

MITIGATION OF THE VAPOR HAZARD FROM SILICON TETRACHLORIDE USING WATER -BASED FOAMS

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Summary

The list of volatile hazardous chemicals contains a significant number of inorganic chlorides. Most react exothermically with water releasing a toxic, corrosive hydrochloric acid aerosol cloud. Spills of such materials provide a significant hazard to people, property and the environment and pose a major problem in clean up and disposal.

In a co-operate program, MSA and Wah Chang have investigated the potential of aqueous foam to mitigate the vapor hazard of one water reactive chloride, silicon tetrachloride. These tests investigated both low and high expansion foams generated using MSA Type V concentrate, a hydrocarbon surfactant based system with a slow drainage and stability over a wide pH range.

The tests conducted were successful in markedly reducing the vapor hazard from the spill. Foam blankets reduced the chloride concentrations in the air at the spill site by some two orders of magnitude over that of an uncontained spill.

Introduction

Shortly after 12.30 p.m. on April 26th 1974, several Bulk Terminal employees heard a sudden "thud" and "noticed fumes rising out of the dike surrounding tank 1502". Within hours the ruptured tank would affect the lives of tens of thousands Chicagoans. As the escaping silicon tetra-chloride reacted with the moisture laden air, an enormous, breathtaking, eye-watering, nausea-inducing, acid cloud was spewing forth. At times, the cloud measured from five to ten miles long as it moved across the city, disrupting traffic, work and normal living activities.

These words are taken from the opening paragraphs of a report on a major spill of silicon tetrachloride [1]. This is the only major spill of this type of material but it has served to accentuate the reactive chlorides as hazardous chemicals.

The inability to control the leak and the vapors being released extended the spill duration to some eight days. The toxicity and irritating character of the fumes caused significant problems for those concerned with the spill and its clean up, forced evacuation of large downwind areas and necessitated extended periods of traffic re-routing.

The difficulty with this spill prompted serious consideration of the avail-

able spill technology not only for silicon tetrachloride but for related materials — titanium tetrachloride, thionyl chloride and others. In this context the applicability of foam to control the vapor release came under investigation.

During the actual spill, foam was recommended as one approach but was only given a cursory test. The application of water to reactive chlorides results in severe reaction with the release of a heavy vapor which is principally a hydrochloric acid aerosol. The reaction of the released vapor with the moisture in the air provides the same result but with less violence and at a slower rate.

Foam is a form of water and it reacts in the same way. Although the reaction violence may be less than with a direct water application, a large dense cloud is formed. There will be little visible change in this cloud until a blanket of foam can be developed over the total spill surface. Failure of the foam to be effective in the Chicago spill has never been addressed by personnel at the site. Any of three factors alone, or in combination, would have been responsible; insufficient time allowed to develop a full blanket, an application rate too slow for the spill size, or a foam not sufficiently resistant to the acid character of the chloride. One might deduce that the first item was most significant. The cloud which developed as the foam was added surprised most observers and it was difficult to convey the information that this was a necessary but temporary situation.

Foam technology

The evaluation and development of foam for controlling the vapor hazard from spilled volatile chemicals has for some time been an active area under both private and government sponsorship. Efforts in this area by MSA have produced two foam systems which, on the basis of laboratory tests, were effective in controlling the vapor hazard from the reactive chlorides.

The first development was a high water retention foam with good stability over a wide pH range, both acidic and alkaline. The second involved an ammoniated foam system. By incorporating ammonia into the foam solution at concentrations up to 14 wt%, not only was vapor release controlled but the chlorine portion of the spilled material was converted to ammonium chloride rather than hydrogen chloride. This resulted in a considerable reduction of the overall hazard of the spill. The vapor hazard decreased and the spill residue was primarily solid NH_4Cl rather than a hydrochloric acid solution.

Field tests — Arrangement and procedures

To test the laboratory results on a larger scale, a co-operative test program was arranged between the Wah Chang Division of Teledyne and MSA. Wah Chang provided a test site and silicon tetrachloride. MSA provided the foam system and chemicals.

Tests were conducted in a remote area using a square test pan with 64 square feet of surface area, and were run using both crude silicon tetrachloride, which contains measurable quantities of free chlorine and phosgene, and with commercial grade silicon tetrachloride. Test runs were made at two expansions; 8 to 1 and 350 to 1. Both expansions were made using MSA Type V foam, a highly stable low draining foam developed originally for use against liquefied gas fires and spills, but recently listed by UL for use in both low expansion and high expansion equipment for fire service.

Tests with both forms of SiCl_4 were made with normal foam at both expansions. Foam appliances were two MSA Model IV-6 generators, 250 cfm output each for high expansion and with a 60 gpm Rockwood SG all purpose nozzle for the low expansion application.

In addition to the normal foam, tests were run in the high expansion mode using a 14% ammonia solution — 28% aqueous ammonia diluted 2 to 1.

