Reducing Vapor Loss in Ammonia Tank Spills

Experiments lead to development of methods for reducing vaporization of liquid ammonia flowing into the atmosphere or into the moist earth around tanks.

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The great increase in recent years in storage tank capacity for liquid ammonia has led BASF to develop measures for reducing the evaporation of the material into the atmosphere, both directly and indirectly, the latter by constructing earthen dikes around the storage tanks.

The experimental work aimed at these measures led the company to conclude that earthwork diked areas around ammonia tanks must be covered with a layer of clay, asphalt, plastic film, or a similar material that is impermeable to the liquid ammonia. Otherwise, the ammonia will flow through the moist earth without forming a solid phase and there would be no point in installing such a catch basin in the first place. Furthermore, the loss of ammonia by evaporation would be even greater in the absence of the impermeable layer over the dike.

It is useful to point out that storage capacity for liquid ammonia had risen in the United States and Canada alone to between 150 and 200 tanks by 1972. In one recent report, data were given for 149 atmospheric ammonia storage tanks in the two countries with capacities between 7,000 and 30,000 ton, and 44 of 30,000 or greater. About 90 of the 149 tanks are protected by earth dikes, in a few cases more than one tank being in the same diked area.

To date, no reports of damage have been received in which a diked area has been filled with liquid ammonia. In a few cases, the dikes have been damaged from the outside by flood waters from nearby rivers. There have been some discussions among ammonia industry technologists on the use of these dikes and the need to restrict the overall surface area of the liquid by using tall dikes. However, the height of an earthen dike is limited by the damage expected by erosion and by the space required for tank maintenance. In most cases, all that is permitted by these restrictions is a diked area with comparatively large surfaces of contact between the liquefied ammonia and the air and the soil. It is for this reason that BASF carried out the simple experiments mentioned.

The experiment on reducing vaporization by covering the liquid surface of the ammonia was carried out as follows:

Two rectangular sheet metal tubs, each measuring 3.3 x 2.3 x 0.3 ft., were laid in a bed of sand and then filled with liquid ammonia—9.3 gal. in each tub. Figure 1 shows the tubs. The liquid surface in one tub was not covered, while that in the other was covered with various materials. Measurements were made of the time of sinking of the liquid surface between two depth marks in each tub.

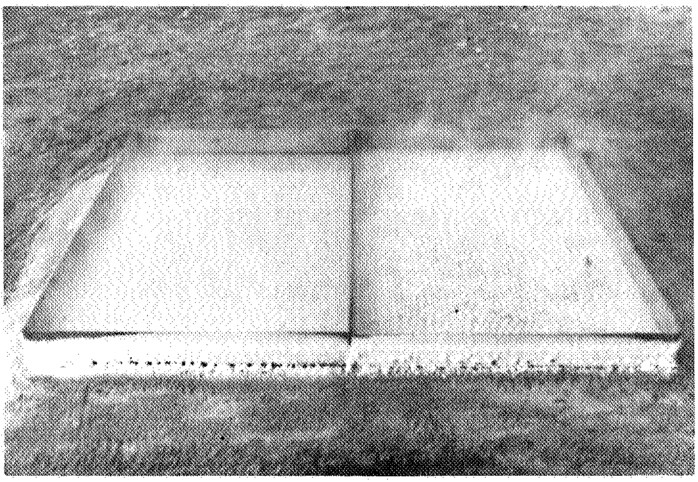


Figure 1. Side-by-side sheet metal tubs filled with liquid ammonia.

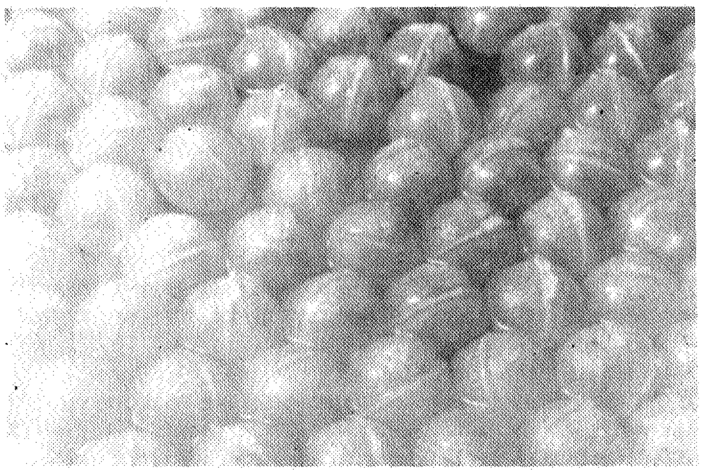


Figure 2. Hollow polypropylene spheres, 0.8 in. diameter, covering some 78% of the liquid ammonia surface.

