

HAZARD OF LIQUID AMMONIA SPILLS FROM LOW PRESSURE STORAGE TANKS

H. W. Husa and W. L. Bulkley
American Oil Co.
Whiting, Ind.

Catastrophic brittle failure of atmospheric pressure storage tanks has occurred at low temperatures. Although the probability of failure is very small, an evaluation of the hazard created by sudden failure of low pressure ammonia storage tanks or fittings provides an estimate of the worst condition. Inasmuch as ammonia is combustible as well as toxic (1-3) analysis of the hazard of a large spill involves consideration of both properties.

Tank failure produces a large pool of liquid ammonia within the diking. (Undiked tanks are not considered here.) Fortunately, the liquid initially is at its atmospheric boiling point so the vaporization, which creates both hazards, is determined only by heat transfer from the ground and the atmosphere and by auto-refrigeration. Discussed herein are the vaporization rate, meteorological considerations, and the burning properties of the liquid pool.

Vaporization considerations

Recent work by the Bureau of Mines (4) with liquid methane spills in large earthen dikes provides a basis for estimating vaporization rates and the characteristics of the cloud of ammonia. For the purposes of this analysis, a 15,000 ton atmospheric storage tank with a 300 x 300 ft. diked area is considered. A tank of this capacity is roughly 120 ft. in diameter and 68 ft. high. The full volume of the tank would give a liquid depth of 7 to 8 ft. in the diked area.

Because of the low temperature of the liquid ammonia in atmospheric pressure storage, all vapor evolved initially is the result of heat input from the ground, the air, and the sun. Of these, the heat input from the ground is dominant during the first minute or two of the spill. The heat stored in the upper layer of the soil is rapidly lost to the ammonia; thereafter, the soil acts as an insulating barrier to the transfer of heat from the lower strata. Heat input from the air and sun is relatively constant and eventually becomes controlling. As a result, the vaporization rate ultimately stabilizes.

Effect of soil characteristics

The initial vaporization from ground heat depends in major part upon the nature of the soil and the

size of the rubble within the dike. For coarse rubble, it can be an order of magnitude greater than for "average" soil, and 20 times that for dry sand (4), because of the larger surface exposure of the rubble and the ability of the liquid ammonia to rapidly penetrate and wet a deeper layer of stone. Soil and sand offer a surface exposure approximately the same as the ground area within the dike and offer more resistance to liquid penetration during the boiling period. Dry sandy soil is superior to average soil because it offers more resistance to heat flow to the liquid ammonia.

Vaporization rates were computed for a 4 mile/hr. wind, strong sunlight, and a ground surface temperature of 70° F. Somewhat different values would be obtained at other atmospheric conditions. Seasonal changes are significant only as they affect ground surface temperature. On this basis, rates of vaporization are in pounds per minute:

	Coarse rubble	Average soil	Sand
Initial flash	110,000	10,000	5,200
Steady state	1,800	1,800	1,800

The initial flash lasts about one to two minutes. The contribution of ground heat to vaporization then rapidly diminishes and at steady-state conditions is relatively unimportant. Because the initial and steady-state conditions are of principal interest here, the heat conduction equation (4) has not been modified to account for changes in ground temperatures with depth.

Meteorological considerations

The evolved vapor will be carried downwind in a rising cloud. The distance at which toxic or flammable conditions exist depends upon both the rate of vapor evolution and wind velocity. Meteorological data on the dissemination of lighter-than-air gases are not extensive. However, calculations based on generally accepted techniques (5) for the initial vaporization rates indicated above and a wind velocity of 4 mile/hr.

indicate the approximate extent of downwind hazard at grade:

	Maximum distance downwind, ft.		
	Immediate Eye irritant*	Dangerous for short exposure**	Flammable mixture
Coarse rubble	5,000	2,500	1,000
Average soil	2,000	700	100
Sand	1,300	300	50

*The "immediate eye irritant" criterion is based on an average concentration of 700 ppm at grade downwind; however, momentary peaks of much higher concentration will occur. Duration of this concentration at the indicated distance will range from about 2 min. for sand to 5 min. for coarse rubble.

**The "dangerous for short exposure" criterion is based on an average concentration of 3,000 ppm at grade downwind. Concentrations both higher and lower will occur. Effects of momentary exposure to the higher concentrations are not known. Duration of this concentration at the indicated distance will range from 1 min. for sand to 3 min. for coarse rubble.

