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Technical Paper #7

Estimating Refrigerant Release Quantities

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Abstract

End users are continuing to make strides toward increasing refrigeration system safety. Programs such as OSHA's Process Safety Management (PSM) standard and EPA's Risk Management Program (RMP) have provided a framework for end users to drive continuous improvement in plant refrigeration system safety. Nevertheless, incidents and accidents involving the unintended and uncontrolled loss of refrigerant from pressure-containing parts of a system can and do occur. In this paper, we review techniques suitable for use in estimating the quantity of refrigerant lost as a result of a leak. First principles models are presented for vapor-only, liquid-only, and flashing liquid leak scenarios. Qualitative indications as to what constitutes a reportable quantity of ammonia lost during an incident are also provided. The paper concludes by providing a number of examples of leak quantity estimates for various leak scenarios.

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Introduction

Occasionally, plants will have incidents that result in the unintended release of anhydrous ammonia from their industrial refrigeration systems. When a release does occur, there is usually a need to estimate the quantity of refrigerant lost from the system. This need to estimate the quantity of refrigerant loss ranges from regulatory reporting requirements to determining whether or not additional refrigerant should be purchased. In this section, we discuss some of the regulatory framework in the U.S. that underpins the need for leak estimates, provide comparative information on reportable release quantities, and present a review of the literature as it relates to leak quantity estimation.

Regulatory Requirements

In 1986, the U.S. enacted the Emergency Planning and Community Right-to-Know Act (EPCRA) establishing requirements for Federal, State, and local governments for reporting of hazardous and toxic chemicals with the overarching intent of improving chemical safety and protecting the health of the public and the environment. The regulation requires any facility using or storing more than the threshold quantity (which is 500 lb (227 kg) for ammonia) on-site to notify their Local Emergency Planning Commission (LEPC) and State Emergency Response Commission (SERC) within 60 days of its first use or storage. In addition, these facilities must *immediately* notify the LEPC and SERC if there is a release equal to or greater than the reportable quantity of the hazardous substance (100 lb (45 kg) for ammonia).

Also in 1986, the U.S. amended the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) with the intent of better managing hazardous materials — including hazardous waste streams. Among other provisions, CERCLA requires that facilities accidentally releasing quantities of hazardous substances in excess of the reportable amount notify the National Response Center (NRC) immediately. The NRC is a Coast Guard-operated single point of contact for reporting incidents involving hazardous materials. Since the NRC does not notify the LEPC or the SERC, these bodies must be separately notified by the end user. Finally, there are likely other state, county, and local jurisdictional reporting requirements that apply in situations of accidental releases of hazardous chemicals.

These and other regulations require end users of industrial ammonia refrigeration systems to make quick determinations as to whether an accidental release of ammonia is likely to exceed 100 lb (45 kg) prior to initiating the above-mentioned notifications. In addition, end users will have to develop a more refined estimate of the total quantity lost following successful mitigation. In this paper, we review the literature seeking those methods suitable for release quantity estimation, we present basic methods to help aid in quickly determining if a release is likely to exceed the reportable quantity, and we provide the technical basis for more formal release quantity calculation.

Literature Review

Much of the literature in the area of leak rate estimates has grown out of research in the nuclear industry and safety concerns from high pressure and high temperature water escaping through breaks or cracks in piping and equipment. One study investigated the two-phase mass flow rate through cracks in walls of nuclear or chemical plant equipment under "leak-before-break" incident scenarios (John, et al, 1988). The authors of this paper compare the predictive performance of four separate models with experimental data using subcooled water up to 15 MPa (2175 psig) in rectangular slit leak area openings ranging from 20–51.2 mm^2 (0.03-0.08 in^2). The authors modified a previously published homogeneous equilibrium model to include a friction coefficient which improved leak estimates to within 20%.

Another report provides guidelines for estimating mass flux rates for subcooled and saturated volatile liquids under both non-equilibrium and equilibrium conditions for accidental breaks in vessels or piping and relief devices (Fauske, 1985). This study compares the model results with data for water, R-11, and R-12 refrigerants. Because this model for flashing flow compares well with measured data and it is relatively simple, we recommend its use in this paper for release estimation in ammonia refrigeration applications.

Another paper reviews several models for estimating leak rates through small slit-shaped cracks (Friedel and Westphal, 1990). The authors emphasize the volume of literature that investigates single and two-phase flow in leaks with water/air and water/steam but point out that extension of these models to other chemical systems is problematic due to fluid property differences. The models reviewed are more complex than the Fauske model without an appreciable increase in accuracy.

One study provides guidelines for estimating ammonia releases based on equations included in the 1993 edition of the Dow Chemical Company "Chemical Exposure Index Guide" (Richards, 1995). The refrigerant release estimates using this approach tend to over-predict the quantity lost in saturated liquid leaks because effects of choking are ignored. Richards also presents a simplified approach for estimating the release quantity through a pressure relief device based on its capacity, set pressure, and blowdown.

In 1999, the USEPA published a guidance document on offsite consequence analysis for owners with covered processes. Although it is primarily focused on the atmospheric dispersion of chemicals following a release, it does include some information on leak rate estimation. The technical source for the release rate estimating methods in the EPA document originated in FEMA's *Handbook of Chemical Hazard Analysis Procedures* (1993). Within this document, estimates for gas leak rates (choked and non-choked) are presented but unlike the approach proposed here, they do not take into account dynamic losses through upstream components or the leak opening. Flashing liquid flow rate estimates in the EPA/FEMA document are based on Fauske (1985).

With possibly the exception of the EPA guidance document on off-site consequence analysis, none of these papers provide a comprehensive look at refrigerant release estimates using models that are both approachable and reasonably accurate. This paper aims to provide basic guidance that allows end users to quickly assess a given situation in order to determine the likelihood that a specific incident will exceed the reportable quantity threshold. In addition, we present models that are suitable for estimating the release rates of vapor, saturated liquid, and subcooled liquid ammonia.

Reportable Quantity – How much is 100 lb (45 kg) of ammonia?

Any accidental release of ammonia that is anticipated to exceed 100 lb (45 kg) requires immediate notification to the appropriate regulatory agencies as previously discussed. One difficulty plant personnel have is recognizing what constitutes a 100 lb (45 kg) release. To overcome this difficulty, we begin by reviewing the basic properties of ammonia in liquid and vapor states followed by some basic comparisons to enable personnel to gauge the extent of a release in order to more confidently judge whether an incident is expected to involve a reportable quantity.