Atmospheric conditions, the same for both tubs during one test run, were as follows: air temperature, 4 to 23°C.; relative humidity, 37 to 71%; barometric pressure, 29.5 to 30 in. Hg.; and wind speed, 1.5 to 6.5 ft./sec.

Several ammonia-resistant materials tested

For covering the liquid surface the following materials (all resistant to liquid ammonia) were tested:

1. Hollow spheres of polypropylene with 0.8 in. diameter, shown in Figure 2. The spheres cover 78% of the liquid surface in maximum packing density. There was no appreciable difference of the vaporized liquid ammonia out of the covered and the exposed surface.
2. Plates of expanded polystyrene 0.4 in. thick. We covered the shell with 12 plates for measuring the effect of the split between the plates. The width of the splits was 0.4 in. The quantity of vaporized liquid ammonia out of the covered surface was 25% less than out of the exposed surface.
3. A layer (about 0.4 in. thick) of expanded polystyrene spheres with a sphere diameter of 0.1 in. The quantity of vaporized liquid ammonia out of the covered surface was 30% less than out of the exposed surface.
4. Plates of expanded polystyrene 1.6 in. thick. The arrangement was the same as in item 2. The quantity of vaporized liquid ammonia out of the covered surface was 65% less than out of the exposed surface.
5. Aqueous foams cover the liquid ammonia for the present, but by reaction of the water content with the ammonia the foam is destroyed quickly. We also made an experiment where the foam covered a layer of expanded polystyrene spheres, as in 2. In this case a part of the polystyrene spheres was deposited by the foam and the foam was destroyed quickly by contact with ammonia. Another disadvantage of the foam is its large area is more subject to wind effects than the smaller area of the polystyrene sphere layer.

Further considerations to cover the liquid ammonia with other liquids like silicon oils for instance are not practicable because the specific weight of the liquid ammonia has the low value of 42 lb./cu.ft.

A result of all our tests is our belief that the best measure is to cover spilled liquid ammonia with spheres or plates of expanded polystyrene.

During the tests just described the liquid ammonia in the tub with the exposed surface a short time after the filling had a temperature of about –60°C instead of –33.4°C, caused by evaporation. The temperature in the tub with the covered surface was between –37°C and –60°C, depending upon the intensity of evaporation.

The second experiment was aimed at developing measures to reduce the vaporization of liquid ammonia into the atmosphere indirectly. In addition, it was our aim to investigate any interaction that took place between the ammonia and the water in the soil. The mass transfer between the ammonia in the diked area and the water in the soil considerably influences indirectly the evaporation of ammonia to the atmosphere. In addition, the ground water may be greatly polluted if the bottom layer of the diked area is not correctly designed.

The interaction between moist soil and liquid ammonia was observed and measured in the apparatus shown in Figure 3. The bottom of a cylindrical sheet-metal tank with a volume of 60 gal. consisted of two wire screens and a 2.5 in. layer of coarse gravel; it was thus permeable to liquids. Five outlet nozzles at the bottom allowed the liquid to be withdrawn. A 26-in. layer of sand with an average grain size of 0.0055 in. was on top of the gravel for the first experiment. Resistance thermometers were inserted into the sand along the axis of the tank at the points of measurement shown in Figure 3. Thus, the temperature in the layer of sand could be recorded as a function of time. The tank was wrapped with a 4-in. layer of thermal insulation to exclude the effect of the ambient temperature.

