REFRIGERATION REVIEW

CLEANUP PROCEDURES FOR REFRIGERANT AMMONIA SPILLS

The following information is provided as a tool for cleanup of refrigerant spills for ammonia. Although prevention by properly designed, safe, automated systems is the best solution, experienced operating personnel as well as good emergency procedures for informed and capable fire departments are all contiguous to optimizing a safe working environment.

The following are excerpts from talks given by the late William Ostner, former President of Jax Cold Storage and graduate Chemical Engineer, regarding procedures they use for cleanup of ammonia spills. Several methods are available. As Mr. Ostner has said, "The one thing worse than the smell of ammonia is the fear of it due to ignorance." Ammonia has many commonplace uses, including household cleaning agents, blueprinting processes, and medical resuscitating. Ammonia, and many other common elements and compounds, are basic building blocks of life itself; its chemistry are found in amino acids, which are at the heart of life-sustaining cell production. Ammonia, the same as water, carbon dioxide, oxygen, and nitrogen, is a very necessary part of our chemistry, when present in proper quantities. The dangers can occur when these quantities are out of balance (too concentrated or too diluted to perform their life-sustaining properties). Many of these common compounds or elements in concentrated forms can be harmful. Knowing how to handle, contain, and correct harmful concentrations is the key to life safety.

Ammonia is used in a concentrated form in closed refrigeration systems. Occasionally, leaks will occur, and depending upon the size of the leak, operators of these systems should be familiar with corrective measures. If the leak is sizeable, more extensive corrective measures may be necessary. The following discussion concerns the primary methods used for cleaning up after ammonia spills or leaks. These are:

1. Ventilation, using outside air
2. Absorption, using the absorbing ability of water to pick up the ammonia
3. Neutralizing, using an acid in some form to neutralize "basic" ammonia (combine it chemically to form harmless precipitates)
4. Reducing ammonia to another chemical form

PART 1 – Ventilation

If we could rapidly replace the ammonia vapors with cold fresh air, our problem would be solved. This is not as easy as it might sound. Let us take a hypothetical case involving a million cubic foot warehouse containing the normal amount of product and assume that the spill is of such magnitude as to fill the air space with ammonia gas. Assuming that stored product occupies half the air space, we would have 500,000 cubic feet of ammonia vapor.

From tables of saturated ammonia, at 0 psig, one cubic foot of ammonia weighs .05555 lbs. So, 500,000 cubic feet would weigh 27,775 lbs. A ¾ HP exhaust fan at .1" static pressure, delivers 11,000 cubic feet per minute. In 45 minutes and 100% efficiency, the fan could replace the air in the room one time, or reduce the 27,775 lbs. by half. In 1½ hours, there would be ¼ of the original ammonia, or 6,944 lbs. remaining. In six hours, we might reduce this to less than 100 lbs. With 0° ambient air, we could continue this delusion process until all detectable ammonia trapped in crevices is removed, however, in the summer we would have injected 6 million cubic feet of warm air into the room. Rising room temperature conditions would limit the quantity of air. In addition to the temperature of the product, we must remember that at very low temperatures ammonia vapor is not as damaging to product as at higher temperatures. If warm humid air is allowed to condense on cold product, the water would then absorb ammonia which would retard its removal. A standard must be set as to how high this temperature can be allowed to go. Some degree of ventilation is a must, but let us consider the second method.

PART 2 – Absorption

Cold water and ammonia have a high affinity for each other. As a rule of thumb, we say that one cubic food of water can absorb 1300 cubic feet of ammonia gas. Using our hypothetical room with an atmosphere containing 500,000 cubic feet of ammonia gas, it would be necessary to bring into the room: 500,000 ÷ 1300, or 385 cubic feet of water, or about 12 tons of water. This water would have to be drained off to the outside. If the room was equipped with water defrost equipment, the refrigeration and fans could be turned off and the water allowed to run at intermittent intervals, as long as temperatures would permit. Some freezers use large water defrost air units, which are an ideal way to remove ammonia vapor by running the fans.

Let us see what could happen if we set an upper temperature tolerance of 0°F using tables on properties of air mixed with saturated water vapor. At 0°F we have .00078 lbs. of water for each lb. of air, and each lb. of air occupies 11.59 cubic feet. It follows then, that (500,000 cubic feet x .00078)/11.59 = 34 pounds of water in our room.

The introduction of water vapor into our room in excess of 34 lbs. would only result in frost forming on the walls, ceiling, product, and the coils. Extrapolating for -8°F, the amount of water vapor in the room at -8°, +34°, +90° is shown in Exhibit C.