Steady-state conditions

At the steady-state condition, flammable mixtures may exist only near the liquid surface and at the top of the downwind dike wall; eye irritant concentrations will extend for only about 500 ft. from the dike.

The computed steady-state values will change with wind and solar input. However, the dispersive properties of the atmosphere change correspondingly. For example, at night the reduction in vaporization rate due to the absence of solar heat will be compensated, in part, by the absence of the dispersive convective currents generated by that heat. Consequently, downwind toxic levels may not decrease in proportion to the reduced vaporization, but may even increase. Similarly, stronger winds, which provide more dilution air at grade, will also increase the vaporization rate and will direct the vapor cloud toward the ground, thereby, reducing dispersion into the upper atmosphere. In view of these compensating factors and the approximate nature of the diffusion equations, the tabulated values are reasonably typical.

Burning of liquid ammonia

Although flammable properties of ammonia vapor-air mixtures have been studied (1), the extent of burning above a liquid pool has not been reported. The fire hazard of the vapor evolved from liquid ammonia contained within diking was discussed, with no conclusions, in the Air Separation and Ammonia Plant Safety Symposium at the 1963 San Juan meeting of the A.I.Ch.E. In view of this question, simple tests were made with small pools and with spills on open ground.

The tests were conducted in a 3 ft. × 3 ft. × 2 in. deep pan filled with liquid anhydrous ammonia. Studies with burning pools of hydrocarbons (6) indicate that data obtained in pans of this size can be extrapolated to larger pools. During the test periods air temperature was 83 to 84°F with bright sunshine. Wind was steady at 17 mile/hr. for some tests and was variable at 7 to 12 mile/hr. for the balance of the work.

The pan was placed at grade in an area of crushed, compacted steel-mill slag. Liquid ammonia was poured into the pan with violent initial boiling.

After a few minutes, the boiling subsided and near steady-state conditions were established. An ignited railway fusee was then passed through the vapor above the liquid surface and through the vapor cloud rolling over the downwind lip of the pan. All areas of the pan were probed from the surface of the liquid upward for several inches. No sustained flame was observed. Brief local flashes occurred when the flare was brought near the liquid surface. Touching the liquid with the fusee tip did not intensify or extend the flame. Submerging the tip extinguished the flare.

Spillage to surroundings

A portion of the liquid in the pan was spilled onto the surrounding slag where it boiled vigorously. Moving the flare into the vapor cloud resulted in ignition. The vapor burned with a colorless flame which persisted after the flare was removed. The flame was stable in the brisk wind, and some tongues of fire were 10 ft. long. Radiation from the flame could be felt, but its intensity was considerably less than that from a hydrocarbon fire of comparable size.

Burning ceased when boiling stopped. With the addition of liquid ammonia, the fire could be rekindled, but it was smaller. With each successive addition of ammonia, the fire diminished in size and eventually degenerated into a wisp of flame in the lee of the pan lip. The ammonia-wetted slag was quite cold to the touch.

When water was sprayed onto the cold ammonia-wetted slag, vigorous boiling occurred. The vapor burned and the flames were stable in the wind. The burning sequence was repeated with spills onto fresh slag. However, at no time could the flame be made to propagate back into the liquid ammonia pool in the pan.

Although the ammonia flames were noticeably less intense than hydrocarbon flames, subsequent tests demonstrated that ammonia flames can ignite hydrocarbon-air mixtures and readily combustible solids such as paper and wood splinters.

Reduction of toxic hazard

Inasmuch as the combustion products of ammonia contain only small quantities of oxides of nitrogen (7), the products are less toxic than the unburned ammonia. It has been suggested that the toxic hazard from a spill could be lessened by burning ammonia vapor as it evolves. Obviously, this procedure would be effective only if the ammonia vapor were nearly completely consumed.

Ammonia-air mixtures were burned in bench-scale, closed equipment that permitted recovery of the combustion products. Even with a stable flame, only a portion of the ammonia was consumed. This effect is similar to results obtained in earlier studies of ammonia explosions in closed vessels (1). Figure 1 shows the ammonia consumed in these explosion tests as a function of mixture composition.

