A Review of Atmospheric Ammonia Research Study

A study, discussed here, on handling large quantities of ammonia has provided a better understanding of atmospheric vapor-dispersion patterns and indicated the reliability of atmospheric-ammonia storage systems.

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Production and use of ammonia have grown tremendously in recent years, at average compound rates of 10% to 12% annually. U.S. consumption rose from 5 million short tons in 1960 to 13 million tons in 1968. Although future annual growth rates may decline to 6% to 8%, consumptions in 1975 and 1980 are likely to be about 20 million and 30 million tons, respectively. Similar patterns are manifest in many other countries. About 80% to 85% of current production is used in fertilizer manufacture, the remainder being taken by other industries.

Corresponding increases in production have not been achieved by building a multitude of small plants in the once common 100 to 200 tons/day range, but by installing relatively few large plants in the 750 tons/day to 1,500 tons/day category. The technical innovations making this feat possible have been well publicized. (1,2). Less familiar, however, is the progress made in storing and handling the huge tonnages now produced. Because most of the demand is for fertilizer purposes, the highly seasonal nature of farming creates additional storage problems. Not only must inventories be built throughout the year; they must be rapidly shipped during a few weeks, as soon as favorable weather conditions appear.

As with production, these challenges were met, not by installing large numbers of small units, but by designing and building relatively few large ones. Whereas 50 ton capacity storage tanks were commonplace a decade ago, current installations are in the 10,000 to 30,000 ton capacity range, or even greater (3). This has been made possible by changing from high-pressure storage at atmospheric temperatures to atmospheric-pressure storage at low temperatures (about −28°F). Simultaneously, drastic reductions in unit capital investment costs have resulted, with benefits to producers and their customers.

Atmospheric-pressure, low-temperature operations have also been extended to long distance ammonia shipments by barge and ocean going carriers, with further advantages and benefits to all.

The author is chairman of the Ammonia Storage Committee of the Compressed Gas Assoc., Inc., sponsor of the research study performed by University Engineers, Inc., Norman, Okla.

Like many chemicals, ammonia is a hazardous material which must be stored and handled properly. Although accidents have always been remarkably few, one might expect that their number would tend to increase in some direct relation to the rapidly increasing tonnages stored and handled. This has not been the case, undoubtedly due to careful precautions taken by the industry. As with earlier methods, atmospheric-pressure storage has proven extremely safe and reliable; nevertheless, there may still be improved ways of ensuring trouble-free operation.

For many years, the AIChE has provided technical guidance on ammonia storage and handling via its Subcommittee on Safety in Air Separation and Ammonia Plants, plus various symposia, articles and surveys—including one on atmospheric-pressure storage in 1964 (4,5). This voluntary work (mostly based on shared experience) has proved immensely helpful, as have the contributions of others, (6,7) in achieving a good safety record.

The industry felt it would be beneficial to supplement this knowledge by learning more about those potential hazards where little experience existed. It was decided to direct and finance the work via an Ammonia Storage Committee under the aegis of the Compressed Gas Association. To date, the following 38 domestic and overseas companies have appointed ammonia specialists to this committee and have given financial and technical support to an appropriate theoretical research program:

Air Products & Chemicals, Inc.
Allied Chemical Corp.
American Cyanamid Co.
Ammoniak Unie N.V. - Holland
The Borden Chemical Co.
Canadian Industries Ltd. - Canada
Central Farmers Fertilizer Co.
Central Nitrogen, Inc.
Chevron Chemical Co.
Chicago Bridge & Iron Co.
Cominco Ltd. - Canada
Cooperative Farm Chemicals Assn.
The Dow Chemical Co.
E.I. DuPont DeNemours & Company, Inc.
Farmland Industries, Inc.
The Fluor Corporation, Ltd.

Foster Wheeler Corp.
General American Transportation Corp.
Graver Tank & Mfg. Co.
W. R. Grace & Co.
Gulf Oil Corp.
Houilleres Du Bassin De Lorraine - France
Imperial Chemical Industries Ltd. - England
Kaiser Aluminum & Chemical, Inc.
The M. W. Kellogg Co.
The Litwin Corp.
Mississippi Chemical Corp.
Mobil Chemical Co.
Monsanto Co.
N. V. Nederlandse Stoatsmijin - Holland
Olin Mathieson Chemical Corp.
Phillips Petroleum Co.
Pittsburgh-Des Moines Steel Co.
J. F. Pritchard & Co.
Tuloma Gas Products Co.
United States Steel Corp.
USS Agri-Chemicals, Inc.
Valley Nitrogen Producers, Inc.