It should be obvious from the above that steam injection would be the ideal, except for our temperature standards. For short periods of time, at intervals, it is acceptable. The reaction of water and ammonia results in the formation of weak alkali ammonium hydroxide. (See Formula 1, Exhibit C.) This product is similar to household ammonia and should be removed. The absorption method has its good points, but let us continue to look at the third method.

PART 3 – Neutralize the Ammonia with an Acid

Ammonia can be neutralized by strong or weak acids. See Equations 2, 3, 4, and 5, shown in Exhibit C.

Both sulfuric acid and muriatic acid (hydrochloric acid) are strong acids, and therefore are good reagents to neutralize ammonia. Years ago, I had a warehouse operator call me in a panic because he had sprayed liquid ammonia on top of product in a blast freezer, and he wondered what he could do. I suggested he put pans of muriatic acid out, leave the fans running, and it should help neutralize the ammonia. He called back the next morning excited. “Hank, it removed all the ammonia fumes!” I asked how many pans of muriatic acid he put out, and he said 30! So, it does work, but since both muriatic acid and sulfuric acid are both dangerous to handle and care should be taken to use PPE when necessary.

PART 4 – Reducing Ammonia to Another Chemical Form

Carbon dioxide gas (CO_2), can be used directly to react with ammonia (NH_3). This can be accomplished by simply releasing carbon dioxide into the air, making sure there is enough moisture available. In the presence of water vapor, CO_2 will combine with ammonia gas to form ammonia carbonate, which is a white powder. This is often the most expedient way to void a mild ammonia leak, but it requires follow up because now you have to sweep up the powdered ammonia carbonate and take it outside the cold room. Once the ammonia carbonate is warmed up outside the cold room, it will break down into ammonia and CO_2, so you need to be aware of where you discard the white powder.

One of the most expedient ways to get CO_2 into a room is with a CO_2 fire extinguisher. For large leaks you can order in truck loads or cylinders, but you need to be aware of the CO_2 percentages in the air and follow the OSHA guidelines.

As we have seen from Equation 5, for each 34 lbs. of ammonia, we will need 36 lbs. of water and 44 lbs. of carbon dioxide. As previously mentioned, this is a very weak bonded compound, and when warmed up to ambient conditions will break down to its original form, NH_3, CO_2, and H_2O.

Let us examine a typic spill using the assumptions above and begin the clean up operation. Our first consideration, of course, is to verify that the leak has been fixed and that **refrigeration is operating**. Ventilation should continue. Carbon dioxide should be introduced. This can be done by placing one or more drums of CO_2 in the doorway with the valve partially open and directed into the room. Care should be used to not open the valve fully, as this will cause a "jet" stream at the nozzle and could knock the cylinder over. A gas mask is not needed for this operation. It is in reality a hindrance at this time. Some ventilation should be maintained to assure oxygen is available to breathe. The room should be continuously checked for oxygen content when CO_2 is being injected. Be mindful that moisture (water vapor) needs to be added by spraying some into the room or by opening a door occasionally to let in warm moist air.

A second drum can be brought in a little further into the room to continue the injection of CO2. Please note that we are now using two of the four methods, namely Ventilation and Neutralization. Remember, however, that neutralization will not occur unless there is sufficient moisture.

In review from our calculations above:
at -8°, 500,000 cubic feet x .0039 ÷ 11.38 = 17 lbs. of moisture
at +34°, 500,000 cubic feet x .0041 ÷ 12.4 = 165 lbs.
at +90°, 500,000 cubic feet x .0319 ÷ 13.86 = 1150 lbs.

As long as the temperature of the room allows us to do so, we will bring in warm moist outside air for our reaction to be complete, otherwise we must use another means such as a water hose with a fine spray or even wet sacks. A separate device, with spray headers, fan and water drain could be used, or existing air units (particularly if water defrost) with a water hose spray could be used.
NOTE: Should shortness of breath be noted, it indicates a temporary excess of CO2, or there may not be enough moisture present, or that the ammonia has been

neutralized. The latter is not likely to be the case since the ammonia has a habit of lingering in unventilated places. As the neutralization proceeds, the daily amount of carbon dioxide can be reduced until it is no longer needed.

EXHIBIT "C"

Calculations for moisture in a room at:

-8°F (500,000 x .00039) ÷11.38 = 17.1 lbs.

+34°F (500,000 x .0041) ÷ 12.44 = 164.8 lbs.

