in the building wake of a typical refrigeration facility and the fact that the worst-case weather condition will likely not persist while the vapor cloud travels large distances. An attempt has been made to take these issues into account in providing guidance for the atmospheric dispersion modeling for anhydrous ammonia facilities (see Figure B-6).

5.0 **RESPONSES TO COMMENTS**

5.1 Use of SACRUNCH and Associated Models

Some reviewers expressed concern that the hazard assessment guidance has been developed using proprietary models (SAIC, 1994). As noted above, these were adopted for ease and convenience in the performance of sensitivity studies; the final product (the guidance in Chapter 2 of the main body of the report) can and should be used without reference to any model. In addition, the "General Guidance on Modeling" in Section 5.0 of Appendix A gives reference to a whole host of other models that can be used. Therefore, this guidance does not imply any bias towards any particular model.

In order to further address this concern, the International Institute of Ammonia Refrigeration (IIAR) sponsored independent analyses, one with DEGADIS and one with ALOHA.

5.1.1 DEGADIS

IIAR's consultant performed a number of DEGADIS (USEPA, 1989) analyses of the consequences of the release of 5,000 pounds of anhydrous ammonia over a period of 10 minutes in worst-case weather conditions. The results of these studies, and the input assumptions, were carefully reviewed with IIAR's consultant, who eventually concluded that he could reproduce the generic guidance to within 5 to 10%, and that the assumptions made in developing the guidance are reasonable.

5.1.2 ALOHA

Another of IIAR's consultants used ALOHA (NOAA, 1995). A comparison between the generic guidance and ALOHA is shown on Figure B-8 for the worst-case scenarios. For the rural case, ALOHA is almost identical to the generic guidance. This good agreement is purely fortuitous. For the urban case, the ALOHA results lie about 30% below the generic guidance. Within the uncertainties expected in atmospheric dispersion modeling, these results are quite close.

IIAR's consultant also looked at the guidance for alternative scenarios (see Figure B-8). His ALOHA predictions are higher than the generic guidance for both the urban and rural cases.

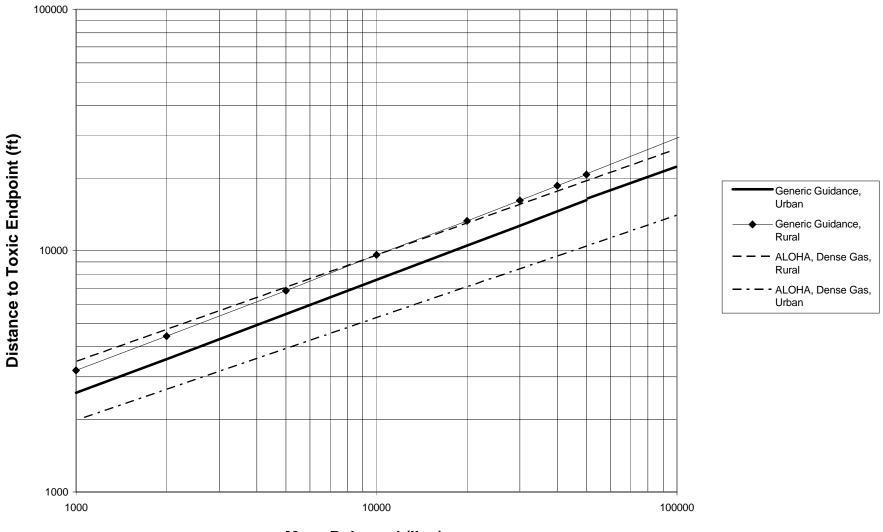


Figure B-8 - Worst-Case Ammonia Release over 10 minutes Comparison of Generic Guidance with ALOHA Model

5.1.3 Conclusion

Limited comparisons with other models do not reveal either great conservations or concerns about underprediction.

5.2 <u>Comparison with Lookup Tables</u>

In other documentation, EPA has produced generic lookup tables (USEPA, 1996). Figure B-9 compares the generic worst-case release scenario guidance with the lookup table guidance for dense gases. As can be seen (and as several reviewers have pointed out), the lookup table guidance gives greater distances (by factors of 1.5 to about 2 at a given mass). The computer model SLAB was used for the lookup tables. There are some reasons why the lookup tables might be expected to differ from the generic ammonia guidance:

The generic ammonia guidance was developed using a model that is specifically able to take account of the initial aerosolization of ammonia as it is released from a pressurized vessel. For the lookup tables, SLAB was run as a generic heavy vapor model.