A sampling system was employed in each test which consisted of an air sampling pump drawing 600 cc per minute through an impact bubbler for a sampling time of one minute. Sample stations were set one pool diameter away at a height of one foot, and 5 pool diameters away at a height of five feet. Due to changes in wind direction after tests had started, meaningful samples were not obtained for all test sequences.

The tests were run by charging approximately one inch of SiCl_4 into the test pan. A one minute delay was allowed to obtain a measure of downwind vapor levels from the free spill. The foam generation was begun and continued until a full blanket was developed over the entire pan surface. With the low expansion foam the cover time was approximately two minutes, with the high expansion foam the cover time was between 60 and 70 seconds.

Air samples were taken for one minute durations immediately after development of a full blanket, and then at both five minutes and ten minutes after foam discharge.

Field tests — Observations and results

In all tests three stages of vapor release were observed. The first stage was that of free spill vaporization which resulted in a dense downwind vapor cloud. The second stage was that of initial foam discharge; in this stage the rate of vapor release and the intensity of the downwind cloud were exaggerated over that of a free spill. The third stage began when the foam blanket was complete, here the rate of vapor release was strongly reduced, visibility in the spill area was restored and continued vapor release was by intermittent vapor surge through the foam blanket. This stage persisted as long as the blanket was maintained. These three stages are shown in Fig. 1.

Standard foam creates a blend of acidic solution and solids. The solids entrain reactive material, and their breakup and hydrolysis during wash-down results in the redevelopment of an intense downwind cloud. It is expected that long term maintenance of the foam blanket would result in slow but

complete hydrolysis of the total spill. In these tests, however, water was added after 15 to 20 minutes of control. This was principally to shorten the test time and permit movement to the next test sequence, but it also served to prove that unreacted SiCl_4 still existed beneath the blanket and that the reduction in the vapor hazard was not due simply to total reaction of the spilled material.





Fig. 1. Spill sequence for foam—silicon tetrachloride test. (a) Free spill; (b) foam on; (c) foam blanket in place.

Based upon visual observation, the low expansion foam reduced vapor release to its lowest level. It took the longest time to cover, however, and one difficulty was experienced. To avoid plunging discharge of the foam directly into the spill, a backboard was used. Foam discharge was impacted against the backboard and flowed onto the spill. The design of the backboard was such that it was placed within the spill and masked the areas behind it from direct foam application. Spread of low expansion foam is poor and as a result foam did not effectively flow behind the backboard. A similar occurrence is possible in real situations where obstacles to flow are present. High expansion foam is not hindered by such obstacles.

The straight foam in high expansion showed a degree of control almost equal to the low expansion mode. The following data is typical of that from the bubbler samples, it is expressed as mg of chloride per liter of air.

1. Background — 40—46
2. Free spill — 17,000
3. Foam blanket complete — 190
4. 5 minutes after foam application — 165

The result with the ammoniated foam were not as impressive, development of the foam blanket took longer and after it was complete the vapor release in terms of visibility was greater than for straight foam. The difference can be seen by comparing Fig. 2 which shows the vapor release through an ammoniated foam blanket with Fig. 1C for normal foam. The delay in obtaining coverage appears due to the higher rate of reaction between SiCl_4 and aqueous ammonia than between SiCl_4 and water alone. This was not observed



Fig. 2. Vapor release through foam blanket using ammoniated foam.

in laboratory tests, but the difference in spill size is a factor.

The ammoniated foam produces a more visible, but less hazardous, vapor cloud due to the fact that NH_4Cl is released rather than HCl . Much of the NH_4Cl formed is entrained as a solid along with SiO_2 . The solids layer tends to float, and over a long term acts to slow the reaction by impeding the movement of water into, and SiCl_4 vapor out of, the spill. There is little, if any, entrainment of acidic solution in the solids.

Conclusions

These tests show fairly dramatically that surfactant foams can be employed to reduce the vapor hazard from spilled silicon tetrachloride materials. For large impounded areas, high expansion would appear to be the best mode in light of its faster cover and insensitivity to obstacles in the area. For small localized spills the lower expansion range may be a better choice.

The application rate in the case of the high expansion foam was approximately 4 cfm per square foot of spill surface and the control time slightly greater than one minute. It is interesting to note that this is within the 3 to 6 cfm range which has been found to be optimum for the control of other spills within a two minute time limit. This is a function of the spread rates of the foam, which differ only by virtue of the influence of the spill on the collapse rate.

The application rate for the low expansion foam was some 2 gpm of solution per square foot of surface. This is an order of magnitude greater than re-

commended rates for other hazards. It is possible that lower rates will be adequate but additional testing is necessary.

References

- 1 W.C. Hoyle and G.R. Melvin, A toxic substance leak in retrospect: Prevention and response, Proceedings of 1976 National Conference on Control of Hazardous Materials Spills, Information Transfer Inc., Library of Congress No. 76-12218, 1976.