+90°F (500,000 x .0319) ÷ 13.86 = 1150 lbs.

EQUATIONS

1. (18) H_2O + (157) NH_3 → (35) NH_4OH

2. (98) H_2SO_4 + (34) $2NH_3$ → (132) $(NH_4)_2SO_4$

3. (35) HCl + (17) NH_3 → (53) NH_4Cl

4. (62) H_2CO_3 + (17) NH_3 → (79) NH_4HCO_3

5. (36) $2H_2O$ + (44) CO_2 + (34) $2NH_3$ → (114) $(NH_4)_2CO_3$*H_2O

EXHIBIT "D"

NAME	**SYMBOL**	**MOLECULAR WEIGHT**
Acetic Acid	$CH_3\ COOH$	60
Ammonia	NH_3	17
Water	H_2O	18
Carbon Dioxide	CO_2	44
Ammonium Carbonate	$(NH_4)_2CO_3*H_2O$	114
Ammonium Acid Carbonate	NH_4HCO_3	79
Ammonium Sesqui-Carbonate	$(NH_4)_4H_2(CO_3)_3*H_2O$	272
Hydrochloric (Muriatic) Acid	HCl	36
Sulfuric Acid	H_2SO_4	98
Sal Ammoniac	NH_4Cl	53
Sulfur	S	32
Ammonium Sulfate	$(NH_4)_2SO_4$	132
Ammonium Bisulfate	NH_4HSO_4	115
Ammonium Mono Sulfite	$(NH_4)_2S$	68
Ammonium Sulfite	$(NH_4)_2SO_2*H_2O$	118
Ammonium Hy-dioxide	NH_4OH	35

AMMONIA LEAK PLAN OF ACTION

On discovery of an ammonia leak in a storage room, the liquid and hot gas lines feeding this room should be turned off (later the suction may need to be turned off if the leak persists). At first, this may be the valve on the manifold in the machinery room, but the valve closest to the leak is the most important one to close. When this one is off, others should be turned back on. The "king" valve (main liquid valve from the receiver) will not be turned off except for necessary work in the machinery room itself, and when all the compressors are turned off. In some old plants, "King" valves fed high pressure liquid directly to the entire system's air units. In modern plants today, they would normally feed the recirculating vessel, which pumps liquid to the air units. Also, liquid is used to cool compressors which may need to operate to help evacuate residual liquid where the leak occurred.

The suction line to the room should be inspected to determine if a valve should be closed to isolate the affected area. An inspection must be made to determine if a vacuum (suction pressure) needs to be maintained to remove ammonia. The leak should be repaired ASAP in order that refrigeration may be restored. Sulfur dioxide and ozone are alternative neutralizing agents that should not be considered under any condition for removing ammonia. Where water defrost units are the means of refrigeration, then they will also be used as an absorbing means by having the water run over the coils.

CHECKLIST OF "DOs AND DON'Ts"
DO use any of the methods mentioned.
DO allow temperatures to climb to the upper tolerance limit.
DO provide circulation within the room.
DO know where there is a supply of carbon dioxide.
DO learn what to do and do it without fear.
DO practice and plan so that prompt action takes place.
DO make safety first, not last.
DO use proper breathing apparatus. (Canister type masks should be replaced with SCBA equipment.)
DO have a plan of action in case of an ammonia spill.
DO train your fire department.
DO monitor oxygen and CO_2 levels when injecting CO_2 gas.
DON'T forget the water needed for neutralization to complete the CO_2/NH_3 method discussed in Part 4.
DON'T put an open flame or electrical arc in a room heavily laden with refrigerant.

Click HERE to download a Refrigeration System Safety Checklist you can use to assist you in operating your plant.

NOTES
There are numerous regulator requirements affecting life safety as well as environmental impact by Federal, State and Local regulatory agencies. These include the following:

NEPA – The National Environmental Policy Act of 1969
RCRA – The Resource Conservation and Recovery Act
TSCA – The Toxic Substance Control Act
Superfund
The Clean Air Act
The Clean Water Act
The Right to Know – Toxic and Hazardous Materials
Asbestos Regulations

Quite often regulations will conflict with each other. The ability to apply the most practical solutions is important for life safety. Experienced operating personnel as well as good emergency procedures for informed and capable fire departments are all contiguous to optimizing a safe working environment.

REMEMBER: Although some refrigerants are "self-alarming," like ammonia, most have very mild odors and displace air, similar to carbon dioxide or natural gas. Be sure air or oxygen is available in open and closed spaces before entering.