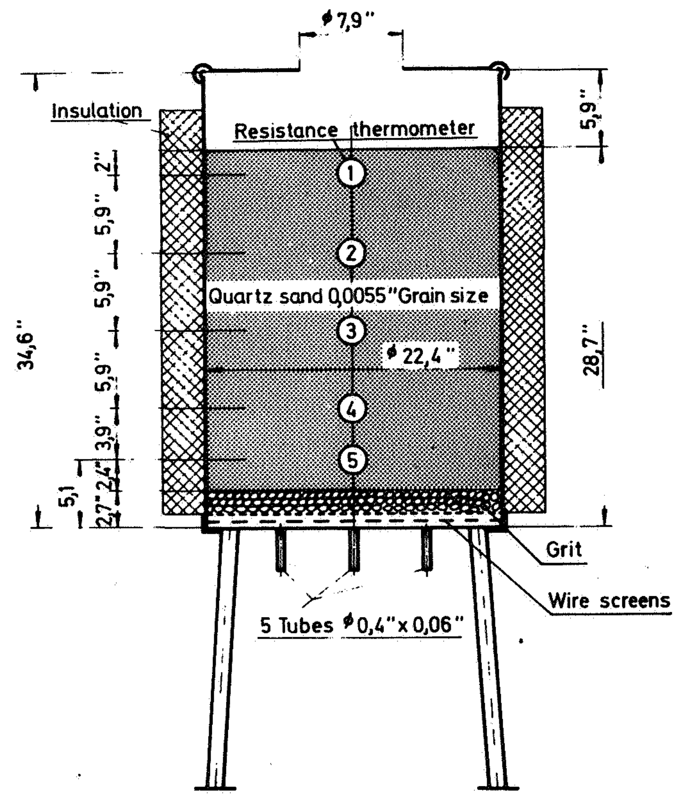


Figure 3. Test apparatus for first experiment, with moist sand.

The first experiment was with a 26-in. layer of water-saturated sand. After the temperature of the moist sand had equalized at the five points of measurement at 3°C, a layer of liquid ammonia was poured on top of it. The ammonia level was kept constant by replenishing that which evaporated or trickled away. The temperature curves shown in Figure 4 were thus obtained at points of measurement 1-5. The time sequence at these points revealed a rise in temperature of up to a maximum of +35°C and then a sudden drop to –33.4°C, the boiling point of ammonia at atmospheric pressure. The rise in temperature observed initially

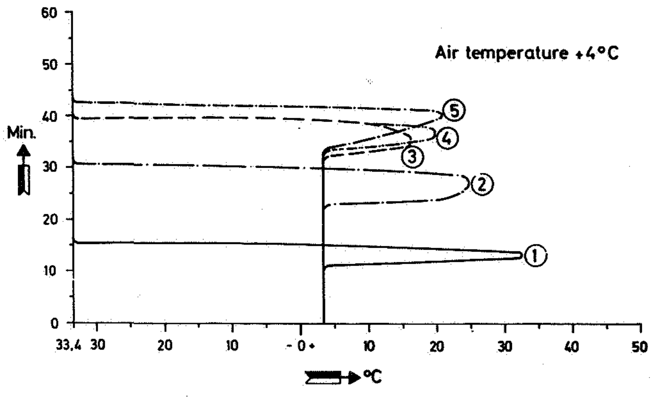


Figure 4. Temperature of moist sand with ammonia.

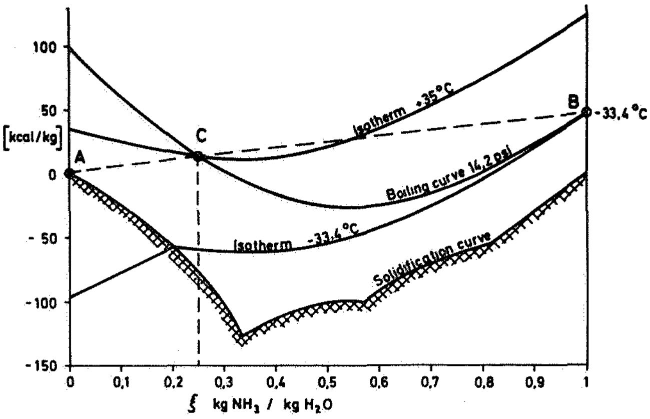


Figure 5. Enthalpy-composition diagram, water-ammonia.