When pressurized liquid ammonia is released from a system, a mixture of liquid and flash gas will result whenever the temperature of the upstream liquid is warmer than the saturation temperature corresponding to the local atmospheric pressure, which is –28°F (–33°C) at sea level. If the temperature of the upstream liquid is colder than the saturation temperature for the local atmospheric pressure, no flash vapor is formed and the refrigerant will remain in its liquid state as it flows through the leak opening, entering the atmosphere until it has absorbed enough heat from the surroundings to raise its temperature to saturation. Additional heat gain will cause the liquid ammonia to evaporate at a rate based on the heat input.

At a temperature of –28°F (–33°C), the density of saturated liquid ammonia is 42.7 lb/ft^3 (16.0 kg/m^3) which means that a loss greater than 2.3 ft3 (0.067 m^3) or 17.6 gallons (66.5 l) would exceed the reportable quantity of 100 lb (45 kg). When the upstream liquid refrigerant is at a temperature above saturation, a portion of the upstream liquid will flash to a vapor as it cools to –28°F (–33°C) upon entering the atmosphere. The fraction of refrigerant liquid flashing to a vapor will increase as the temperature of the upstream liquid increases. If the upstream liquid is saturated at 95°F (35°C), 23wt% will flash to a vapor while cooling to –28°F (–33°C). This means that by the time a total of 17.6 gallons (66.5 l) of visible liquid has accumulated outside the system, approximately 130 lb (59 kg) of refrigerant has actually been released. Of the 130 lb (59 kg) released, 30 lb (14 kg) is in a vapor state and the remaining 100 lb (45 kg) is in a liquid state.

The volume of vapor that equates to 100 lb (45 kg) of refrigerant mass will depend on the specific volume of the refrigerant vapor. At atmospheric conditions, the pressure of the ammonia vapor is fixed; however, the specific volume of ammonia vapor is very temperature-dependent (Figure 1).

With a specific volume of ammonia of 18 ft^3/lb (1.125 m^3/kg), a vapor release of 100 lb (45 kg) of pure ammonia would occupy 1,800 ft^3 (51 m^3). As the ammonia vapor is diluted by mixing with ambient air, the volume requirement to reach 100 lb (45 kg) of refrigerant mass grows substantially as will be shown in the last example given in the next section. The specific volume of ammonia vapor increases by more than 15% when warming from –28°F (–33°C) to 40°F (4°C) (Figure 1). This increase in specific volume is particularly important when attempting to relate concentration readings (volumetric) in enclosed spaces to the mass of ammonia in a vapor state.

Because the density (reciprocal of the specific volume) of ammonia in a liquid state is significantly greater than the vapor state, releases that involve liquid ammonia more rapidly approach the reportable quantity compared to vapor releases. A comparative measure of liquid and vapor releases that reach the 100 lb (45 kg) reportable quantity is provided (Table 1).

In considering the above comparative liquid measures, there are a number of additional considerations that need to be kept in mind. Accumulating 17.6 gallons (66.5 l) of liquid ammonia outside of a refrigeration system will result in a refrigerant loss in excess of 100 lb (45 kg) when the temperature of the upstream liquid is warmer than –28°F (–33°C). This is due to a portion of the upstream liquid flashing to vapor as a result of the decrease in pressure from the upstream to the downstream condition. Second, the hygroscopic nature of anhydrous ammonia leads to a dilution of the liquid ammonia with water from either the atmosphere or another source of water in the neighborhood of the leak. Since the ammonia will preferentially evaporate compared to water, the concentration of ammonia in a pool of liquid will tend to dilute over time.

Release Estimation Methods

Following the successful mitigation of an ammonia release, refinement of any rough estimate of the quantity lost during the incident is in order. A refined estimate is needed for multiple reasons, including: providing a written response as a follow-up to the LEPC and SERC, inclusion in the incident investigation report, 5 year accident history update and the corresponding RMP re-submittals, as well as other local jurisdictional requirements. In this section, we present techniques that can be used for estimating refrigerant release rates as vapor-only, liquid-only, and flashing flow scenarios. All too often, sufficient details on the specific conditions during the incident are not known or unavailable, making release quantity estimating quite difficult and error-prone. The following are details that are particularly important in refining a release quantity estimate:

- Time incident began
- Location of refrigerant release
- State of the refrigerant upstream of the leak site (vapor, liquid, two-phase)
- Geometry of the leak site (size of opening, shape of opening, physical characteristics of the opening)

- Pressure of the refrigerant upstream of leak location
- Temperature of the refrigerant upstream of the leak location
- Behavior of the leak: intermittent, steady, decreasing rate, increasing rate, etc.
- Room concentrations
- Leak duration

This information can then be used as input to the methods presented below to estimate the leak rate. The product of the leak rate and leak duration provides an estimate of the total quantity of refrigerant lost.

Vapor-only Leaks

Refrigerant vapor leaks can occur on the discharge gas side of compressors (booster or high-stage) as well as on high-stage dry suction lines operating above atmospheric pressure. It is important to keep in mind that releases from hot gas defrost piping are often vapor-only but could also include some quantity of condensed liquid.

In estimating flow rates of vapor state refrigerant, it is important to recognize the changes in density that can occur which leads to the need for consideration of compressibility. In compressible flow scenarios, choking can readily occur and needs to be considered. Choking is a phenomenon whereby increasing upstream pressure does not result in increasing downstream vapor velocity. It is important to emphasize that although choking results in no further changes in vapor velocity with increasing upstream pressure, the mass flow rate of vapor will increase due to the increasing density of the upstream vapor with increasing pressure.