The storage study program

The three subjects covered by the research program were:

1. A literature survey and analysis of industrial data relating to the theory and practice of atmospheric-pressure ammonia storage.

2. Theoretical calculations involving the formation and extent of ammonia dispersion patterns, assuming large spills under hypothetical conditions.

3. Possible causes and effects of temperature stratification and roll-over in atmospheric-pressure ammonia storage tanks.

The committee retained University Engineers, Inc. of Norman, Okla. to perform the literature search and make the theoretical studies. The assignment was carried out in 1965-66, under the direction of C. M. Sliepcevich. This report is based on an analysis of that work.

The program was supplemented by a questionnaire distributed to the industry by the committee, requesting information on previous experience with ammonia leaks and spills, with special reference to atmospheric-pressure storage.

The literature survey encompassed about 750 pertinent references and revealed that theoretical approaches were relatively advanced, but experimental and practical data were scarce. Similarly, little pertinent information resulted from the industry questionnaires; of the 47 spill incidents reported, only two specifically involved atmospheric ammonia storage. In one of these, a leak developed from a crack in the floor plate of a small tank, while in another a seal failure occurred on a transfer pump located within the dike area of a large atmospheric ammonia storage tank.

Other reported mishaps included ten cases of failure in flexible hoses or couplings; 11 instances of leaks from small piping, gaskets and appurtenances; five ruptures due to premature movement of tank cars or trucks; and 19 miscellaneous incidents. Reported fatalities were few; one occurred when a liquid ammonia manifold on a barge ruptured, and another when a maintenance worker mistakenly removed a valve from a loaded tank car.

Nevertheless, despite the absence of data which could be used for research purposes, the industry survey revealed two important facts. First, in some cases when a spill occurred, although safety equipment had been installed and safety procedures had been provided, it was impossible to carry them out promptly because of escaping ammonia. Second, canister-type masks proved to be inadequate in the high concentration of ammonia vapor found to exist.

Apart from some instances of sticking valves, which were remedied by using appropriate trims and lubricants, the survey yielded little information about potential spills, one of which was ten tons in size. Two accounts of temperature stratification were received along with several reports on the effects of sudden, significant barometric changes. Two theorectical contributions on large scale spills and temperatures stratification were also offered.

Without adequate practical data, the only way to predict the dispersion of ammonia into the atmosphere following a liquid spill was to undertake a theoretical analysis involving the simultaneous application of heat and mass transfer rates. It was, of course, realized that the initial flash, the transient decay and eventual attainment of steady state evaporation, plus variable soil and weather conditions, could introduce significant complexities. Using certain assumptions, these factors were taken into consideration.

Likewise, the study of possible causes of roll-over, such as temperature stratification and hydrodynamic instability was hampered by the paucity of practical data. Bump-boiling, another atmospheric ammonia-storage phenomenon which might possibly induce a potential hazard, was also examined in terms of available theory. Where applicable, relevant information from the literature search and the industry survey was used to supplement the research study.

The initial consequences of a large liquid-ammonia spill would be the resulting evaporation and release of relatively large amounts of vapor to the surrounding area. In a theoretical approach, the first problem is to determine evaporation rates, and the second is to define dispersion rates and patterns.

Evaporation rates can be estimated by heat and mass transfer calculations. Enough energy must, of course, be available to vaporize the liquid ammonia, which can come from:

1. Ground conduction. This will decrease as the soil is cooled.

2. Ambient air. As the pool temperature drops, the

temperature difference will increase.

3. Solar radiation. Contribution will be appreciable in hot weather, but low on cloudy days, and negligible at night.

4. Sensible heat of the liquid. This will contribute to evaporation as the pool cools down.

5. Free moisture in the soil. When present, it will react with seeping ammonia and liberate heat.

6. Other factors such as rain, wind, fog, water, and possible chemicals used in combating the spill.

Initial flash

Immediately upon release to the atmosphere, a portion of any liquid ammonia spilled would flash off as vapor. For ammonia from a refrigerated tank operating at about 0.5 psig, this fraction would amount only to about 0.2% of the total. In a pressure-storage system under 126 psig and 75 F, for example, about 20 per cent of the spilled ammonia would be flashed. Hence the per cent initially flashed is reduced by a factor of 100 when liquid ammonia is stored under atmospheric-pressure, refrigerated conditions. Figure 1 shows the relation between the per cent of ammonia flashed and initial temperatures and pressures.