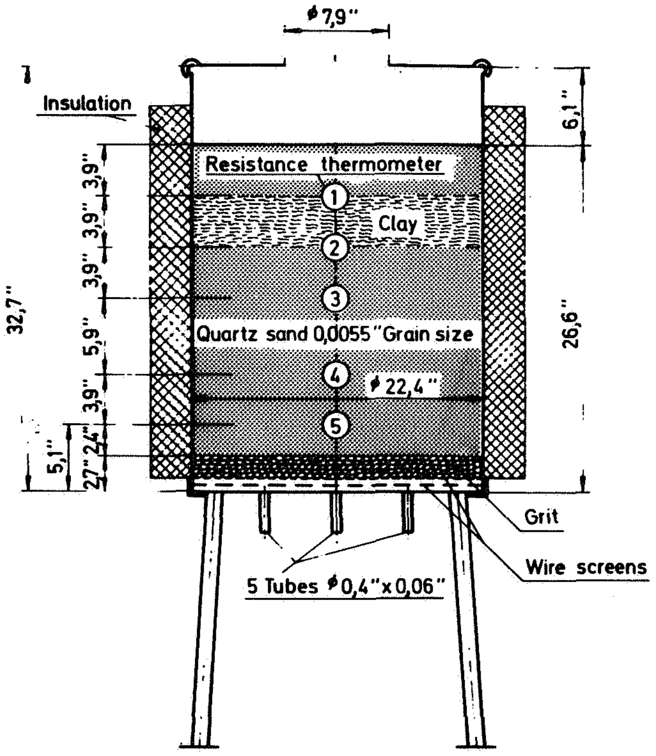


Figure 6. Test apparatus for second experiment, with moist sand and a layer of clay.

is explained by the enthalpy-composition diagram for mixtures of water and ammonia in Figure 5.

The intersection of the boiling curve at atmospheric pressure with the line connecting point A (water at +3°C) and point B (liquid ammonia at –33.4°C) represents the equilibrium condition. It occurs at a temperature of +35°C and a concentration of 25%-wt. of NH_3.

As the temperature curves in Figure 4 demonstrate, this equilibrium is attained momentarily in the upper part of the sand layer. As a result of rapid flow through the layer of sand, only part of the water is absorbed by the ammonia. The remainder is displaced, as in plug flow. Consequently, equilibrium is no longer attained in the lower part of the bed of sand.

In accordance with this, water is observed to flow first, from the outlets of the experimental tank. It is followed by ammonia water and, finally, after a period of about one hour, by liquefied ammonia. As the experiment demonstrates and the phase diagram proves, no solid phase is formed. As long as flow through the bed and mass transfer of ammonia and water in the layer of sand proceed more rapidly than the thermal conductivity and the associated cooling of the layer of sand, no ice can be formed. This applies to permeable soils that do offer virtually no resistance to flow or trickling of the liquid; i.e., layers of sand and gravel and other porous strata.

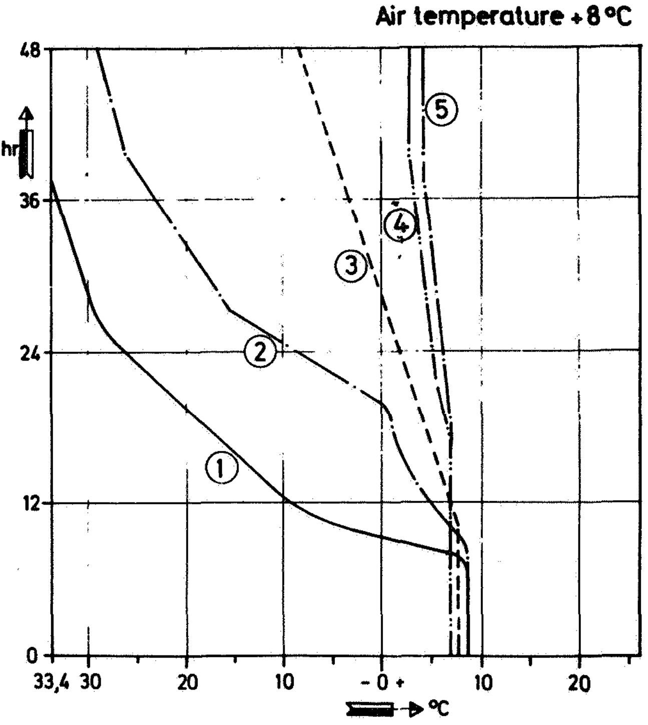


Figure 7. Temperature of moist sand with a clay layer and ammonia.