We begin by looking at a fundamental relationship that relates pressure drop to the kinetic energy of a frictional fluid flowing - the basic Darcy-Weisbach equation (White, 1998):

$$\Delta P = f\frac{L}{D}\cdot\rho\cdot\frac{V^2}{2g} \qquad (1)$$

The dimensionless group *fL/D* represents a frictional resistance coefficient sometimes referred to as, $K_{friction}$. This grouping can be replaced by a total resistance coefficient, *K*, that includes both frictional effects and fitting losses. Crane (1988) applies a correction factor to the Darcy-Weisbach equation to accommodate the compressibility associated with fluids discharging through a small area to significantly larger area. Rearranging Eq. 1, formulating it in terms of mass flow, and including a correction factor for adiabatic compressible flow gives:

$$\dot{m}\left[\frac{lb}{min}\right] = 5778 \cdot Y \cdot A_{leak} \cdot \sqrt{\frac{\Delta P \cdot \rho}{K}} \tag{2}$$

If the leak opening is circular, the area can be simply expressed in terms of the leak diameter as:

$$\dot{m}\left[\frac{lb}{min}\right] = 31.5 \cdot Y \cdot d^2 \cdot \sqrt{\frac{\Delta P \cdot \rho}{K}} \tag{3}$$

For most leak geometries, the total resistance coefficient can be expressed as the sum of an entrance and exit loss (frictional component of the resistance coefficient is small). The resistance coefficient for a flush entrance is $K = 0.5$ and for a sharp-edged or projecting exit $K = 1.0$ (Crane 1988) for a total resistance coefficient of 1.5. Crane also provides estimates of the net expansion factor for correcting the Darcy-Weisbach equation to accommodate the compressibility of the vapor flow (Figure 2).

The net expansion factor, *Y*, decreases with increasing pressure ratio with the total resistance coefficient as a parameter. In this case, the pressure ratio is defined as the difference in absolute pressure upstream minus absolute local atmospheric pressure divided by the absolute upstream pressure. It is also of interest to note that the net expansion factor terminates at a pressure ratio where the flow becomes choked. As such, the pressure difference used in Eq. 2 is necessarily limited to that determined by the product of the terminal pressure ratio shown in Figure 2 and the upstream pressure. In the case of the total resistance factor $K = 1.5$, the maximum pressure ratio is 0.550 and the maximum pressure difference would be the pressure ratio multiplied by the absolute pressure upstream of the leak site. A relationship for the net expansion factor for a total resistance coefficient of 1.5 is given by:

$$Y = \max\left(\left(1 - 0.6725 \cdot \frac{\Delta P}{P_{upstream}}\right), 0.631\right) \tag{4}$$

Figures 3 and 4 summarize the results of applying these equations to a range of differing leak geometries in two classifications that might be considered "small leaks" and "larger leaks." Figure 4 shows the resulting vapor leak rates for a range of small openings while Figure 4 shows the vapor leak rates for larger openings. Knowing the average upstream pressure during the incident and matching the characteristics of the leak geometry with those shown in the respective figures leads to an estimate of the vapor leak flow rate. Multiplying the resulting vapor leak rate by the active incident duration leads to an estimate of the total mass of vapor lost. Because the method outlined in EPA (1999) does not include dynamic losses attributable to either upstream fittings or flow through the leak site itself, the EPA method predicts higher vapor mass flow rates.

Another common vapor release scenario is from actuation of pressure relief valves. A characteristic of a relief valve that yields its mass or volume flow rate based on its upstream overpressure is called the *slope*. The mass flow rate of air through a pressure relief device is given by:

$$\dot{m}_{air,rated}\left[\frac{lb}{min}\right] = \text{slope}_{\dot{m}}\ (P_{set} \cdot 1.1 + 14.7) \tag{5}$$

Slope data is provided by the National Board in its publication NB-18 for all relief devices that are National Board rated. It is important to note that this mass flow rate is defined for when the valve is fully open and assumes the flowing fluid through the relief device is air. Therefore, the flow rate needs to be converted to a refrigerant basis prior to use for release estimation.

During a release from an overpressure situation in a refrigeration system, the relief valve will likely cycle open and closed intermittently. Since the closing pressure of a relief valve is significantly less than its opening pressure, the mass flow rate through the valve will be proportionally lower as the inlet pressure to the valve decreases prior to the valve closing. As a first approximation, the mass flow rate through a relief device can be determined knowing the inlet pressure to the valve that causes it to open (this is the set pressure unless the valve drifts over time). Using a mass flow rate based on the set pressure is conservative and could be refined downward if the closing pressure of the valve was known. Since closing pressures are not widely available for relief valves used in industrial refrigeration applications, we will not pursue this refinement here.

Once the mass flow rate of the relief valve is determined (either by the above slope for air or by consulting capacity tables provided by the relief device manufacturer), the air basis mass flow rate must be converted to a refrigerant basis. This can be accomplished by the following (ASHRAE 2007):

$$\dot{m}_{NH_3} = \dot{m}_{air,rated} \cdot \frac{C_{NH_3}}{C_{air}} \cdot \sqrt{\frac{T_{air} \cdot MW_{NH_3}}{T_{NH_3} \cdot MW_{air}}} \tag{6}$$

The conversion factor for mass flow from an air basis to an ammonia basis is dependent on the temperature and pressure of the upstream ammonia; however, the resulting conversion constant is relatively insensitive. We recommend using a constant value of 0.72 which yields a refrigerant mass flow:

$$\dot{m}_{NH_3} \approx 0.72 \cdot \dot{m}_{air,rated} \qquad (7)$$

The total mass of ammonia lost in the event of a relief device lifting can then be approximated as:

$$M_{Total,NH_3}[lb] = 0.72 \cdot \dot{m}_{air,rated} \cdot f_{open} \cdot t \qquad (8)$$

Liquid-only Leaks

In situations where the leak source is liquid refrigerant at a temperature below the saturation temperature corresponding to the local atmospheric pressure, the liquid will not flash but remain in its pure liquid state as it moves from a higher pressure within the system to atmospheric pressure. An appropriate model for estimating the quantity lost in this incident scenario is the non-flashing or what is sometimes referred to as the "frozen flow" model. The governing equation in this simple flow regime, based on the orifice equation, is given by

$$\dot{m}_{liquid,leak,Frozenflow}\left[\frac{lb}{min}\right] = 96.3 \cdot C_D \cdot A_{leak} \sqrt{\Delta P \cdot \rho_{liquid}} \qquad (9)$$

where the discharge coefficient, C_D, is approximately 0.6. Figure 5 shows liquid leak rates based on the non-flashing or frozen flow model for small openings, and Figure 6 shows leak rates for large openings. It is important to note that the leak rate is a strong function of the pressure difference across the leak site. In some incidents, the pressure upstream of the leak site will decrease over time, thereby requiring consideration of a varying leak mass flow and time-integration of the dynamic leak quantity to arrive at a reasonable estimate of the total refrigerant quantity loss.

Two-phase Flashing Flow Liquid Leaks

In situations where the temperature of liquid upstream of a leak site is above the saturation temperature for the prevailing ambient pressure, a portion of the upstream liquid will flash to a vapor as it flows to and through the leak opening. With ammonia, there is a substantial increase in specific volume in moving from a liquid to a vapor state. This large increase in volume during the expansion decreases the effective size of a leak opening.