Following an initial flash, evaporation behavior would depend on the relationship between evaporation rates and the flow of heat into the pool from the ground, the air, the sun, and the rate at which the vaporized ammonia is removed from above the spill. Heat transfer from ground to pool is a function of soil thermal conductivity, density, specific heat and temperature. Calculations show that the thermal-conduction rate decreases with time and approaches zero when steady state conditions are reached.

The rate of heat transfer by convection from ambient air to a pool is dependent on the corresponding heat transfer coefficient (h) and the temperature difference. A lack of experimental information on this phenomenon made (h) difficult to assess directly, and an analogy between convective heat and mass transfer had to be used to calculate this coefficient before the heat contributed by convection could be determined.

The amount of solar radiation energy that can be absorbed by a pool varies widely, from about zero on a dull day or at night, to some 80 per cent of the solar constant, which is about 360 B.t.u./ft.^{2}/hr. on hot days. Re-radiation would be negligible at the low temperatures prevailing.

Energy required to evaporate the ammonia spilled is a function of the total mass, the heat of vaporization, and the mass evaporation rate (m). Because appropriate practical information was lacking, (m) was calculated using the film theory of mass transfer in an analogous way to determining the convective heat transfer coefficient (h.)

By solving simultaneous equations for heat and mass transfer, pool temperatures and evaporation rates were determined for various conditions, as illustrated in Figures 2 and 3. Steady state temperatures and evaporation rates
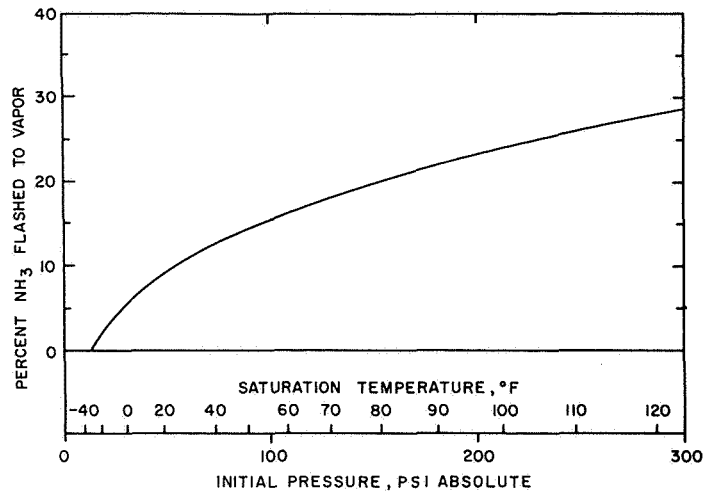

Figure 1. Per cent of ammonia flashed to vapor following spill of pressurized liquid ammonia.
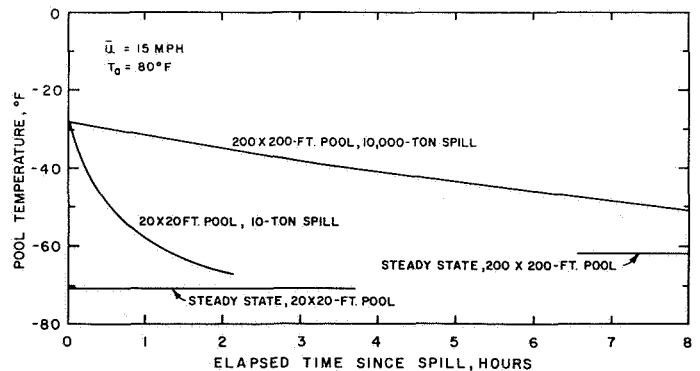

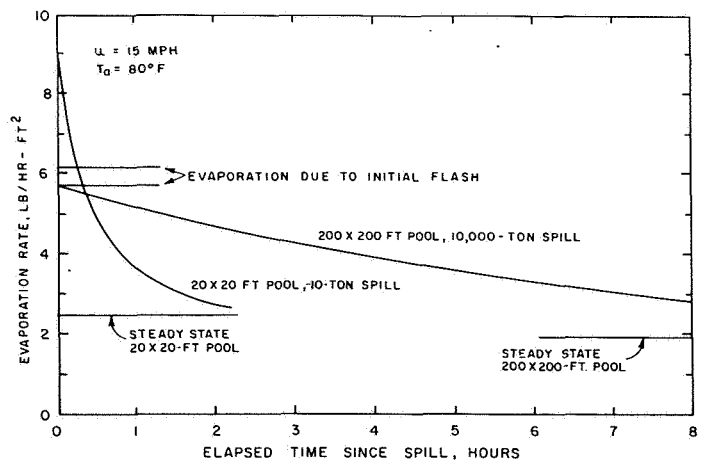Figure 2. Temperature of liquid ammonia pools as a function of time following 10 ton and 10,000 ton spills.