Ammonia is highly reactive. Therefore, relatively high dry deposition velocities and relatively rapid depletion of the plume it travels downwind is to be expected. On this basis, lower predicted distances to the toxic endpoint are plausible for ammonia.

The structure of the lookup tables is such that toxic endpoints cannot be exactly matched. The toxic endpoint for ammonia is 0.14 mg/L; the closest available value in the lookup tables is 0.1 mg/L, leading to some overprediction in the lookup tables.

Figure B-10 compares the generic guidance for altherative scearios with that from the lookup tables. As for the worst-case, the lookup table guidance is somewhat higher.

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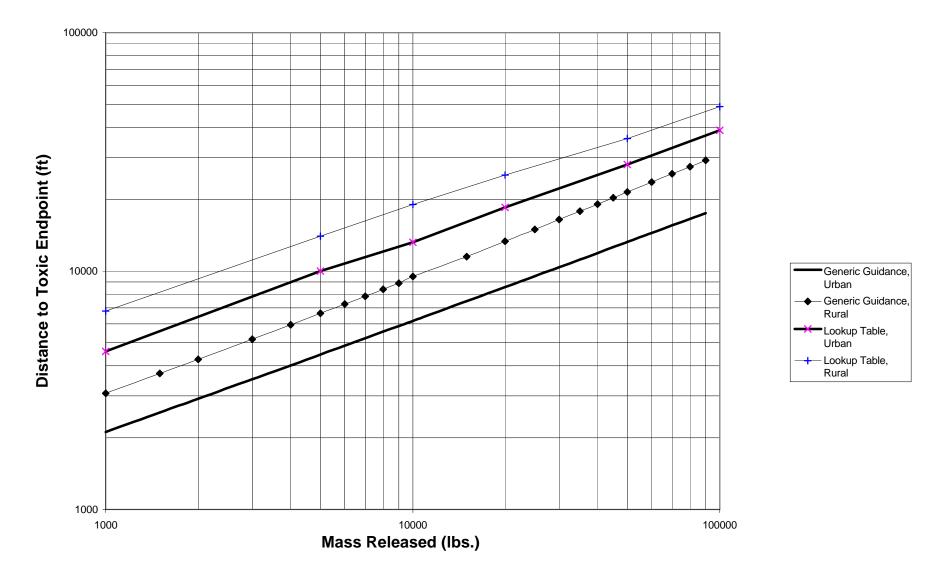


Figure B-9 - Worst-Case Ammonia Release over 10 minutes Comparison with Lookup Tables

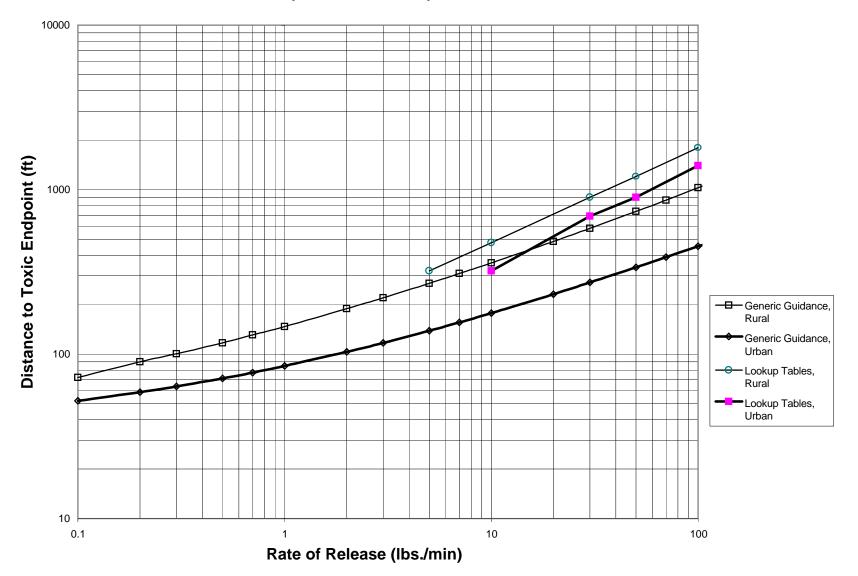


Figure B-10 - Alternative Release in Typical Weather Conditions Comparison with Lookup Tables

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APPENDIX C

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APPENDIX C

EFFECT OF AMMONIA RELEASES ON STRUCTURES

The purpose of this appendix is to discuss the consequences of releases inside rooms, such as the compressor room. In Appendix A, Section 2.4, it was stated that "it is not easy to show that a typical building that houses compressors and vessels will effectively contain and mitigate a release of ammonia if the worst-case scenario occurs inside. Appendix C shows that, for many building configurations, the sudden loss of the contents of a high-pressure receiver (for example) would generate pressures that could not be withstood by a typical cinder block or unreinforced concrete structure".