Field tests to determine ammonia consumed during the burning of vapors above open pools were not attempted. The laboratory data indicated adequately that open burning would not consume a substantial fraction of the ammonia because of the apparent requirement that the mixtures with air would need to be nearly stoichiometric. The toxic hazard downwind would be alleviated only to a small degree by partial combustion of ammonia. For example, calculations show that the extent of the downwind toxic zone would be reduced only 25%, for the initial vaporization condition, if 50%

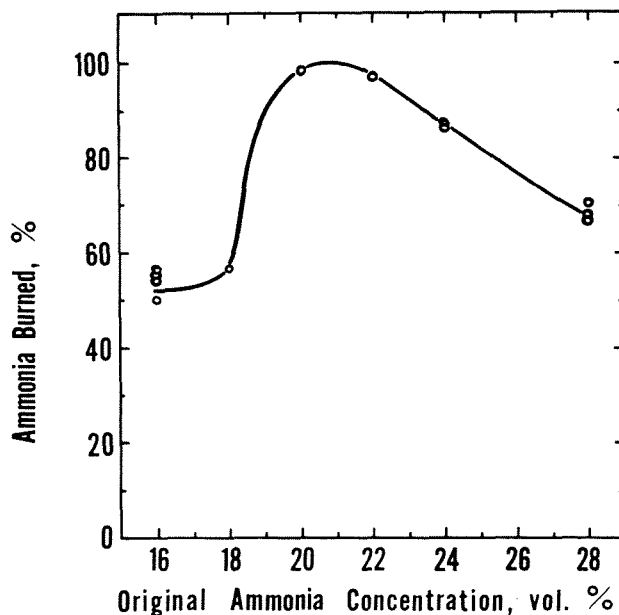


Figure 1. Combustion of ammonia-air mixtures in a closed vessel 25 in. long and 5 in. in diameter.

of the cloud were burned. Further, the requirement that an adequate ignition source be available as the initial vaporization occurs, and at the proper location, makes protection by burning highly unreliable.

Conclusions

The initial high rate of vaporization following a large spill of low temperature ammonia is controlled

primarily by heat transfer from the ground and may be minimized by retaining the liquid within dikes and by having smooth packed sand or soil in the enclosed area. This initial vaporization can create toxic and fire hazards a considerable distance downwind for a short time. Subsequent steady-state vaporization is controlled by atmospheric conditions and provides a minimal, local fire hazard and a moderate toxic hazard only a short distance downwind. Flames above liquid ammonia do not radiate adequate heat to maintain the vaporization rate necessary for continued burning. Therefore, fires above large pools should not be fought with water but permitted to burn out. Intentional burning of ammonia vapor can reduce the toxic hazard somewhat, but reliable ignition is difficult.

LITERATURE CITED

1. Bulkley, W. L., and H. W. Husa, *Chem. Eng. Progr.*, 58, p. 81 (1962).
2. Henderson, Y., and H. W. Haggard, "Noxious Gases," Second and Revised Edition, Reinhold Publishing Corp., New York (1943).
3. Sax, N. I., "Dangerous Properties of Industrial Materials," Reinhold Publishing Corp., New York (1963).
4. Burgess, D., and M. G. Zabetakis, U. S. Bureau of Mines Report of Investigation 6099 (1962).
5. Magill, P. L., R. F. Holden, and C. Ackley, "Air Pollution Handbook," McGraw-Hill Book Co., Inc., New York (1956).
6. Blinov, V. I., and G. N. Khudiakov, *Academia Nauk, SSSR Doklady*, 113, p. 1094 (1957); review by Hottel, H. C., *Fire Research Abstracts and Reviews*, 1, p. 41 (January, 1959).
7. Kirk, R. E., and D. F. Othmer, ed., "Encyclopedia of Chemical Technology," Vol. I, p. 773, The Interscience Encyclopedia, Inc., New York (1947).

ADDENDA

In the calculation of vaporization rates and downwind conditions, it was assumed that the liquid ammonia temperature remained at the atmospheric boiling point as in the studies with liquefied natural gas (ref. 4 in the paper). However, as the paper by G. O. Morgan and J. D. Reed (this volume) correctly notes, additional vapor will be released and the liquid temperature will decrease as a result of auto-refrigeration. This discussion considers this additional vaporization as it affects the downwind conditions. Only the case in which the diked area contains coarse rubble will be covered inasmuch as it provides the maximum hazard situation.