For liquid ammonia incidents that result in flashing flow, we recommend using the Fauske model (Fauske 1985). The Fauske model is capable of accommodating a range of scenarios that include the formation of flash gas upstream of a leak site (that might result from a rapid depressurization in a long liquid line) as well as flash gas formed by the liquid refrigerant moving through a leak opening. Assuming choked conditions exist for the flashing liquid flow, the mass flow rate of liquid through the leak site for equilibrium conditions is given by Fauske for short lengths of upstream piping (approximately 3 ft (1 m)).

$$\dot{m}_{liquid,equil,Fauske}\left[\frac{lb}{min}\right] \approx 60 \cdot A_{leak} \cdot \frac{h_{fg}}{v_{fg}} \sqrt{\frac{1}{T \cdot cp_l}} \tag{10}$$

Figure 7 shows the results of the Fauske model applied for small leak openings assuming equilibrium conditions are attained (Eq. 10) and Figure 8 shows results for larger leak openings. Also included is the impact of subcooling the upstream liquid (dashed lines). As expected, subcooling the upstream liquid reduces the mass fraction of flash gas generated, thereby increasing the mass flow rate of liquid through the leak site. The effects of flash gas in reducing the mass flow rate through the leak site are apparent when the results of the Fauske model under equilibrium conditions are compared with the frozen flow model. In the next section, we present examples of applying the models presented for estimating the quantities of refrigerant lost following an incident.

Examples

In this section, we apply the principles and results presented in the previous section to estimate the total quantity of refrigerant lost during an incident. Although the equations presented for leak rate estimation are applicable for other refrigerants, the mass flow rate plots for different leak site sizes included here are all based on anhydrous ammonia. As a result, we will consider ammonia as the working fluid in all the examples presented in this section. We present examples of small vapor leaks, severed high pressure liquid piping, pressure relief device actuation, and estimation of the mass of ammonia vapor within an enclosed space based on measured concentration.

Small Openings

At 6:15 am, an employee reports the strong smell of ammonia in the dock area of a cold storage warehouse. A refrigeration mechanic confirms the odor and believes it is originating from a ceiling-hung evaporator located in the dock and decides to evacuate the area. A second operator is contacted by two-way radio to check the operating status of the suspect evaporator unit using the system's computer-based controls. He confirms that the unit in question is presently in defrost mode and notes the current system head pressure is at 160 psig (11.03 barg). Refrigeration personnel quickly close the globe isolation valve in the hot gas supply line located on the roof immediately above the unit. The decision is made to manually close the unit's liquid supply, and suction globe valves as well. The elapsed time from initial notification of the leak to the isolation of the unit was 13 minutes.

Following the release mitigation, the operators visually inspect the evaporator and discover a pinhole leak in the hot gas supply line to the unit's drain pan. The pinhole leak measured approximately 5/32" (4 mm) in diameter. Figure 3 includes leak rate estimates for vapor-only leaks for openings of 1/8" (3.2 mm) and 3/16" (4.8 mm) but none for a 5/32" (4 mm) leak. Because the leak rate increases approximately linearly with leak area, Figure 9 shows a sketched line for the leak rate that would be expected for the 5/32" (4 mm) pinhole leak. Assuming a 5 psig (0.34 barg) pressure drop in the hot gas line from the engine room to the unit gives an estimate of the pressure immediately upstream of the leak site at 155 psig (10.55 barg). The intersection of the assumed leak rate line and the 155 psig (10.55 barg) source pressure yields a leak rate estimate of 2.35 lb/min (1.07 kg/min). The quantity lost from the dynamic hot gas leak is given by:

$$M_{leak} = \dot{m} \cdot t = 2.35 \frac{lb}{min} \cdot 13\ min \approx 31\ lb\ [14\ kg] \qquad (11)$$

Assuming the hot-gas supply to the pan and the evaporator are piped in series, it may also be reasonable to estimate the residual quantity of ammonia vapor in the evaporator unit itself and assume the entire vapor inventory of the evaporator was discharged into the space following the remote isolation of the unit.

*(**Note:** this scenario would require the failing of the pan check.)*

Data listing the internal volume of evaporators are typically available from the unit's manufacturer. In this case, the internal volume of the evaporator is listed as 3.9 ft^3 (0.11 m^3). To find the density of the refrigerant vapor, assume the ammonia occupying the evaporator is saturated vapor at the relief regulator set pressure (75 psig (5.2 barg)). In this case, the density of vapor in the evaporator is 0.3065 lb/ft^3 (4.91 kg/m^3). The product of the unit's internal volume and the density of the ammonia at this pressure provide an estimate of the residual ammonia vapor in the unit.

$$M_{residual} = \rho_{vapor} \cdot V_{coil} = 0.3065 \frac{lb}{ft^3} \cdot 3.9\ ft^3 = 1.2\ lb\ [0.54\ kg] \qquad (12)$$

The contribution to the dynamic loss from the residual vapor is quite small. If the leak occurred early during the defrost period, there would be a significant amount of condensed liquid ammonia available to leak out of the coil which would increase the loss estimate.

Severed Piping

The forks on a lift truck impacted the ¾" schedule 80 (0.742" ID) (18.9 mm) oil pot drain line causing it to sever upstream of the pot's globe isolation valve. The oil pot is connected to an intercooler operating at pressure of 25 psig (1.72 barg). Saturated liquid at 25 psig (1.72 barg) leaks through the short section of severed pipe for a period of 15 minutes prior to mitigation. The quantity lost can be estimated using both the frozen flow and Fauske models.

The leak rate for frozen flow can be obtained from Figure 6 and the leak rate for the Fauske model from Figure 8. At an upstream pressure of 25 psig (1.72 barg), the leak rate for frozen flow is 330 lb/min (150 kg/min) and the leak rate for the Fauske model is 100 lb/min (45.4 kg/min). The total mass lost is the product of the leak rate and the leak duration.

$$M_{frozen\ flow} = \dot{m}_{frozen\ flow} \cdot t = 330 \frac{lb}{min} \cdot 15\ min = 4{,}950\ lb\ [2{,}245\ kg] \qquad (13)$$

$$M_{Fauske} = \dot{m}_{Fauske} \cdot t = 100 \frac{lb}{min} \cdot 15\ min = 1{,}500\ lb\ [680\ kg] \qquad (14)$$

Since the frozen flow model does not include the effects of flashing flow, it predicts more than triple the quantity of refrigerant lost when compared to the Fauske model.