Figure 3. Evaporation rates from liquid ammonia pools as a function of time following 10 ton and 10,000 tons spills.

3

per unit vary only slightly with pool size. However, early temperatures are much lower and early evaporation rates are higher for shallow pools than for large ones; accordingly, a shallow pool will reach steady state conditions more quickly.

In experimental tests on one ton and ten ton pools of liquid ammonia, evaporation rates of 6.8 lbs./hr./sq. ft. were obtained which, if extrapolated to steady state conditions, indicated an apparent evaporative loss rate of about 3.7 lbs./hr./sq. ft. Some ammonia was also lost by seepage into the soil; thus the true evaporative loss was less than indicated by the figures given above. Comparing the results of these tests with those in Figure 3, and considering all of the inherent variables and assumptions, there is good accord between the theoretical approach and the practical tests.

Calculated steady state values for pool temperatures and evaporation rates under different atmospheric conditions and for a range of pool sizes are depicted in Figures 4 and 5. In deriving the results shown in Figures 2 through 5, it was necessary to make several simplifying assumptions, e.g., that pool temperatures would be uniform en masse, and that the physical properties of the soil and ammonia would remain unaffected.

Vapor dispersion

A theoretical study of dispersion (8,9) of ammonia vapor into the atmosphere following a spill is complicated and difficult to interpret in a practical way because of the widely different conditions existing at each site.

Wind velocity and gustiness, humidity and atmospheric stability are major factors affecting diffusion rates and dispersion patterns. High humidities promote formation of an ammonia fog which can retard dispersion. Stability, or the propensity for displacing air to different altitudes, is largely controlled by temperature gradients. A profile having a temperature rise with increasing altitude is termed an inversion, while the converse is known as a lapse state. The latter will tend to disperse a mass of ammonia-laden air much more rapidly than will an inversion. A condition where no temperature difference exists is known as an isothermal.

Because of temperature and density factors, neutral atmospheric conditions can prevail under strong gusty winds or overcast skies, when heating or cooling at the earth's surface is small. Daytime solar heating tends to promote super-adiabatic or rising air flows and nighttime cooling induces sub-adiabatic or inversion conditions. These different patterns could greatly affect dispersion of ammonia vapor, following a spill. Similarly, buoyancy differences between parcels of air-ammonia vapor and air could be expected to influence dispersion behavior, but lack of data precluded theoretical consideration of these effects. However, high initial concentrations of ammonia vapor could be expected to increase buoyancy and therefore assist vapor dispersion to some extent.
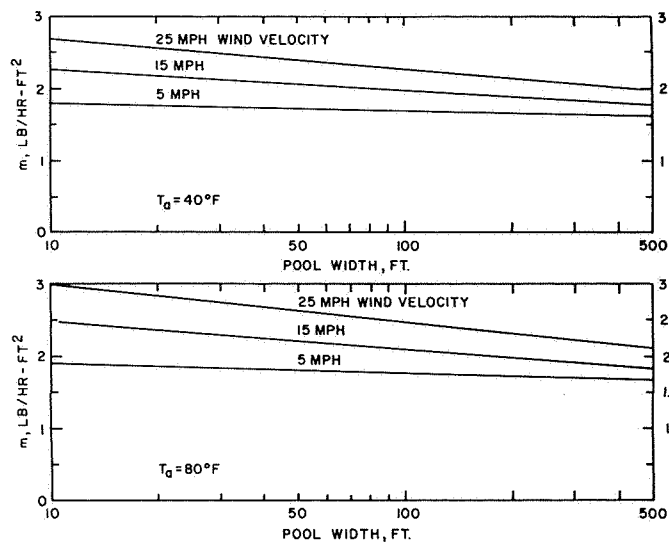