Russian work

A Russian paper, now available in translation (8) provides equations for calculating evaporation rates for liquids exposed to moving air. Under the conditions assumed in the paper—300 × 300 ft. diked area, 4 mile/hr. wind—the computed rate is 12,000 lb./min. at the initial temperature, -28°F. Hence, heat transfer is the controlling factor initially, and the maximum downwind effects indicated in the paper are unchanged. After the initial boiling period, the decrease in liquid temperature through auto-refrigeration is accompanied by a decrease in the evaporation rate so that conditions after the initial period of rapid vaporization are substantially less hazardous. Ultimately, a steady-state condition will be attained with liquid temperatures of

-60°F or lower. Calculations indicate that the rate of vaporization at this condition is very little different from that previously calculated for a pool temperature of -28°F.

Inasmuch as the equation used above had not been experimentally verified with ammonia, a few simple tests were made to check its validity. Tests were made in open air using sheet metal pans of dimensions 72 in. × 12 in. × 1 in. and 17 in. × 11 in. × 7 1/2 in. and in a glass dish 18 in. × 12 in. × 2 1/2 in. Wind velocity was about 8 to 10 mile/hr.

Liquid temperature variations

Following the initial high vaporization rate when liquid ammonia was added, liquid temperature fell with time and finally stabilized in the -60 to -80°F range. The time required for the liquid to drop in temperature from -28°F to -60°F varied from about 4 min. for a depth of about 2 in. to 15 min. for a depth of about 5 1/2 in. In the long narrow pan, a difference in liquid temperature of as much as 5°F was measured between the upwind and downwind ends of the pan.

Evaporation rates from auto-refrigeration were computed for many of these tests. Although the values can be considered as only approximate, they are consistent among themselves and in reasonably good agreement with the Russian correlation. For example, with a 9 mile/hr. wind and a liquid temperature of -37°F, ob-

served and calculated rates were 0.088 and 0.19 lb./min.-sq. ft., respectively. The latter is expected to be higher as it includes heat input effects as well as auto-refrigeration.

Practical considerations

Several practical considerations should be noted. The calculations assume that the pool is formed instantly. In an actual tank failure, a measurable time period would be required to fill the diked area; thus, the initial vaporization period would be prolonged, but the peak rate would be lower. Calculated evaporation

rates assume a negligible partial pressure of ammonia in the air. Actually, in the case of a large pool, air near the surface will become partially saturated, thereby, decreasing evaporation rate. Near the low temperature steady-state condition, the vapor cloud will become heavier than air and less readily dispersed. However, vaporization rate is low, which tends to minimize this effect.

LITERATURE CITED

8. Matsak, V. G., "Vapor pressure and evaporation of Substances in Movable Air," *Gigiyena I Sanitariya*, p. 35-41. Translation: U. S. Air Force, Foreign Technology Division, No. FTD-TT-63-1044/1+2.

DISCUSSION

SCHWAB—Factory Insurance: Dr. Bulkley, would you care to comment on the effect of ammonia fire on a polyurethane foam-insulated or styrene foam-insulated tank?

BULKLEY: I have no experimental evidence. We have not looked at this. However, ammonia flames did not ignite test materials readily, and I have a feeling that the ammonia flames would not ignite the more fire resistant urethane foams.

SCHWAB: Most of the TDI-based foams and the polystyrene foams are evaluated on their fire-resistant qualities, by the two ASTM tests. These tests are on a very small scale and are generally unreliable, at least when you are trying to extrapolate the results to large quantity. To illustrate the example of how unreliable they can be, if you would substitute wood in those ASTM tests, you would have to come to the conclusion that most of the woods that are commonly used are self-extinguishing. I don't think there's anybody in this room who would accept this.

The Factory Mutuals, some time ago, ran some tests, which were published*, which illustrated this rather interesting conclusion rather nicely. Balsa wood was the only one that turned out to be combustible at that time.

*Wilson, J. A., "Plastic Fire Hazard Classifications," *Natl. Fire Prevention Assoc. Quarterly*, 56, No. 2, p. 162 (October, 1962).