Pressure Relief Valves

An area-wide utility power outage caused a complete shutdown at a plant during summertime operation. Heat gains from the ambient caused a pressure relief valve on a surge drum located on the roof to actuate. Plant staff noted that the suction pressure was at 90 psig (6.2 barg) when the relief valve began to actuate even though the set pressure on the relief device was 150 psig (10.3 barg). The leak persisted for 100 minutes before a partial restoration of power to the plant allowed compressors to be re-started to lower the suction pressure. Just prior to compressor re-start, operators noted the suction pressure had risen to 100 psig (6.9 barg). During the period of time the relief valve was lifting, the operators observed that the fraction of time the valve dwelled open was 30%. The total quantity of refrigerant lost due to the relief device intermittently lifting can be estimated.

The first step is to estimate the relief valve capacity at the reduced pressure. For the purposes of the release quantity estimate, we will use the average inlet pressure to the valve during the event (95 psig (6.55 barg)). The relief valve capacity at the reduced inlet pressure can be determined using the slope on air for the relief valve in service. The slope for the installed relief valve is 0.1753 lb of air per minute per psia. The revised capacity for the relief valve at the lower inlet pressure is given by

$$\begin{aligned} C' &= \text{slope}_{\dot{m}} \cdot (P_{suction} \cdot 1.1 + 14.7\ psia) = \\ & 0.1753 \cdot (95\ psig \cdot 1.1 + 14.7\ psia) = 20.9\ \frac{lb_{air}}{min} \left[9.5 \frac{kg}{min} \right] \end{aligned} \tag{15}$$

Since the relief device capacity is based on air, we need to convert the mass flow rate from an air basis to an ammonia basis. Alternatively, we can estimate the total quantity of refrigerant lost using Eq. 8 because it includes the conversion from an air basis to refrigerant basis.

$$M_{Total,NH_3} = 0.72 \cdot \dot{m}_{air,rated} \cdot f_{open} \cdot t = 0.72 \cdot 20.9 \cdot 0.3 \cdot 100 = 451\ lb\ [205\ kg] \qquad (16)$$

It is important to note that good estimates of the fraction of time open and the total incident duration will significantly affect the estimated total quantity of refrigerant lost during the incident.

Enclosed Spaces

In some cases, refrigerant leaks occur in spaces that are enclosed with no ventilation and little infiltration of outside air. If an ammonia detection system is in place and calibrated, the quantity of refrigerant emitted into the space can be estimated. Typically, detection systems report the concentration of ammonia in parts per million (ppm) by volume. This reported concentration represents the ratio of the volume of ammonia to the total volume of the space.

$$ppm[-] \equiv \frac{V_{NH_3}[ft^3]}{V_{Total}[ft^3]} \cdot 1E06 = \frac{v_{NH_3}\left[\frac{ft^3}{lb}\right] \cdot M_{NH_3}[lb]}{V_{Total}\ [ft^3]} \cdot 1E06 \qquad (17)$$

Since the specific volume of ammonia is temperature dependent, it is important to determine the space temperature if this approach is used for estimating the total quantity present in a space.

For example, determine the concentration of ammonia that would result from 100 lb (45 kg) of ammonia vapor being released into an enclosed space measuring 100 ft

(30.5 m) long by 50 ft (15.2 m) wide by 20 ft tall (6.1 m) at a temperature of 40°F (4°C). The specific volume of ammonia at this temperature is 21.12 ft^3/lb (1.32 m^3/kg). The resulting concentration can be found by using Eq. 18 as follows:

$$ppm[-] = \frac{21.12\left[\frac{ft^3}{lb}\right]\cdot 100\,[lb]}{100\cdot 50\cdot 20\;[ft^3]}\cdot 1E06 \;=\; 21{,}120\; ppm \tag{18}$$

Again, this result is intended to provide an indication of a reportable quantity released into an enclosed space. It should also be noted that any infiltration of air into this space will result in diluting the ammonia concentration. This fact should be kept in mind when using ammonia concentration readings to estimate quantities of refrigerant lost from a system.

Conclusions & Recommendations

Although the emphasis of safety standards such as PSM is to *prevent* incidents from occurring, they will still happen from time to time. In the event of a refrigerant leak from a system, the quantity of refrigerant lost must be estimated as accurately as possible. In this paper, we review principles of leak estimates for vapor-only, flashing liquid, and liquid-only incident scenarios. Results are provided for a number of leak site geometries in both vapor and liquid leak scenarios. Regardless of the method used for leak quantity estimation, it is essential that operations staff gather the following information:

- Time incident began
- Location of refrigerant release
- State of the refrigerant upstream of the leak site (vapor, liquid, two-phase)
- Geometry of the leak site (size of opening, shape of opening, physical characteristics of the opening)
- Pressure of the refrigerant upstream of leak location

- Temperature of the refrigerant upstream of the leak location
- Behavior of the leak: intermittent, steady, decreasing rate, increasing rate, etc.
- Room concentrations
- Leak duration

Using this information, the total quantity of refrigerant lost from the system following an incident can be obtained through either the model equations or the summary charts presented in this paper.

Nomenclature

A_{leak} = area of the leak site, ft^2

C_{air} = constant for air, 356

C_D = discharge coefficient for the leak geometry (approximately 0.6)

C_{NH_3} = constant for ammonia,

cp_l = specific heat of upstream liquid, ft^2/s^2-R

d = equivalent diameter of opening, in

D = inside diameter of pipe, ft

f_{open} = fraction of time relief device is open

g = gravitational constant, ft-lbm/lbf-s^2

h_{fg} = enthalpy of vaporization of upstream liquid, ft^2/s^2

k = ratio of specific heat at constant pressure to constant volume at upstream condition

K = total resistance coefficient (frictional plus fitting losses associated with leak area)

L = length of piping upstream of leak site where upstream pressure is known, ft

$\dot{m}$ = mass flow rate, lb/min

M_{air} = molecular weight of air, 28.97

$\dot{m}_{airrated}$ = rated relief device capacity on an air basis, lb/min

$\dot{m}_{liquidleakFrozenflow}$ = liquid leak flow rate through leak site for frozen flow model, lb/min