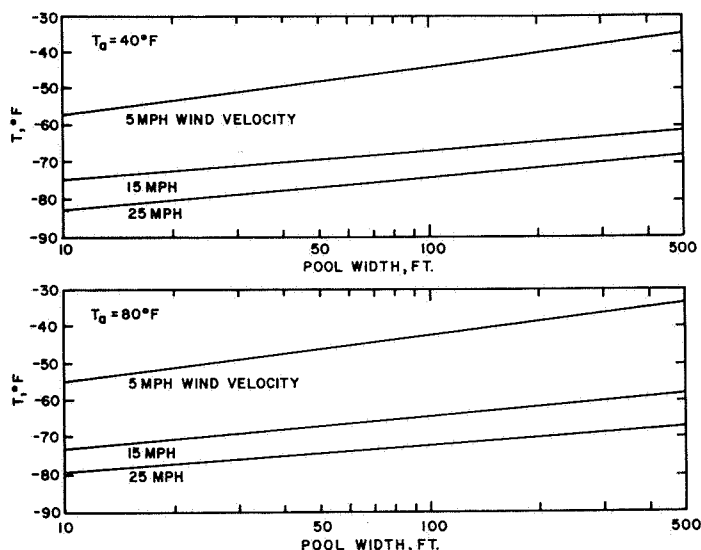Figure 4. Steady-state evaporation rates for square liquid pools.

Figure 5. Steady-state pool temperatures for square liquid ammonia pools.

Several mathematical approaches to the study of atmospheric dispersion exist, one of the earliest being the K theory by which coefficients of diffusion along spatial coordinates from a point source can be calculated in a manner analogous to Fick's parabolic law. But it was soon apparent that under typically varying atmospheric conditions, these coefficients could not be constant; moreover, they varied with distance from the source (which also is rarely a point). By making several simplifying assumptions (10), it was possible to use the K theory in conjunction with a digital computer to calculate vapor concentrations under point-source conditions. However, area-source studies could not be made because of complexity and time considerations, even with the aid of a large computer. Consequently, other approaches were examined.

One applicable method was found to be statistical

4

route *(11-13)* which assumes wind movement to result from a combination of steady and unsteady components along the three spatial coordinates. By making various simplifying assumptions (such as the reduction of variable components to zero), expressions could be obtained for point-source diffusion. Then, with the aid of dimensionless analysis and experimental data such as obtained in "Project Prairie Grass" studies *(14)*, diffusion coefficients and concentrations could be calculated under inversion, neutral and lapse conditions for various source-configurations and distances.

Calculations were made for square pools ranging in size from 30 ft. x 30 ft. to 500 ft. x 500 ft. and for wind velocities of 5 mph and 25 mph. Downwind drift concentrations of 100 ppm and 1,000 ppm were used as examples since usually 100 ppm of ammonia can be tolerated for an extended period of time, but at 1,000 ppm a person experiences coughing and severe eye irritation and is impelled to leave the area.

With a neutral atmosphere, calculations disclosed that a 1,000 ppm concentration can occur at a distance of about ten pool diameters downwind when the wind speed is 5 mph. At 25 mph wind speed the distance for 1,000 ppm concentrations reduces to about four pool diameters. When there is an atmospheric inversion, these distances can increase between two and three times. An atmospheric lapse state will substantially reduce the downwind drift.

The only practical data available to date on ammonia vapor dispersion indicated concentrations of 1,000 ppm and greater, reaching downwind to 150 ft. from a 5 ft. x 22 ft. pool. Concentrations in the 50 ppm to 1,000 ppm range were found up to distances of 500 ft. These figures were obtained long before steady state evaporation was reached, and when extrapolated to steady rate conditions, reasonably close correlations with theoretical results were obtained.

To conclude: all theoretical results emphasize the retarding effects of inversions on atmospheric ammonia dispersion, and the favorable influence of winds, which not only can sweep away evaporated ammonia, but can stimulate helpful conditions—provided they do not carry vapor into a critical area. Under absolutely calm conditions, dispersion might even take longer than with an inversion plus a slight wind. Regarding pool sizes, calculations indicate that larger areas will increase distances at which high concentrations of ammonia vapor might occur. The possible effects of topography and buildings could not be included in the general approach undertaken.

Roll-over and temperature stratification

A few operators have observed occasional, spasmodic pressure fluctations in atmospheric-pressure ammonia storage tanks, sometimes accompanied by vibrations and rumbling noises *(4)*. These phenomena have been attributed to sudden migrations of warm liquid from the bottom of the tank to the surface, with the release of a large volume of vapor. A theoretical study of conditions which could promote this behavior (known as "roll-over") was undertaken and attempts were made on the following lines to define possible hazards.