This Appendix provides technical justification for the above statement. In addition, methods for prediction of pressures inside buildings and the rate of release to the atmosphere for prolonged releases are discussed. Important parameters include the quantity of ammonia available for release, the volume of the room, the presence of airborne liquid droplets, leakpaths in the structure and the characteristics of the ventilation system.

1.0 SUDDEN RELEASES

Worst-case scenarios for ammonia releases include catastrophic failure of storage tanks or receivers containing liquid ammonia under pressure. The presence of containment buildings will play a role in defining the conditions under which a release occurs and in controlling the rate at which ammonia is released to the atmosphere. In the case of sudden releases, forced ventilation or leakpath flow are likely to be ineffective in mitigating the initial pressure pulse, and the structure serves to enforce a constant volume constraint on the conditions of the initial release. Sudden releases occurring indoors may involve expansion of pure ammonia to pressures above atmospheric pressure and/or reduction of pressure following the mixing of ammonia and air and the subsequent evaporation cooling process. If the estimated pressure differential exceeds the design capacity of the confining structure, the structure could fail and release ammonia directly to the atmosphere.

In order to develop a conservative representation of potential conditions, sudden releases inside buildings are represented as occurring in two steps--an expansion of pure ammonia and compression of room air in the first step and mixing of ammonia with room air in the second step. This conceptual approach is similar to that applied for investigation of the release of chlorine into building containments (Brighton 1989). In the present analysis, the quantity of ammonia evaporated in the first step and the temperatures and pressures of both the ammonia and air at the end of the first step can be calculated as follows. The fraction of ammonia evaporated in the first step is estimated from an energy balance:

where:

$$\mathbf{Y}_{1} = [\mathbf{C}_{\text{pl,nh3}}(\mathbf{T}_{0,\text{nh3}} - \mathbf{T}_{1,\text{nh3}})]/\lambda_{\text{nh3}}$$
(1-1)

\mathbf{Y}_1	=	mass fraction of ammonia vapor at the end of the first step
C _{pl,nh3}	=	heat capacity of liquid ammonia, kJ/kg/K
	=	temperature of stored ammonia, K
	=	ammonia temperature at the end of the first step, K
	=	heat of vaporization of ammonia, kJ/kg

The temperature, pressure, and density of ammonia at the end of the first step are related by the vapor/liquid equilibrium constraint:

where:

$$P_{1,nh3} = F_{sat}(T_{1,nh3})$$
 (1-2)

$$P_{1,nh3}$$
 = equilibrium partial pressure of ammonia at temperature $T_{1,nh3}$, Pa
 F_{sat} = equilibrium relation between pressure and temperature for ammonia

 $T_{\rm 1,nh3}$ is defined as above, and the vapor/liquid equilibrium relationship is available in tabular form (ASHRAE 1981) .

The volume occupied by the ammonia at the end of the first step is estimated from the mass fraction evaporated and the ammonia vapor and liquid densities at equilibrium conditions. The volume occupied by air at the end of the first step is estimated by the difference between the specified total room volume and the calculated ammonia volume. The pressure and temperature of the air at the end of the first step may then be estimated assuming isentropic compression:

$$\mathbf{P}_{1,\text{air}} = \mathbf{P}_{0,\text{air}}(\boldsymbol{\phi}/\mathbf{V}_{1,\text{air}})\boldsymbol{\gamma}$$
(1-3)

$$T_{1,air} = T_{0,air} (101,325/P_{1,air})^{(\gamma - 1)/\gamma}$$
(1-4)

where:

$P_{1,air}$	=	absolute air pressure at the end of the first step, Pa
$P_{0,air}$	=	absolute air pressure prior to vessel failure, Pa
	=	room volume per unit mass of stored ammonia, m ³ /kg
$V_{1,air}$	=	air volume at end of first step per unit mass of stored ammonia, m ³ /kg
γ	=	ratio of constant pressure to constant volume heat capacities for air, dim
T _{1,air}	=	air temperature at the end of the first step, K
T _{0,air}	=	air temperature prior to vessel failure, K

The unknown mass fraction of ammonia evaporated and the ammonia and air temperatures and pressures are calculated from the above four equations and the constraint of equal ammonia and air pressures at the end of the first step.