$\dot{m}_{liquidnonequilFauske}$ = non-equilibrium liquid leak flow rate estimate for Fauske equation, lb/min

$\dot{m}_{NH_3}$ = ammonia mass flow rate through relief device at rated capacity, lb/min

M_{NH_3} = mass of ammonia, lb

M_{leak} = mass of ammonia lost during a dynamic leak, lb

$M_{residual}$ = residual mass of ammonia remaining in a section of a system with the potential for being lost during an incident, lb

$M_{TotalNH_3}$ = mass of ammonia lost during relief valve actuation, lb

MW_{air} = molecular weight of air, 28.9

MW_{NH_3} = molecular weight of ammonia, 17.0

P_{set} = relief device set pressure, psig

$\text{slope}_{\dot{m}}$ = relief device flow characteristic, lb of air/min per psia

t = total time of relief device operation, min

T = absolute temperature of the upstream liquid, R

T_{air} = absolute temperature of air at relief device rating condition, 520 R

T_{NH_3} = absolute temperature of ammonia vapor at upstream condition, R

v_{fg} = change in specific volume from vapor to liquid, ft^3/lb

v_{NH_3} = specific volume of ammonia vapor, ft^3/lb

V_{coil} = internal volume of an evaporator coil (or other piece of equipment), ft^3

V_{NH_3} = volume of ammonia vapor in an enclosed space, ft^3

V_{Total} = total volume of enclosed space, ft^3

Y = net expansion factor

Symbols

ΔP = difference in absolute pressure upstream and downstream of the leak (equivalent to the gauge pressure upstream of the leak) with consideration of the choking flow condition, psi

ρ = density of ammonia upstream of leak, lb/ft^3

ρ_{liquid} = density of liquid upstream, lb/ft^3

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Figure 1. Temperature-dependent vapor specific volume.

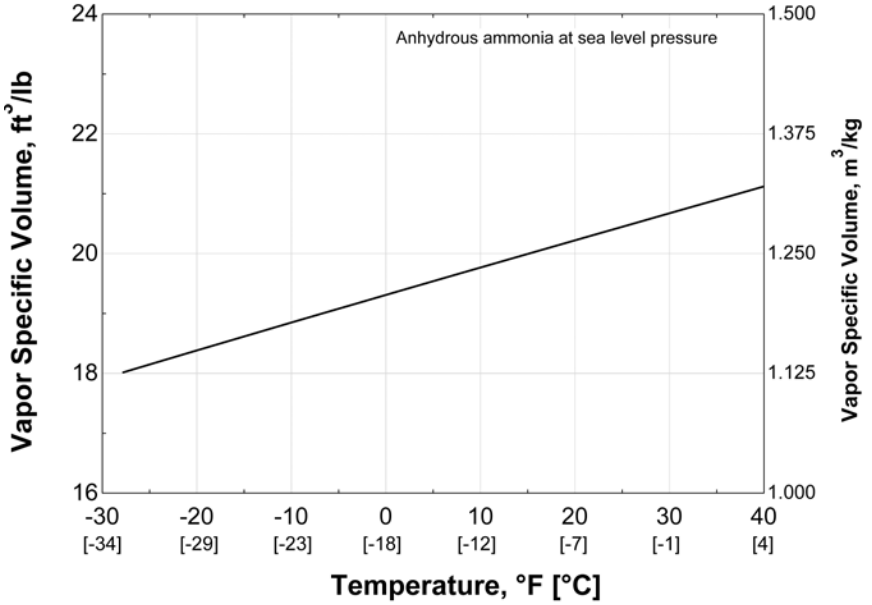

Figure 2. Net expansion factor accomodates for compressibility.

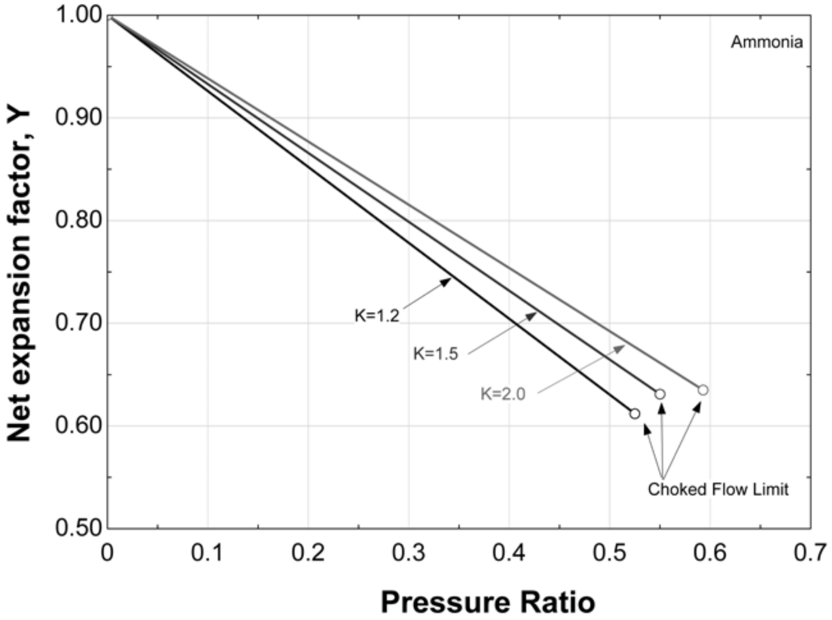

Figure 3. Leak rate estimates: packing leaks.

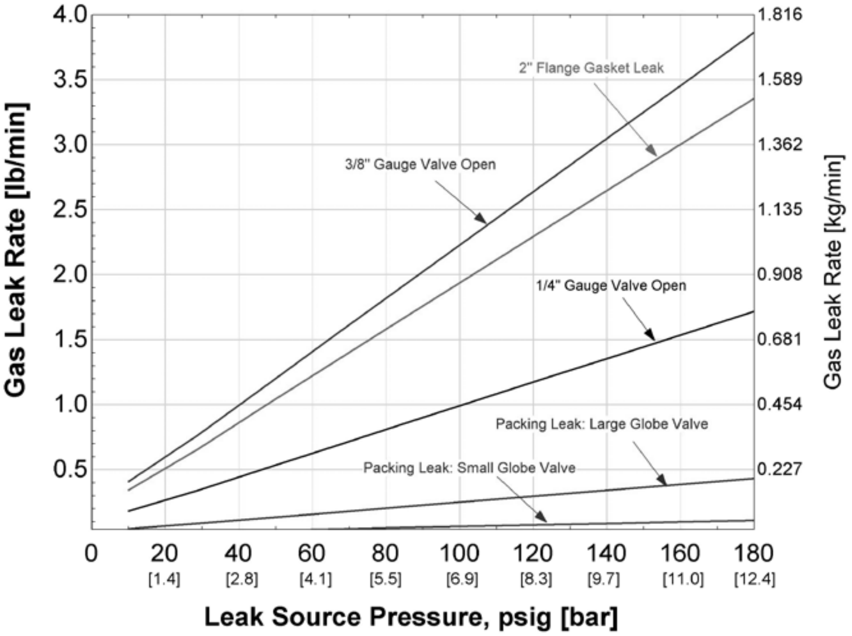

Figure 4. Leak rate estimates: sheared lines.

