Hazards of Liquid Ammonia Spills

A progress report summarizing experimental and analytical results of a continuing study of such accidental releases on both the surface and under water.

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Preliminary findings of an on-going, 18-month study of the hazards of liquid ammonia spills on water have been judged worth reporting to the industry, and are therefore presented in this progress report.

The study program was initiated by the United States Coast Guard and is being carried out by the U.S.C.G. and Arthur D. Little, Inc. The program comprises four major studies, or tasks: 1) liquefied anhydrous ammonia spills on water, 2) analytical modeling of such spills, 3) study of liquefied anhydrous ammonia release underwater, and 4) study of neutralization methods.

During the past decade there has been a rapid growth in the maritime transport of liquid anhydrous ammonia (LNH_3) on the inland and coastal waters of the United States. (1) Anhydrous ammonia is carried as a high-pressure liquefied cargo in barges with heavy-wall steel tanks as well as a low-temperature cargo in essentially atmospheric-pressure refrigerated barges.

The frequent movement of bulk quantities of LNH_3 on U.S. waters poses a potential hazard to the public, to aquatic life and other shipping, should there be an accidental release of ammonia either on or under water. Although the explosion and fire hazard of such a spill is limited (2), (3), the health and pollution hazard is not insignificant.

The United States Coast Guard recognized the need to evaluate the hazards due to large accidental spills of LNH3 and initiated the 18-month program with Arthur D. Little, Inc. to study the important aspects of ammonia spill on and under water. The main objective is to develop a thorough understanding of the physico-chemical behavior of large accidental releases of LNH_3 on and under water. It calls for the development of analytical models and the conduct of a scaled experimental program to verify and modify these models so that they can be used to predict the potential hazards due to spills of up to 3000 tons of LNH_3.

Four major tasks in the program

To achieve the objectives of this investigation, a program consisting of four major tasks was planned.

Task I. Experimental study of LNH_3 spills on water. This involves the experimental determination of the following:

1. The determination of the amount of initial vapor flash (or aerosol formation) as a function of spill quantity.

2. Measurements of evaporation rates of ammonia as a function of time elapsed from moment of spill, size of spill and distance from spill origin.

3. Concentration and dispersion measurements of ammonia in water as a function of time, spill size, distance from spill origin and water currents.

4. Dispersion measurements of the ammonia vapor cloud as a function of time, wind speed and distance from spill origin.

5. The rate of pool spread as a function of spill size and time elapsed from moment of spill.

Task II. Analytical modeling of LNH_3 spills on water. This task requires the development of analytical models to predict the behavior of large scale anhydrous liquid ammonia spills on water. Included in this phase of the work are:

1. Analytical modeling of the initial vapor flash.

2. Development of a transient ammonia evaporation rate model which includes functional dependence of the rate on size of spill and distance from the spill.

3. Development of a theoretical model relating ammonia concentration and dispersion rate in water to time and distance from spill origin.

4. Analytical study of ammonia vapor cloud dispersion and concentration attenuation as a function of wind speed, time, and distance from spill site.

5. Theoretical study of rate of pool spread as a function of spill size and time elapsed since spill.

Task III. Study of LNH_3 release underwater. For this task, an analytical model to predict the behavior of a continuous release of ammonia below the water surface is being developed and verified by conducting laboratory and field experiments. The analytical model will provide esti-

mates of ammonia vapor concentration and aqueous ammonia concentration as a function of: water temperature, type of release, depth of release, distance from origin of release, and physical characteristics of the tank.

In addition, the task will develop a model to study the heat transfer through the walls of a sunken tank and the resulting pressure build-up inside.

Task IV. Neutralization. Here, a literature survey to identify the most effective procedures available to neturalize the detrimental effects caused by a large release of liquefied anhydrous ammonia on and under water is being undertaken. Methods of effectively neutralizing both atmospheric and water hazards are being considered. Comparisons between various systems will be made and emergency response procedures suggested.

The results are to be presented in manner to facilitate rapid calculations necessary to assess the hazard due to a spill under any studies condition. This means that once an analytical derivation has been experimentally verified, its solutions will be presented in graphs, tables, and memographs that are amenable to quick information retrieval.

The actual approach to these tasks consisted of conducting a program of laboratory scale spill tests to develop an initial understanding to the pertinent LNH_3-air-water interactions, and to develop preliminary analytical models to explain the physical interactions observed. This was then followed by larger scale tests in an 18-ft. diameter pool and further model refinement. The largest scale spills will involve quantities up to 50 gallons of ammonia in a lake and final model refinement.

As of late summer, 1973, the laboratory spill tests and the 18-ft pool tests had been completed and preliminary analytical models to explain various LNH_3-air-water interactions developed. The largest scale spill tests of up to 50 gallons of ammonia were to be conducted in a lake in Vermont during October, 1973. A final report on the complete study is to be available in January, 1974.

Since this article constitutes a progress report we will not present details of the experimental setup and procedure or the mathematical analysis involved. More detailed progress reports are available from the U.S. Coast Guard. Major findings to date are summarized.

Surface spills results summarized

1. In the surface spill tests, the partition ratio (defined as the fraction of spilled ammonia that is absorbed by water) seems to be essentially constant and unaffected by a great variety of variables.