Figure 6 shows the apparatus with a 4-in. layer of clay inserted in the sand, which offers considerable resistance to liquid flow. The other experimental conditions were unchanged. Figure 7 shows the temperature curves at the points of measurement 1 to 5 taken over a period of two days after filling in the liquid ammonia and maintaining it at a constant level.

Observation of the layer of clay and the underlying sand immediately after the experiment had ended revealed that ice had formed at the points of measurement 1, 2, and 3. In this experiment, mass transfer of water and ammonia and the flow of ammonia were impeded by the clay layer. Owing to the comparatively good thermal conductivity of the moist sand and clay, ice formation eventually occurred, as can be seen from the temperatures in Figure 7.

If an 0.002-in. polyethylene film is inserted in the sand instead of the layer of clay as shown in Figure 8, the temperature curves in Figure 9 are obtained for the same experimental conditions. In this case, mass transfer between water and ammonia and flow into the underlying layer of sand are prevented by the film even more efficiently than by the clay in the previous test. Thermal conductivity is almost unobstructed, and ice is formed as can be seen from the temperature curves 1, 2, and 3. After the experiment had finished, a 3.5-in. layer of ice had formed in the sand above the film.

In these experiments, the measuring range of the temperature probes was restricted to the boiling point of ammonia under atmospheric pressure. After the experi-

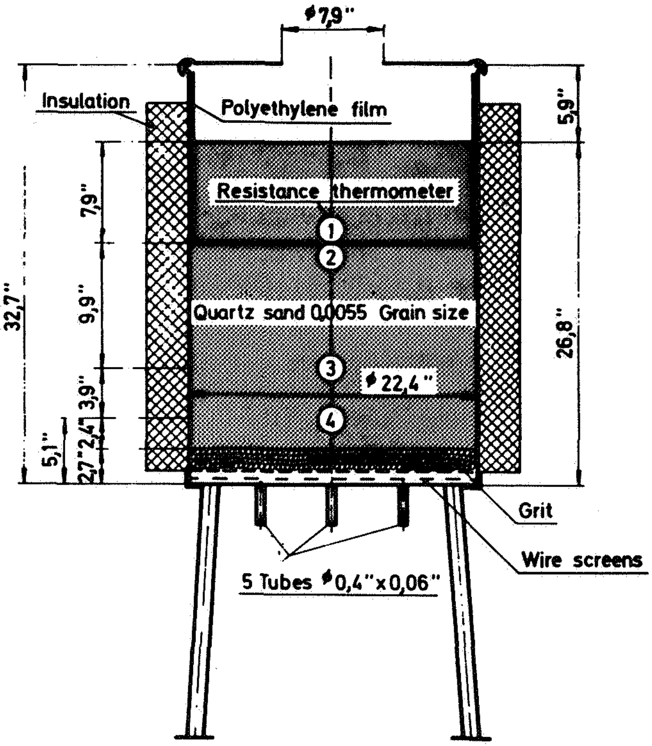


Figure 8. Test apparatus for third experiment, using moist sand and a polyethylene film insert.

ments have been run for a few hours and the apparatus has cooled sufficiently, the ammonia will evaporate at below the boiling point. Thus, the ammonia partial pressure above the liquid drops, and the temperature of the liquid falls correspondingly, e.g. the temperature curves 1 and 2 in Figure 9. The same would occur if a tank of liquid ammonia were to burst and the diked area had cooled sufficiently.

After the experiment in Figure 8 had proceeded for 51 hr., the ammonia evaporating above the surface of the sand was at a temperature of –54°C. The NH_3 partial pressure corresponding to this temperature is 4.65 lb./sq.in. It can