When a liquid is warmed at a depth, a lower layer will tend to move from a level where its vapor-pressure is below local hydrostatic pressure, to a higher level where its vapor-pressure exceeds or equals the hydrostatic head. The liquid becomes thermodynamically unstable and returns to its equilibrium temperature, simultaneously releasing a certain amount of vapor. Calculations have shown that if 1,000 tons of liquid ammonia at $-27°$F migrated to the surface of a tank kept at $-28°$F and 14.7 psi actual, about 87,000 std. cu. ft. of vapor would be produced, equivalent to a removal of 2.31×10^6 B.t.u. from the liquid. If this were to occur within a one minute period, cusomary pressure-relief systems would be overwhelmed. (This quantity of heat is equivalent to the total heat leak of a 20,000 ton tank full of ammonia over a period of about 39 hrs). With this scale of events in mind, however unlikely or improbable, major constraints were examined and their effects related to typical operating conditions. Included in possible causes of roll-over were:

1. Sudden inducements of convection in an initially static liquid zone.

2. Transitions from laminar to turbulent free convection.

3. Sudden transitions within an established, turbulent, free-convection zone.

4. Changes in absolute tank pressure which might nullify free convection forces.

The only experimental information available showed possibilities of a roll-over due to the above causes were remote. Although these data were based on fluid layers between 1 mm. and 100 mm. (contrasted with 10ft. to 100 ft. typically existing in ammonia storage practice), theoretical analyses supported this conclusion. However, these calculations were based on highly idealized models and additional practical data would have been helpful.

Conjectured causes of noise and vibration were incipient boiling of liquid ammonia at the base or sides of the tank, or in attached piping. Provided insulation is effective and intact, temperatures at the tank bottom and at most of the wall are much lower than needed to initiate boiling. But, when localized failure of insulation has occurred—caused by damage or moisture under the tank for example—boiling can take place in such a region, as the inward heat flow may be much greater than the dispersion possible via free convection. Sudden migration of bubbles to the surface and their collapse would undoubtedly generate some noise and vibration (like the singing of a monstrous kettle) and create the phenomenon known as "bump-boiling." On a sufficiently large scale this could lead to temporary overpressure and might constitute a potential hazard. Obvious remedies are to ensure that insulation is installed properly and maintained effectively and to circulate ammonia externally from the bottom of the tank to the surface, if the problem persists. As a guide,

Figure 7. Vertical temperature profile in a horizontal layer of fluid heated from below.
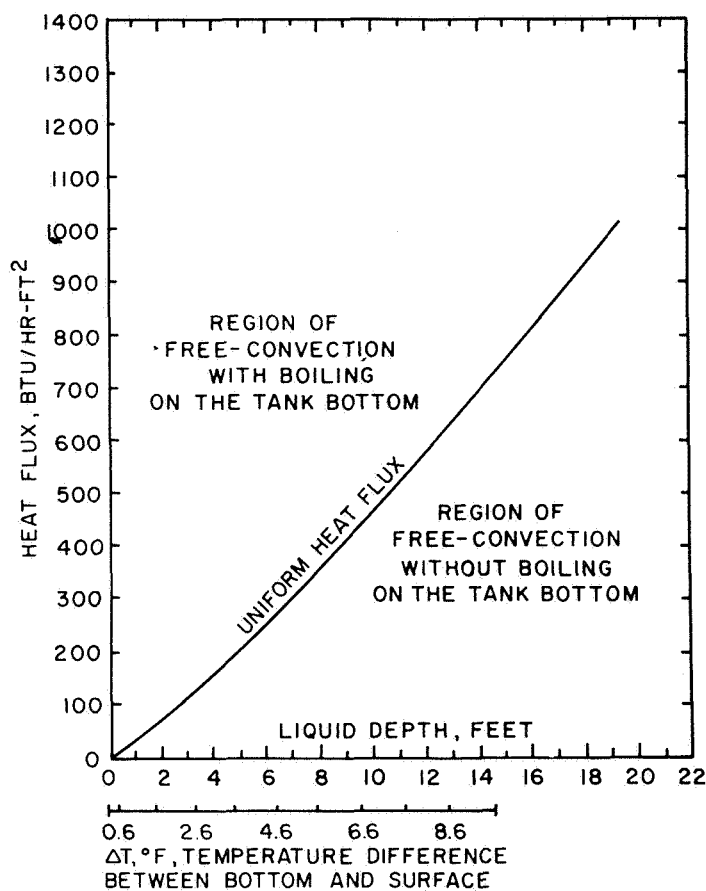

Figure 6. The maximum heat flux for free-convection without boiling on the bottom of a tank as a function of liquid ammonia depth for a horizontal layer of liquid ammonia heated from below.

maximum heat fluxes for free convection without boiling are shown in Figure 6, which is based on uniform heating of a tank bottom (15). No realistic information for a tank with partially damaged insulation has been obtainable, but in such cases the local heat flux would be below the indicated curve.

In addition to the foregoing possible causes of roll-over and noise relative to design and operation, the effects of natural convection were examined with special reference to thermodynamic and hydrodynamic stability. Calculations showed that a layer of liquid ammonia heated from below would be stagnant for a steady heat flux less than 0.00189 B.t.u./hr./sq. ft.

Since the heat leak in atmospheric ammonia storage practice is at least 1,000 times greater, the liquid should be highly unstable mechanically and subject to strong, natural convection. However, this heat-flux figure really indicates the limit above which free convection is possible and not the extent of departure from equilibrium necessary to induce motion.

Further calculations revealed that the required departure from equalibrium conditions (16-18) could be generated by a temperature difference of only 0.0005°F between the top and bottom layers of a 1 ft. depth of ammonia. For a 100 ft. depth, the necessary temperature difference came to 0.055°F. Therefore, it may be concluded that natural convection in an ammonia tank is extremely sensitive to small temperature changes, especially in the vertical plane. Consequently, the likelihood of roll-over occurring with pure ammonia in an insulated tank due to temperature stratification or other thermal causes is remote.
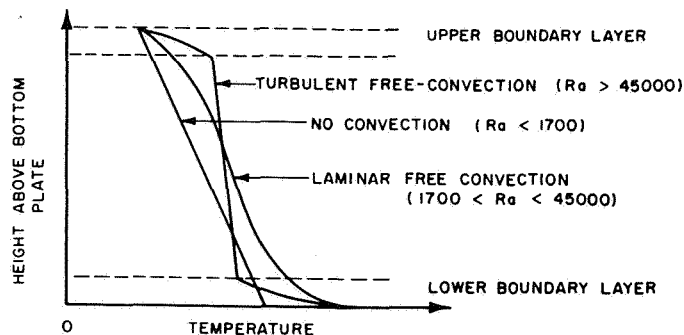
Effects of water

Should an impurity such as water be added to liquid ammonia in a storage tank, the temperature and density gradients needed to impart free convection would change, especially if a concentration gradient were also created by imperfect mixing or stratification. In such a case, the average temperature of an ammonia-water layer subjected to an inward heat leak would steadily increase to several degrees greater than the boiling point of liquid ammonia at tank pressure. This warmed stratum would also gradually overcome opposing density forces and rise to the surface, with a corresponding release of a large amount of vapor within a short period.

Calculations indicate that unstable conditions of this nature might arise if contamination by water approached a level of about 1 mole %, (about 10,600 ppm). While it is unlikely that concentrations of this magnitude would be encountered in normal practice, it must be borne in mind that to reduce stress-corrosion cracking, water is often injected to levels of about 2,000 ppm. Therefore, if there is any likelihood of accidental concentrations greater than about 5,000 ppm occurring, circulation of liquid ammonia in the tank appears advisable to minimize any possibilities of instability and sudden boil-off.

For a horizontal lens of liquid heated from below, the vertical temperature gradient would be uniform for no convection, but under turbulent free convection conditions, temperature differentials could be expected to be concentrated within the thin, horizontal top and bottom boundary layers (19). The bulk of the liquid would be essentially at uniform temperature. Thus, a transition from laminar to turbulent free convection at the upper surface might reduce the bulk average temperature, raise the boundary temperature, and simultaneously result in some boil-off from the upper boundary layer. But this would be dampened by a pressure increase which would repress a sudden evolution of vapor, and the resultant effect should be of little consequence. The empirical temperature profiles involved are illustrated in Figure 7 together with corresponding Rayleigh Numbers.

Heat will also enter an ammonia storage tank via the vertical wall (and roof), but the thickness of the boundary layer compared to the tank diameter is very small. Consequently, the heating effect on the total contents is minimal and only likely to become of any significance at very low tank levels. Hence, no potential danger appears likely from this type of heat leakage.

Other possible origins of instability and roll-over that

were examined included transitions within a turbulent, free convection system and the suppression of natural convection by a sudden increase in tank pressure. However, it has already been shown that under normal, free convection conditions, most of the temperature differences are confined to the thin, horizontal boundary layers. Thus, even if boundary conditions were suddenly changed, it would take several hours before the total contents came into equalibrium with the new conditions. This is well known to operators; tank pressures can be lowered quickly, but maintaining pressures at reduced levels necessitates removal of boil-off for several hours. This indicates a rapid response from boundary layers and a slow one from the liquid bulk. Because of this flywheel effect, hazards due to sudden changes, or errors in temperature and pressure control are greatly minimized.

Also studied were possible effects of variations in tank pressure on the warm liquid which rises from the tank walls and stratifies near the surface *(20,21)*. It was established that under increased pressure, this liquid would accumulate until the rising temperature triggered flash evaporation, and subsequent cooling. The resulting downward movement of denser liquid would contribute to circulation. Accordingly, no potential hazard from this source appears likely.

Summary of research study

A theoretical method of predicting ammonia vapor diffusion and dispersion from area sources under widely different atmospheric conditions was developed. It showed, under adverse conditions concentrations in the 1,000 ppm category might appear as far as 20- to 30-pool diameters downwind, following a large spill.

An analysis was made of circumstances which might lead to roll-over, hydrodynamic instability, and the release of hazardous volumes of ammonia vapor from large storage tanks. It revealed that temperature stratification caused by heat leakage is an unlikely cause, as only about $0.0005°F$ gradient/ft. will initiate and maintain natural circulation. However, concentration gradients (as might be caused by the addition of water) do appear to be possible causes of instability. For this reason thorough mixing is recommended when water concentrations could be in the 5,000 ppm category or higher.

The occasionally observed noises and rumblings from ammonia tanks known as bump-boiling appear to be caused by spasmodic bubble formation. In pronounced cases when tank pressure-control might be affected, better insulation, especially under the tank bottom, or ammonia circulation, should provide a remedy.

Based on the results of this research study and the practical experience of the members of the Ammonia Storage Committee, the following observations and suggestions can be made:

1. Although trite, the best protection against a spill is the prevention of one. Therefore, careful attention to location, design, construction and operation is essential.

2. The most vulnerable items in atmospheric ammonia storage systems are associated connections, fittings and pumps.

3. Fail-safe equipment with *remote*, manual over-rides is often desirable.

4. The study also shows it is desirable to minimize the area of a pool that might result from a spill.

5. Rubber suits and self-contained breathing apparatus are necessary to approach a large spill. Use of water must be undertaken with great caution, as the heat liberated is likely to amplify an already hazardous local vapor concentration.

Literature cited

1. Gambrell, L.M., et al, *Oil Gas J.* (March 27, 1967).
2. Piombino, A.J., *Chem. Week* (September 11, 1965).
3. Cook, J.L., *Chem. Processing* (March, 1969).
4. AIChE, "A Survey of Low-Pressure Storage of Liquid Ammonia," CEP Technical Manual (1964).
5. AIChE, "Safety in Air and Ammonia Plants," CEP Technical Manual (1965).
6. Agricultural Nitrogen Institute, "Standards for the Storage and Handling of Anhydrous Ammonia," ANI Std. No. M-1.
7. "American Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia," USAS K61.1-1966, Compressed Gas Assoc., Pamphlet G-2.1.
8. Pasquill, F., "Atmospheric Diffusion," Van Nostrand Co., New York, (1962).
9. U.S. Weather Bureau, "Meterology & Atomic Energy," U.S. Government Printing Office, Washington, D.C. (1965).
10. Roberts, P.H., "Non-Equilibrium Thermodynamics, Variational Techniques & Stability," R.J. Donelly, et al, Univ. of Chicago, Ill., 115 (1966).
11. Taylor, G.I., "Statistical Theory of Turbulence, Parts 1-4," *Proc. Roy. Soc. London* (1935).
12. Stutton, O.G., *J. Roy. Met. Soc. London*, 73, 420 (1947)
13. ., *Proc. Roy. Soc. London*, Series A, 204, 297-309 (1950).
14. Haugen, D.A., et al, *J. Meterol.* 18, 386 (1961).
15. Dropkin, D., and E. Somerscales, *J. Heat Transfer*, trans.: ASME Series C, 1964.
16. Ostrach, S., and D. Pnueli, *J. Heat Transfer*, trans.: ASME Series 85, 346-54 (1963).
17. Pnueli, D., *J. App. Mech.* 31, Section 3, 376-79 (1964).
18. Pellew, A., and R. V. Southwell, *Proc. Roy. Soc. London*, Series A, 176, 312 (1940).
19. Schmidt, R.J. and O.A. Saunders, *Proc. Roy. Soc. London*, Series A, 165, 216 (1938).
20. Clark, J.A., "Advances in Cryogenic Engineering," 10, 259, (1965).
21. Eckert, R.G., and T. W. Jackson, "Analysis of Turbulent Free-Convection Boundary Layer on Flat Plates," NACA, TN 207, October, 1950.