WHITE—Smith-Douglass: I have recently had occasion to look into the flameproof quality of treated polyurethane foam and also treated polystyrene, and I used wood along with it. On the polystyrene you'd have to have quite a bit more intense heat to get it to char, it would not burn, than you would with the wood. The wood would actually burn. I did not run the test according to API, I just ran it for my own satisfaction. With a piece of wood, you can go ahead and light it off and it would burn. The polystyrene under a hot flame will be hot—it would melt but it would not burn at all.

There is a paint that you can get and spray on polystyrene that will actually char and will not even let the material melt. It is made by the ALBI Manufacturing Co. of Rockville, Conn. However, if I understand Bulkley, you could not draw this flame back to where the liquid ammonia is. Then, if you had a dike full of ammonia boiling up around the tank, you would not be able to have a flame around the insulation.

Again, it is relative, but from the description Bulkley gave of it and from what I saw of this polystyrene and polyurethane foam, where it's been treated, I would doubt that it would even melt.

SOMMERS—Pennsalt Chemicals: These large tanks are frequently located along sizeable rivers. Has any thought been given to merely letting the stuff run into a large body of water, and let it be carried away?

HEPP—Sun Oil: How long was that initial period of very rapid evolution.

BULKLEY: Only a few minutes.

HEPP: And you believe this to be the case in a diked area also. I am optimistic about these results. If I read the data correctly, after the first few minutes the area of maximum danger is pulled very close to the tank. This seems to be at odds with some of the other things we heard today. How do you feel about that?

BULKLEY: If our observations are correct, that there are these two regimes, it looks as if the duration of the extreme hazard is quite short. Of course, it also doesn't take very long to kill people with high concentration so this may or may not be helpful. In connection with Sommers' question, to introduce a brief commercial, there are some data in the "Safety in Air and Ammonia Plants," manuals that we publish concerning a spill of ammonia in a river, and I don't think we could recommend that as a disposal means. You can find the data in the manual but, as I recall, there was considerable damage, particularly to all vegetation for something like three or four miles downstream. It came out very lush the next year, but it was quite damaging.

GIBSON—Atlantic Refining: What's the inevitable? If you don't dispose of it there, your tank is ruptured and you have no place else to put it. Would the river be the best alternative?

MORGAN—Imperial Chemical Industries: We obviously are in disagreement with Bulkley, author of the last paper. There were one or two facts which can, if they are available, determine how much ammonia is flashed. If, for instance, we knew the temperature which was attained in the pool at steady state, I think we could perhaps reconcile our views. I would like to discuss our views outside this meeting to reconcile our papers.

HILL—DuPont: I don't want to prolong this discussion unnecessarily, but DuPont has made the same sort of a study that was made by ICI and Amoco. We are concerned most about the potential 200 hr. of continuing ammonia vaporization from the diked area following a major spill. Some means of quick disposal must be provided.

There's one other point, the sensible heat in the liquid ammonia should be taken into account when con-

sidering the initial flash following a major spill. This source of heat could be significant and as important as the heat from the ground.

STRAUCH—Frick Co.: We of Frick Co. are quite involved in atmospheric ammonia storage and this topic of temperature variance has been of concern to us for some time. We have found this problem both on storage tanks as well as barges transporting ammonia at 0 lb./sq. in. gauge or -28°F .

We believe it to be a simple problem of static head. Ammonia weighs 37 lb./cu. ft., therefore, in a 50-ft. column we have about 12.8 lb./sq. in. difference between the top of the tank and the bottom of the tank. Put this on the saturation table, 12.8 lb./sq. in. is about -4°F . One can readily see how a temperature difference is possible. If a circulation pump is employed, drawing the ammonia off the bottom and placing it on the top, then the temperature would be about the same, -28° top and bottom.

To explain the bubble—when the tank is initially filled with -28°F ammonia, we can probably assume the temperature of the whole tank to be -28°F . As heat penetrates through the bottom of the tank, the small bubbles are held on to the bottom by the static head. The bubbles tend to join themselves together until they have become a giant bubble, say, three or four inches thick, finally the forces of static head are no longer capable of holding this giant bubble down, then it breaks loose and rises to the top; this is where the turnover effect comes from, the giant bubble rising to the top of the tank.

We advocate a circulation pump to prevent the formation of bubble in the first place. One can readily see how, if you are capable of circulating the ammonia, you will keep the same temperature throughout the tank and, as bubbles form, they are picked up by the pump and discharged at the top where they are released to the compressor.