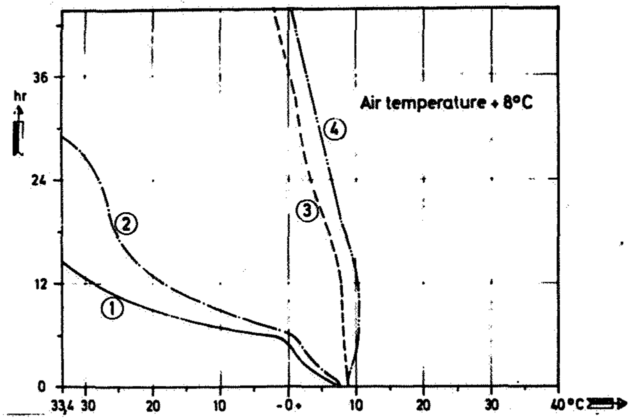
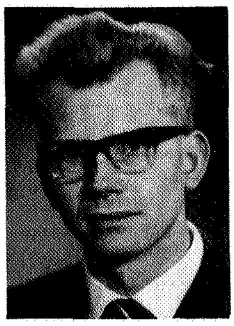


Figure 9. Temperature of moist sand with polyethylene film and ammonia.

be seen from this that the temperature in diked areas may drop below about –60°C. If there were a layer impermeable to liquids in the soil, the formation of the ice layer would be accelerated. This severe drop in the temperature of the liquefied ammonia and the associated material problems are actually observed in concrete wall constructions.

Conclusions

These experiments have shown that a layer of some material impermeable to liquid ammonia must be used to cover earthen diked areas around ammonia storage tanks. It might be material such as clay, asphalt, or plastic film. #



FEIND, K.

DISCUSSION

R.M. OSMAN, Exxon Chemical Co.: You mentioned two experiments, both using plates of expanded polystyrene. One was 0.4 in. thick and the other was 1.6 in. thick, and the 1.6 in. thick layer apparently was much more successful in reducing the ammonia vaporization. Now would you say this is strictly an insulating effect here rather than the effect of covering the surface, because since the geometry was the same in the two experiments, presumably the free surface for evaporation was the same, and the only differences was that the thicker blocks would be better insulators than the thinner blocks?

FEIND: Yes. That's quite right. So more thick is a foam polystyrene plate, so better is the insulation effect. The covering effect was in our experiments with the various plates like the same. But it would be difficult to bring such thick plates upon the liquid surface when you have a large area of spilled ammonia, and it seems to me the best to cover it with polystyrene spheres in a thick layer of about two inches.

JAN BLANKEN, UKF Holland: I understand that other European companies have done experiments with this foam over liquid ammonia, and as I understand the results, if you carefully select the foam, but I am not familiar with foam at all, with a high expansion factor you can have good results.

As far as I understand the working of foam is very much dependent on the quality of the foam.

FEIND: The foam has in all cases a water content. This water content reacts with ammonia and the lifetime of the foam is very short then. And the second disadvantage of the foam is its large area, and when you have larger wind speeds the foam goes away very rapidly.

GENE COMEAU, Farmland Industries, Inc.: As you may know, the ammonia committee is very interested in the subject of ammonia spills into dikes. We have been for a number of years, and I personally have been very involved. I'd like to express my appreciation to BASF and to Dr. Feind for this work. And I would also like to make a clarification.

The paper yesterday afternoon on ammonia spills into water gives an entirely different picture than the work done regarding ammonia spills on to the ground. And this is acknowledged in the paper by Arthur D. Little. I wanted to call it to your attention in case it was not obvious in the paper. The buoyant effect of the cloud which is important in an ammonia spill on water is not important in regard to a long term spill into a dike of an ammonia storage tank. The buoyant effect does not come into play after the initial spill.

If you spill 30,000 tons of ammonia into a storage tank dike, that ammonia is going to stay there for a long time and the downstream concentrations which were presented in the paper several years ago by the Ammonia Storage Committee of the Compressed Gas Association were based on the equilibrium condition after the initial spill.

On the initial spill there's a lot more vapor and the concentrations are higher so that the cloud tends to be buoyant and to get up off the ground. However, ammonia in air at a thousand parts per million is not buoyant and it's pretty well proven that the vapor from ammonia in a dike stays on the ground. So I would like to advise everyone that this is a continuing problem that we don't have the answers for and to not be put at ease by the buoyant effect of ammonia.

W.H. DOYLE, Consultant: Gene, I'd just like to make a comment on your comment. The temperature effect has to be considered. In the case of liquefied natural gas spills there is a large body of evidence that the temperature of the spill equilibrates at a temperature very much below the normal boiling point. And vapors from such a spill have to warm up at least 100 degrees F before they become buoyant with respect to ambient air. And I suspect the same temperature effect exists in a liquid ammonia spill.