2. In over 90% of these tests, the partition ratios fell in the range from 65% to 82%. In almost all instances where points fell outside this range, reruns fell within the expected data band.

3. The nominal spill conditions as observed in the spill tank indicated that the evaporation zone seems to be confined to a reasonably small area, adjacent to the spill. The phenolphthalein dye indications and temperature measurement indicated that a warm layer of ammonium hydroxide propagated from the spill zone along the surface. This layer was about one inch thick, and the temperature in the vicinity of the surface was of the order of 5° or 10°F above

initial water temperature.

4. Neither the partition ratio nor the physical model described above seem to be strongly affected by variables which might be expected to influence interface heat and mass transfer, such as: (a) spill size; (b) spill rate; (c) spill delivery angle; (d) air and water velocity; and (e) salinity.

5. Restricting the total area available to the spill site does influence the propagation of the ammonium hydroxide layer; but, if it does not infringe on the area of the evaporation zone, it does not seem to have any marked affect on either the physical mechanism of the evaporation process or the partition ratio.

6. When the area available to the spill is reduced to less than the nominal boiling zone area (such as is achieved in the beaker tests), the upper layers of the ammonium hydroxide solution experience a temperature drop rather than the rise which was otherwise noted. However, although the reproducibility of partitition ratio was not as good in these tests, the average value of the partition ratio was not greatly affected.

7. The partitioning of ammonia by dissolution into the water and vaporization into the air may be fully explained by thermodynamic considerations alone. As liquid ammonia is dissolved into water, heat is generated which is carried off in part by ammonia vapor generated during mixing. As the dilution process continues toward zero concentration of ammonia, the vapor generated per unit mass of ammonia spilled on water becomes nearly a constant. The liberation of 25% to 30% of the spilled ammonia as vapor (i.e., a partition ratio of 70% to 75%) independent of size of spill or rate is analytically predictable by our spill model.

8. The partition ratio is limited by thermodynamics rather than rate processes.

9. The thermodynamic treatment of the ammonia dissolution and vapor generation process is an extremely useful tool for disclosing the nature of the interaction of liquid ammonia and water. Though the anlaysis does not reveal the rates at which the reaction propagates, it does provide the net partition ratio of ammonia. The thermodynamic analysis also correctly predicts changes in water temperature due to the dissolution-vaporization process.

10. Spreading of the liquid ammonia on water is a difficult interaction to model theoretically. One simple model has been developed, but because of drawbacks inherent in the model it will require further examination so that a more detailed spreading model may be incorporated in the analytic approach.

11. If large quantities of ammonia are discharged on the water surface with much splashing (or other mechanical activity) particles of liquid ammonia are torn from the main spill body and dispersed downwind as a foggy cloud. We call this phenomena aerosol formation.

12. In the event of a spill with associated aerosol formation, the partition ratio can be as low as 50%.

13. Measurements of ammonia concentration in the dispersing vapor cloud indicate Guassion profile behavior.

14. Vapor dispersion can be adequately predicted by the existing dispersion theory of Pasquill *(4)* and Gifford *(5)*.

15. Experimentally measured dispersion coefficients agree well with the values obtained by Turner *(6)*.

Underwater spill results summarized

1. Underwater releases of liquid ammonia at slow rates in large water bodies result in much bubble formation. However, bubbles of ammonia dissolve fast and may not reach the water surface.

2. If liquid ammonia is released underwater from an orifice of diameter D and the rate of release is within a range of Reynolds number of 10^6 to 10^8, complete dissolution of ammonia bubbles occur within a distance 10D up from the orifice.

3. Underwater release of ammonia is analogous to a turbulent diffusion flame in certain ways and drawing on this analogy we have developed a theory to predict ammonia jet lengths for releases underwater. Theory predicts complete dissolution (jet lengths) of above 10D from the orifice.

4. The partition ratio for releases deep underwater (greater than 10D) is experimentally close to 1.0 (complete dissolution).

How a hazard is calculated

Consider a five gallon spill of LNH_3 on water. The wind is blowing at 7.5 mph, and it is a sunny day (atmosphere type B). We wish to know how far downwind people could detect the cloud by odor and mild eye irritation (concentration of 50 ppm).

Spill quantity = 5 gallons = 12.9 Kg.
Partition ratio = 0.7.
Quantity vaporized = 12.9 x (1-0.7) = 3.87 Kg.
Atmosphere type = B.
Time for evaporation $\sim$ 5 seconds.

Utilizing Turner's approach *(6)*, we can now predict that where the concentration falls below 5 ppm., the distance of interest = 1450 ft.

Thus, a five-gallon spill of liquid ammonia or water would, under conditions of atmosphere type B, be detectable by odor and eye irritation 1,450 ft. downwind.
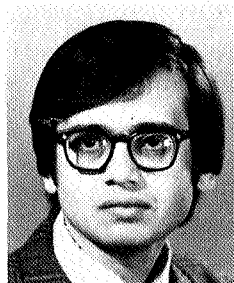
In describing the on-going program to predict hazards of large spills of ammonia on water, some of the results—both experimental and analytical—have been presented. It should be pointed out that much work remains to be done before the program is completed.

Literature cited

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