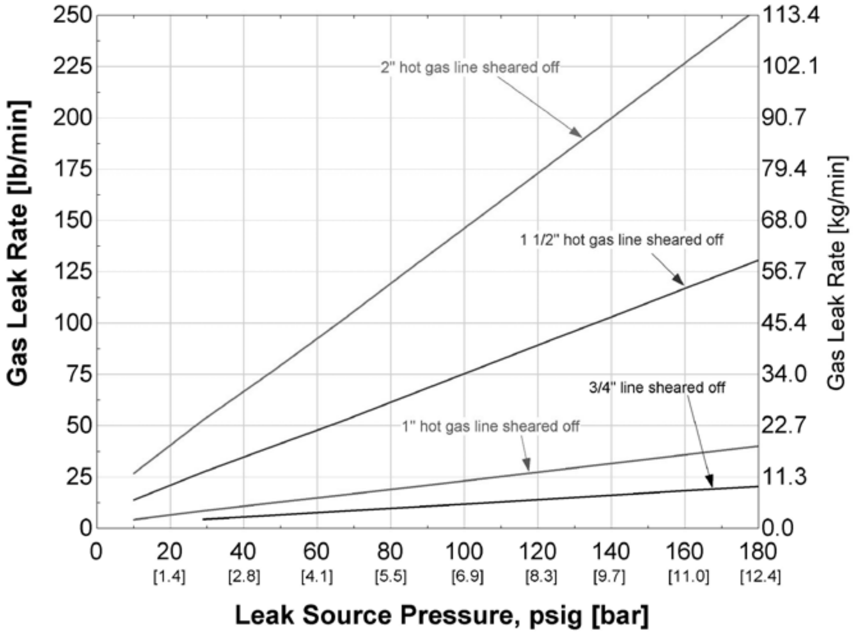

Figure 5. Leak rate estimates: small liquid openings.

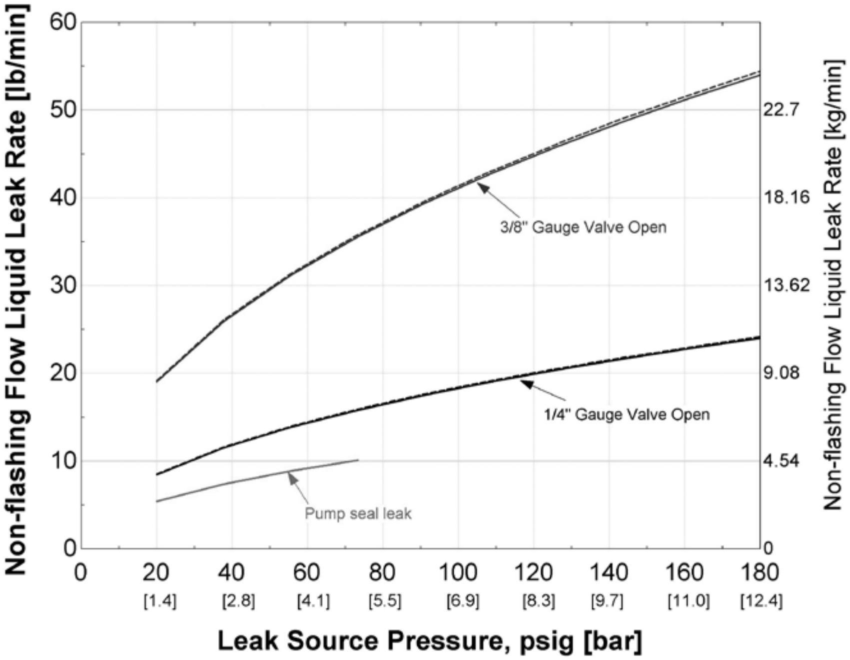

Figure 6. Leak rate estimates: large liquid openings.

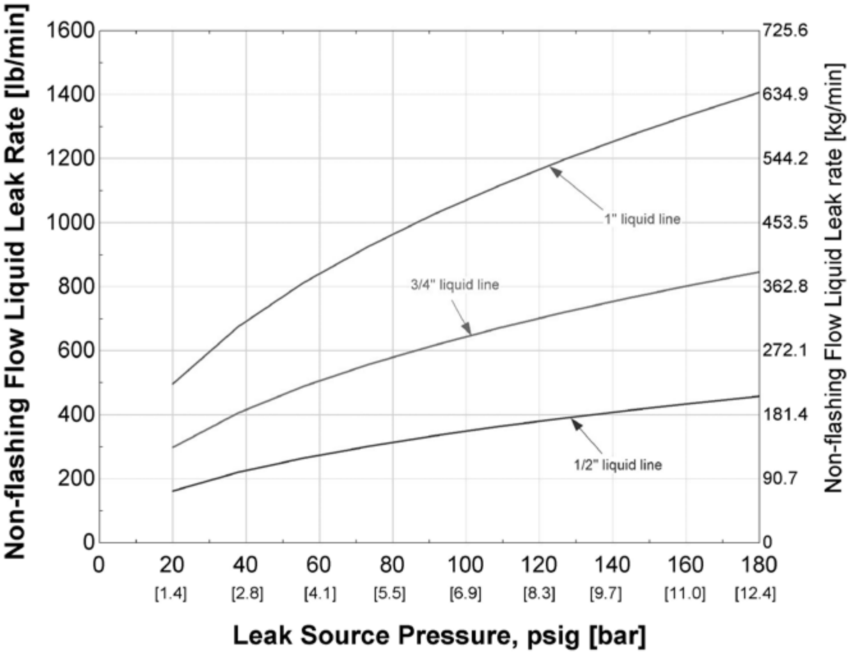

Figure 7. Fauske model applied to small openings.