Following the initial ammonia expansion/air compression, the gases mix at constant pressure and additional evaporation and associated reduction in temperature occurs. An energy balance for this process may be expressed as:

$$\begin{array}{ll} (Y_{2}[C_{pv,nh3}(T_{2}\text{-}T_{r})+\lambda_{nh3}]+(1\text{-}Y_{2})C_{pl,nh3}(T_{2}\text{-}T_{r})+\\ \varphi C_{p,air}(T_{2}\text{-}T_{r})\} & - (Y_{1}[C_{pv,nh3}(T_{1}\text{-}T_{r})+\lambda_{nh3}]+\\ (1\text{-}Y_{1})C_{pl,nh3}(T_{1}\text{-}T_{r})+\varphi C_{p,air}(T_{1}\text{-}T_{r})\} & = \varphi(P_{2}\text{-}P_{1}) \end{array}$$
(1-5)

where:

\mathbf{Y}_2	=	mass ratio of ammonia vapor to total ammonia at end of step 2, dim
C _{pv,nh3}	=	heat capacity of ammonia vapor at constant pressure, kJ/kg/K
$C_{p,air}$		heat capacity of air at constant pressure, kJ/kg/K
-	=	mixture temperature at end of step 2, K
P ₂	=	mixture absolute pressure at end of step 2, Pa
T _r	=	reference temperature, K

and all other variables are as defined above. The pressures appearing in this equation can be eliminated in favor of temperatures using the ideal gas law applied to both ammonia and air. In this form the equation can be solved directly for final temperature (T_2) if all the ammonia is evaporated in the mixing process. If some ammonia remains in the liquid state, the energy balance is solved simultaneously with the vapor/liquid equilibrium relation to determine the conditions at the end of the mixing process.

Potential conditions which could be encountered were established for sudden failure of a tank of liquid ammonia for the expected range of the ratio of room volume to stored ammonia mass (ϕ). Initial ammonia conditions were a temperature of 310 K (98°F) and a pressure of 1.4 MPa (206 psia). Final conditions predicted for the expansion/compression $(Y_1, T_1 \text{ and } P_1 \text{ for step } 1)$ and mixing processes (Y_2, Y_2) T_2 , and P_2 for step 2) are presented on Table C-1. For rooms at the lower end of the range of expected volumes (i.e., 500 m³), ammonia inventories analyzed ranged from 10 to 1,000 kg. For rooms at the upper end of the expected range (i.e., 10,000 m³), ammonia inventories analyzed ranged from 200 to 20,000 kg. The results indicate that under many circumstances, either the step 1 overpressure or the step 2 underpressure would cause significant damage or failure of most structures. Only at the largest room volume to ammonia mass ratios are predicted pressure deviations small enough to support the position that the building would contain the release. This conclusion is based on adoption of an over/underpressure failure criterion of 6,895 Pa (1 psia). Shattering of concrete or cinder block walls is reported for explosion overpressures on the order of 13,900 Pa (2 psia) (Lees, 1980, p. 594). Because resistance of structures to forces decreases with an increase of duration of application, the failure threshold for the predicted ammonia release over/underpressures is approximately a factor of 2 less than that expected for explosion effects (Lees 1980, p. 579). Effects of explosions, such as shattering of small windows at overpressured 700 Pa (0.1 psia) and large windows at overpressured 3,500 Pa (0.5 psia) (Lees, 1980, p. 579) are also expected for ammonia release events.

Table C-1

	<u>Step 1:</u>	Expansion	/Compression		Step 2	: Mixing
		P ₁ *			P ₁ *	
φ	T_1	(Mpa)	\mathbf{Y}_1	T_1	(Mpa)	\mathbf{Y}_{1}
$(\underline{m}^{3}/\underline{kg})$	<u>(K)</u>	[psig]	<u>(dim.)</u>	<u>(K)</u>	[psig]	<u>(dim.)</u>
0.5	250	0.165	0.205	232	0.145	0.304
		[9.24]			[7.34]	
1.0	246	0.137	0.218	223	0.113	0.364
		[5.17]			[1.69]	
2.0	244	0.124	0.225	215	0.094	0.456
		[3.29]			[-1.06]	
5.0	241	0.109	.0234	208	0.082	0.687
		[1.11]			[-2.80]	
10.0	241	0.105	0.237	203	0.076	1.0
		[0.53]			[-3.67]	
20.0	240	0.103	0.238	252	0.088	1.0
		[0.24]			[-1.93]	
50.0	240	0.102	0.239	285	0.096	1.0
		[0.10]			[-0.77]	

Predicted Conditions for Sudden Releases of Ammonia Inside Buildings

* Negative values of gauge pressure indicate subatmospheric or vacuum pressure condition.

2.0 PROLONGED RELEASES

Gradual releases of ammonia may not be capable of producing the pressure differentials predicted for instantaneous releases. Over periods on the order of 10 minutes, ammonia may escape through leakpath and ventilation system flowpaths at rates large enough to relieve the initial pressure disturbance. The potential magnitude of this behavior was investigated for a leakpath flow which would produce a room change-over rate of one-half volumes per hour at undisturbed flow conditions. This assumption does not preclude the possibility that there may be significantly different change-over rates to be investigated on a case-by-case basis. The approach applied was to estimate leakpath resistance factors for representative conditions and use these resistance factor estimates to evaluate the building pressure response to a specified rate of ammonia release from a vessel inside the building.

Wind flowing directly towards the long side of a building produces an over-pressure on the upwind face and under-pressures on the side- and down-wind faces. For a given windspeed, the pressure differential may be estimated using correlations based on experimental data (Blevins, 1984). The pressure differential may then be used in conjunction with the assumed normal condition leakage rate to estimate resistances for the in- and out-leakage paths. This leakage resistance calibration procedure also assumed that the cross-sectional area of each leakpath was proportional to the length of the building, and that building length was twice building width. Leakpath resistance factors estimated in this manner were used in a ventilation system accident analysis computer model to evaluate room temperature, pressure and leakage flows for given mass injection rates. The computer code used for this analysis, FIRAC (Gregory and Nichols, 1986), is a node/branch network model in which nodes represent rooms and branches represent ducts, blowers and filters. In this case, leakpaths were modeled as ducts of small size, and the ammonia release was represented as mass injection with associated evaporative energy loss.

Potential conditions which could be established were investigated for a 10-minute release of liquid ammonia stored at 310 K (98°F) and 1.4 MPa (206 psia). The simulation estimated the ammonia injection rate required to produce an overpressure large enough to threaten structural integrity. An overpressure value of 6,895 Pa (1 psia) was adopted for this criterion. Release modeling predicted immediate evaporation of approximately 20% of the ammonia flow with subsequent evaporation of the remaining mass. High-accident condition leakpath flows were predicted for room volumes from 500 to 10,000 m³ with 6,710 kg/10 min (14,790 lb/10 min) required to produce the 6,895 Pa (1 psia) overpressure for the 500 m³ room. Very large release rates were required to approach the overpressure criterion for rooms in the 1,000 to 10,000 m³ range.

3.0 SUMMARY OF CONCLUSIONS

Worst-case releases of ammonia inside buildings could occur as sudden releases in which case analysis of the expected range of building volumes (500 to 10,000 m³) and ammonia inventories (10 to 20,000 kg) indicated that failure of the confining structure would be likely.

For prolonged releases, such as might be typical of an alternative scenario, analysis indicated that leakpaths that could produce a room air change-over of one-half volume per hour would effectively vent ammonia releases for rooms with volumes greater than 1,000 m³. Thus, prolonged releases from

the building would be modeled as transient releases at rates less than or equal to the estimated equipment release rate. That is, it is reasonable to take credit for the mitigating effects of the structure for "more likely" scenarios.

4.0 COMMENTS

Some comments were received on earlier drafts of this Appendix. There seems to be general concurrence that one cannot automatically assume that a building would effectively mitigate the consequences of a worst-case scenario. Some of the comments that are representative of the concerns raised are reviewed below.

Comment

Release of an entire storage inventory with complete vaporization and heating to 77°F within 10 minutes is an impossible case.

Response

Here, the 77°F (25°C) arises because, in the generic lookup table guidance, the ambient temperature is assumed to be 25°C. This concern appears to arise because the commenter is thinking of the spillage of large quantities of ammonia refrigerated at its atmospheric boiling point. If such spillages were to occur into a diked area, the rate of evaporation would be slow. It is important to realize that the scenarios considered in the present case are quite different, consisting as they do of instantaneous tank failures and breakage of pipes of diameter 1" or more connected to tanks at pressures of up to 200 psig. In either case, standard momentum/energy release analysis indicates that the major portion of the contents of a tank as large as 10 tons could be released within 10 minutes (see also Section 3 of Appendix A). The physical state of the released material is established by energy balance supported by experimental data. For both the instantaneous and pipe releases, the vapor fraction was estimated for isenthalpic expansion conditions. As indicated by the results presented in Appendix C and the discussion of Appendix A, the initial ammonia vapor fraction ranges from 20 to 25 weight percent. As also described in Appendix A, experimental observations indicate conclusively that the liquid fraction remains entrained in the cloud as small droplets. Subsequent entrainment of air into the cloud results in vaporization of the liquid ammonia with an associated decrease in temperature. Experimental observations indicate that substantial amounts of air may be entrained into the cloud near the point of release, but, independent of the location and rate of entrainment, expected conditions are, for the major portion of the initial release, to remain airborne in the form of a dense cloud with temperature significantly less than 77°F (e.g., at or near the atmospheric boiling point of ammonia). Note that there are several instances of instantaneous or nearly instantaneous releases of several tens of tons of ammonia from vessels that failed catastrophically, with the whole contents becoming/remaining airborne virtually at once (Kaiser, 1979; McMullen, 1976; Lousdale, 1975; NTSB, 1971; NTSB, 1978).

Comment

The confined space ammonia release estimates need to reconsider the role of blast, confined space pressurization and potential for retention. The use of the work of Goldwire is inappropriate to justify a blast effect. The EPA has assumed that blast will occur for all pressurized conditions in this guidance document. Liquid depressurization is unlikely to drive isentropic compression of the room air.

Response

The evaluations and conclusions presented in Appendix C for instantaneous and 10-minute releases do not assume and are not dependent upon occurrence of superheated liquid or boiling liquid expanding vapor explosions. Shock waves occurring as a result of the sudden failure of an ammonia vessel would be in addition to the phenomena described in this Appendix,namely overpressurization due to the initial rapid expansion of ammonia. Section 2.4 of Appendix A states that the duration of the excess pressure in such a case will be much greater than that of a shock wave. Visualization of the initial vaporization and expansion as slower than a blast does not imply that it would be no faster than the mixing and secondary vaporization processes. Experimental observations indicate that an initial concentrated cloud is formed on sudden releases. Some overpressurization due to the constant volume constraint of the room is likely to occur prior to vaporization of the entrained liquid ammonia. The reference to the work of Goldwire in Appendix A supports the initial entrainment aspect of cloud formation and does not refer to blast effects.

Even if the intermediate state overpressurization were not to occur, over and underpressurization predicted for the final state (i.e., Step 2) indicate that failure of windows, openings, or panels would likely occur for all room volume-to-ammonia mass ratios, with the exception of a narrow band near room volume-to-ammonia mass ratio of 1.4. This statement is based on constant volume isenthalpic flash and isenthalpic mixing and vaporization modeling as described here in Appendix C.

5.0 **REFERENCES**

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APPENDIX D

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APPENDIX D

LIST OF TABLES

<u>Table</u>		Page
D-1	Summary of Information on Ammonia from ARIP Data Base	D-2

ARIP No.	Event	Operation	Root Cause	Process	Remarks
	Valve disassembled	Maintenance	Contractor selection	Public CS	Error in installing a new accumulator
1770			E/R training	lce cream	Equipment upgrade stated
2579			E/R training	Food production	Sched 40 thd pipe used instead of welded sch 80
			E/R training	Poultry processing	Procedure produced untenable thermal shock
1281	Flange blew out	In operation	M.I. fit for purpose	Citrus concentrate	Cast iron flange
2850	2850 Condenser leak	Maintenance	M.I. inspection	Milk	Corrosion; new unit on order at the time
1078	1078 Heat exch. leak	In operation	M.I. Inspection	Ice Mfg	lce machine tube failure
1080	1080 Valve failure	In operation	M.I. Inspection	Meat Process	No explanation
1338	1338 Pipe joint failure	In operation	M.I. inspection	Milk & ice cream	Fatigue failure on vibration
1901	Valve separation	In operation	M.I. inspection	Food processing	Corrective actions inspection and maintenance
4140	4140 Gasket leak	In operation	M.I. inspection	6	Gasket leak on compressor; shut off valve failed to close
4209	4209 Recip shaft seal	In operation	M.I. inspection	Frozen fish	Main brg failure - broken crank
3320	3320 PRV opens	Maintenance	M.I. inspection	Ge	In pressure test to less than stated relief pressure; opened at lower pressure
1394	1394 Pipe break	Sched shutdown	M.I. inspection	lce cream	Equipment upgrade stated
834	834 Pipe broke	Temp inactive	M.I. Inspection	Turkey Prod	None given; Corr Actions were Inspections; RC inferred
2320	2320 Tube rupture	Temp inactive	M.I. inspection	Frozen juices	Condenser replaced with new design
4269	4269 PRV opens	Temp shutdown	M.I. inspection	Ground beef	Data missing
2456	-		M.I. inspection	Public CS	Solenoid valve fails to close
1770	1770 Tube rupture	In operation	M.I. inspection (Inf)	B	Inspection called out
2202	2202 Valve leak	Sched shutdown	M.I. inspection (Inf)	Frozen desserts	Corrective actions PM. inspection and test
2825	2825 Valve came apart	In operation	M I procedures	Poultry processing	Procedure produced untenable thermal shock
2222	2227 DRV onens	Maintenance	M I procedures	Poultry	Equipment not tied into central controller: restarted improverly after maintenance
VCV	101 Sight glass laak	Waakand shirtdown	M I procedures	Salisada Mfo	Equipriment not used into contrain controlleri, restanced impropenty arter manifection of Contractor left compressor under off
1424	Dipo brook			Cood production	Contractor reit contripressor water on Cohod 40 thd airso troad instand of triadand ash 00
2420	2450 Pipe break				Scried 40 this pipe used instead of weiged scripto
4252	4252 Pump casing worn	Maintenance		Distribution whse	Pumps replaced with a "more reliable design"
1879	1879 Strainer casting	In operation	M.I. QC (Inf)	Meat processing	Strainer casting failure; changed design
799	799 PRV opens	In operation	M.I. test	Public C.S.	Ice buildup; fan destroyed; high-pressure cutout fails
2332	2332 PRV failure	In operation	M.I. test	Citrus juices	RV neither tested nor replaced
2340	2340 PRV opens	In operation	M.I. test	Public CS	Solenoid valve fails to close
1098	1098 PRV opens	In operation	M.I. test	Cheese	R.V. set pressure less than high-pressure trip; would not reseat
1878			M.I. test	ee ee	Inspection called out
1878	1878 Unit failure	In operation	PHA	Meat processing	Improved control at PLC called out
2579	2579 Pipe cap blown off	In operation	PHA	Poultry processing	Procedure produced untenable thermal shock
2907	2907 PRV opens	In operation	PHA	Public CS	Not stated; vent re-routed to accumulator
3218	PRV opens	Normal startup	PHA	Cheese	Failed to start water pump on startup
453				Sausage Mfg	Contractor left compressor water off
1098				Cheese	R.V. set pressure less than high-pressure trip; would not reseat
2227			PHA	Poultry	Equipment not tied in to central controller; restarted improperly after maintenance
3263	Pipe break, forklift	In operation	PHA (siting)	Meat packing	Exposed piping - to be re-routed
3539	3539 Piping damage	In operation	PHA (siting)	Beer	Damaged ammonia piping; PHA called out as corrective action
453			Procedures	Sausage Mfg	Contractor left compressor water off.
1106			Procedures	Cheese	R.V. set pressure less than high-pressure trip; would not reseat
3218			Procedures	Cheese	Failed to start water pump on startup
1106	1106 Open line	construction	PSSR	Public C.S.	New construction; valve left uncapped at startup
3090	3090 Valve left open	Startup new equip	PSSR	Meat products	No check for proper installation prior to startup
4170	4170 Not legible	Startup new equip	PSSR	Not legible	Details illegible
3538	3538 Valve left open	Maintenance	SWP	Beer	Valve left open during maintenance
453	453 Flex Joint break	Temp inactive	Training	Veg mfg	Trapped liquid; operator error; design fault