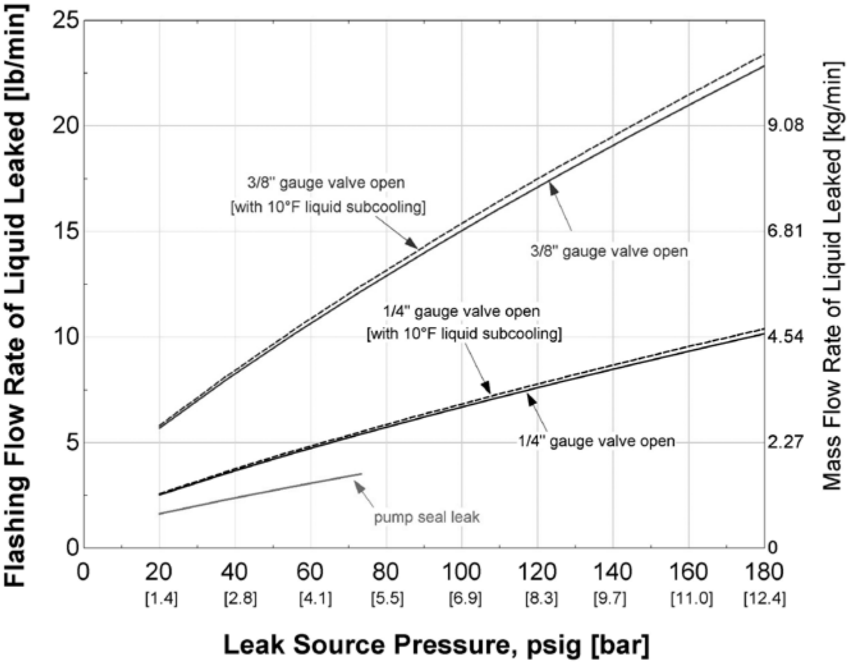

Figure 8. Fauske model applied to large openings.

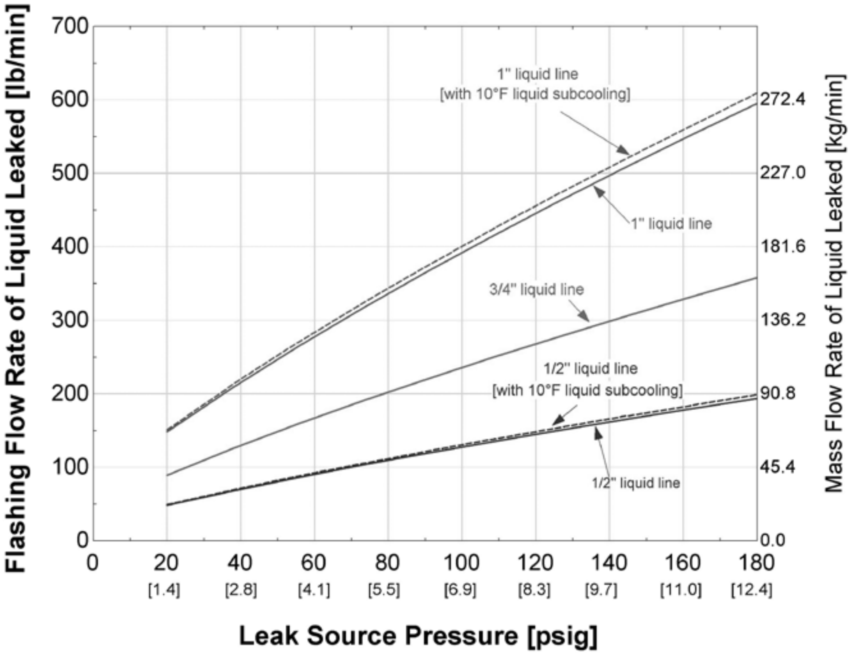

Figure 9. Leak rate estimates: 5/32" (4 mm) pinhole leak.

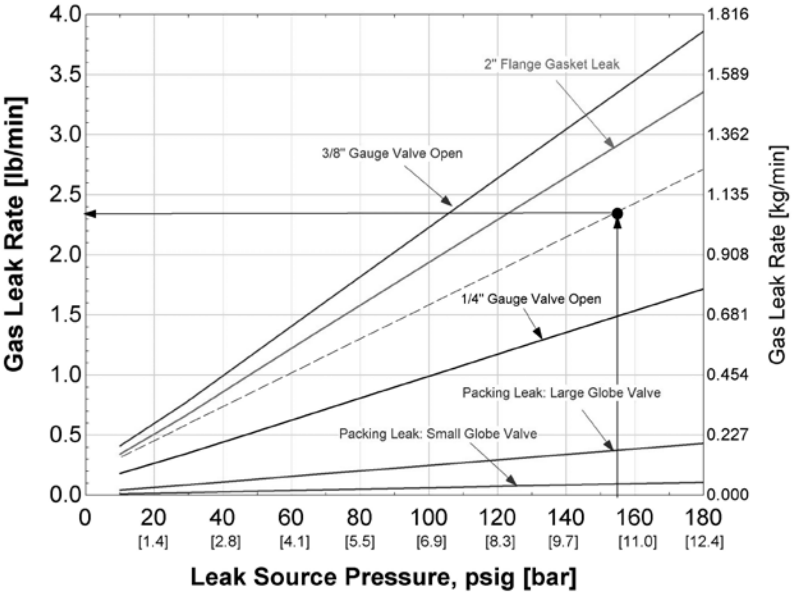

Table 1. Comparisons of liquid and vapor quantities totaling 100 lb (45 kg).

Refrigerant State	Equivalent NH_3 Volume	Comparative Measure	Comments
Saturated liquid at -28°F (-33°C)	17.6 gal (66.5 l)	A 20 gallon (76 l) fish aquarium about 90% full	
		Liquid puddle ½" (1.27 cm) deep and 8 ½ ft (2.6 m) in diameter	
Vapor at -28°F (-33°C)	1,800 ft^3 (51 m^3)	A 90 ft^2 (8.4 m^2) room with 20 ft (6.1 m) ceiling at a concentration of 1,000,000 ppm	Pure ammonia vapor
		A 301,000 ft^2 (27,964 m^2) room with 20 ft (6.1 m) ceiling at a concentration of 300 ppm	Diluted ammonia with a room concentration equal to the IDLH

Notes: