Mitigation of Ammonia Aerosol Releases via Water Spraying

Different types of water spraying systems for absorbing and diluting unconfined releases of ammonia aerosols are evaluated. Examples show how mathematical modeling can help design water spray systems. Alternative mitigation options are also discussed.

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Introduction

Ammonia releases will form either buoyant or denser-than-air mixtures with the surrounding air, and this behavior will govern the way the release can be mitigated. Accidental releases of ammonia from pressurized containers frequently lash into tiny droplets and form aerosol clouds which are heavier than air. Several studies (Kaiser and Walker, 1978; Blanken, 1980; Kaiser and Griffiths, 1982; Kaiser, 1989) have shown that ammonia releases in moist air will form a denser-than-air cloud if the release contains more than approximately 16% aerosol. This behavior is due to aerosol density and cooling effects, that is, aerosol droplets themselves contribute to the higher density and as the droplets evaporate, they cool the surrounding air. For releases in dry air, dense gas may be formed at lower aerosol fractions; reaction between water vapor and ammonia is exothermic, so a mixture of ammonia and moist air is warmer and less dense than a mixture of ammonia and dry air. If the initial release contains less than 4-8% aerosol, its mixture with air always produces a buoyant cloud.

A buoyant release will disperse upwards rather quickly and may not give time for mitigation action. In cases, however, of releases from a pressurized container where a denser than-air cloud is formed, mitigation using water sprays can be very effective.

Background

Removal of water-soluble gases

Water sprays for scrubbing unconfined release of water-soluble gases (such as HF, NH₃) have been studied theoretically, tested in field experiments, and tried in actual emergencies.

Hydrogen Fluoride. The potential of water sprays to mitigate unconfined releases of hydrogen fluoride (HF) has been investigated in large-scale experiments at the Dept. of Energy (DOE) Nevada Test Site (NTS) by Lawrence Livermore National Laboratory and Amoco Corp. (Goldfish tests, Blewitt et al., 1987), and the Industry Cooperative Hydrogen Fluoride
Mitigation/Assessment Program (ICHMAP) (Hawk tests, Schatz, 1993). The Goldfish tests showed that flashing occurred in accidental releases of HF at a temperature and a pressure typical of alkylation units [such as 40°C, 115 psig (792 kPa)]. Flashing resulted in approximately 80% of the material being released as an aerosol of very small droplets and the rest as cold HF vapor. No liquid dropout of HF was observed. The resulting cloud was much denser than air because of the aerosol and cold HF vapor. The entire release remained cold, dense, and compact as it moved downwind. Spraying the plume with water from downwind positions was found to be effective, but the complications and uncertainties of large-scale testing in the open atmosphere did not allow for good quantitative information to be obtained. The next stage was the 1988 laboratory tests and Hawk field tests. The laboratory study comprised 42 tests of HF releases on a small scale. The field tests took place in a large chamber [140 ft (43 m) long, 16 ft (4.9 m) high, and 8 ft (2.4 m) wide]. They comprised a series of 87 tests, involving different water-to-HF ratios, nozzles, manifold and nozzle positioning, nozzle configurations, vessel pressures, wind speed, and humidity conditions. These tests showed that when water is applied in a prudent way, it can absorb up to 95% of the released HF. These tests represent the most comprehensive effort to evaluate a system for mitigating unconfined releases, and they are of a scale unprecedented in the evaluation of any other mitigation system in the chemical industry.

**Dilution of flammable vapors**

Water sprays have been extensively tested for their potential to dilute a released gas by inducing air flow. In the field tests, dilution ratios (ratios of gas concentrations with and without water sprays operating) were in the range of 2 to 5 measured 10 to 20 m downwind of the spray (Moodie, 1985). This dilution provided a worthwhile local enhancement of the dispersion rate of heavy gas releases, which may be sufficient to reduce the concentration of a flammable vapor below its low flammability limit, but the effect of this local dilution is insignificant in reducing health hazards from highly toxic gases (Fthenakis, 1989).

**Water Curtains vs. Water Monitors**

A spray curtain typically is designed as a sectional, peripheral curtain around the unit to be protected. Spray curtains are used when there is space for the curtain at the perimeter of the unit to be protected, and operator's interaction with an accidental NH₃ release is to be kept to a minimum. The simplest way to deal with a gaseous leak is to turn on the entire peripheral water spray curtain surrounding the unit. Thereafter, it can be determined which sections of the spray are upwind from the release and be turned off. This approach, however, requires large amounts of water. Another way is to evaluate the wind direction first and then turn on a U-shaped section downwind from the leak.

The Hawk tests indicated that water monitors (water cannons), when properly located and operated, can achieve HF mitigation efficiencies almost as high as those obtained by water spray curtains. Monitors for HF or NH₃ mitigation have the advantage that they can alternatively be used as fire monitors. Monitors are more flexible as to the size and location of a leak. In most cases an NH₃ mitigation system using monitors is cheaper than a dedicated water spray curtain of the same capacity. A major drawback in the operation of the monitor system is the complexity of manipulating multiple, remotely controlled monitors. While curtains can be operated with a single on-off control, monitors must be individually controlled to achieve optimal mitigation efficiency. Changes in wind speed...
and direction, as well as increases or decreases in NH₃ release rate, require readjustment of the system. Operating a system of six to eight monitors can be a challenge, especially since little opportunity exists to gain experience with the system, unless a comprehensive training program with simulated releases is implemented (Schatz, 1993).

**Computer Simulations as Performance Evaluation Tool**

In actual mitigation applications, source and site-specific factors have to be taken into account to establish the design basis of the water spray curtain. These factors include: storage and process system conditions; accidental release scenarios, usually determined by a hazard and operability study (HAZOP); prevailing wind and atmospheric conditions; wind direction to nearest population; effect of structures on cloud dispersion; availability of water; release detection systems; acceptable exposure limits.

Once the leak rate and the acceptable NH₃ concentrations downwind from the water spray have been determined, the design basis can be specified as to how much water has to be delivered where and how fast, as well as how the alkaline water is removed, neutralized, and disposed of. The next step is to determine manifold locations and elevations, and nozzle type and configuration, to optimize momentum and mass transfer under water pressure and flow rate constraints. For example, spraying near the release with fog-nozzles (small drop size) can increase mass transfer, but it may not prevent penetration of the plume through the water curtain and the drops may remain airborne under strong wind conditions. Such optimization is done by using the computer model HGSPRAY5.

HGSPRAY, a verified mathematical model (Fthenakis, 1993), has been developed to quantify effectiveness of water sprays at specific installations, given specific release scenarios and weather conditions. HGSPRAY5 has the capacity to model chemical reactions in the liquid phase and can be used to evaluate mitigation systems using caustic or oxidizing solutions for removal of various gases. The model has been used in aiding the design of several industrial HF mitigation systems in the U.S. and Europe. HGSPRAY5 is a two-dimensional spray model that describes absorption of gases by water sprays, air entrainment and heat transfer. It is a complete model of coupled mass, momentum, and heat transfer between air/HF and drops injected by water sprays or monitors. The water droplet dynamics are explicitly described by considering a finite number of drops of varying size and trajectory. As drops transverse the computational flow field, they accelerate or decelerate, evaporate or condense, conduct heat or convect enthalpy, and absorb ammonia. HGSPRAY5 has been verified against the 87 Hawk field tests performed in the DOE Nevada test site as part of the ICHMAP: HFSPRAY model predictions are within ±6% of the experimental results obtained in the Hawk field tests (Fthenakis et al., 1993). In addition, the model replicated the dispersion patterns observed from boundary layer wind tunnel modeling of water spray mitigation systems from actual industrial installations (Fthenakis and Blewitt, 1993).

In general, computer simulations of a heavy gas (HG) release mitigation system entail the use of three models, each describing the plume behavior in a different region (shown in Figure 1):

1. HGPLUME (part of HGSYSTEM) for the initial release and near-field dispersion of the released jet.
2. HGSPRAY5, for liquid spray-HG interactions.
3. HEGADAS5 (part of HGSYSTEM) for the subsequent dispersion of the remaining HG downwind of the sprays/monitors.

HGSPRAY5 is linked with the HGSYSTEM models (Puttock et al., 1990) which describe the physical transformations and the dispersion of a jet or plume upstream and downstream of the water spraying region. The HGSYSTEM models describe all the phases of an accidental gaseous release, including depressurization, phase-change, and atmospheric dispersion of buoyant or denser-than-air gases. These models have been independently verified by comparisons with a wide range of experimental databases.

**Ammonia specific modeling**

HGSPRAY5 is a general model which can simulate the scrubbing of any gas with water sprays, once the
gas physical and transport parameters are known. The characteristics of an ammonia plume (such as density, viscosity, diffusivity, concentration, temperature) are a user input to the model.

Ammonia specific parameters in HGSPRAY include the Henry's law coefficient, and other physical and chemical parameters.

\[ \ln H = 4.092 T^{-1} - 9.7 \]  

\[ m_k c_p \frac{dT}{dt} = \text{Nu} \pi d(T_g - T) - m_w h_w - m_{ah_a} \]  

The Henry's law coefficient is described as a function of the drop temperature in Eq. 1. The drop temperature is derived from the solution of the energy equation (Eq. 2) where \( m_k \) is the mass of a drop \( k \), representing a specific drop size and trajectory \( m_w \) is the drop's evaporation rate, \( m_a \) is the rate of \( \text{NH}_3 \) absorption in the drop, \( T \) is the drop temperature, \( T_g \) is the temperature of the surrounding gas, \( k \) is the thermal conductivity, and \( c_p \) is the specific heat of water, \( h_w \) is the latent heat for water evaporation and \( h_a \) is the heat of solution of \( \text{NH}_3(g) + \text{H}_2\text{O} \) mixing.

A series of simulations were conducted to predict the effectiveness of water sprays in mitigating ammonia releases from high-pressure containers. Release scenarios resembling the Hawk HF tests were chosen to compare ammonia removal with the HF mitigation, because the latter has been established both in the field and by earlier simulations (Fthenakis et al., 1993). A comparison of \( \text{NH}_3 \) and HF removal effectiveness, as a function of water-to-gas weight ratio, is shown in Figure 2; the corresponding initial conditions are given in Table 1.

The effectiveness of ammonia mitigation will depend, besides the water-to-gas ratio, on several other parameters (such as location of release, concentration of ammonia in the plume, positioning of spray nozzles, drop size, wind speed, ambient temperature) in the same way that HF removal is affected by these parameters. Such effects are discussed elsewhere (Schatz, 1993; Fthenakis, 1993).

Ammonia is less soluble in water than HF and, therefore, is removed to a lesser extent than HF by water spraying. Nevertheless, the predicted ammonia removal is sufficiently high (about 75% at a 40 to 1 water to ammonia ratio) for water spraying to be an effective tool for mitigation of accidental release of ammonia as well.

Case Studies

Two industrial cases are considered: one involving sprays in a "curtain" setting and the other involving water monitors.

**Case A: water curtain**

This case involves modeling of an actual HF mitigation system based on sprays encircling an alkylation unit (Figure 3). The spray configurations considered are: (a) two headers at about 25 ft (7.6 m) off the ground, one equipped with spray nozzles pointing upwards and the other with the same nozzles pointing downwards, and (b) two headers at different elevations.

| Table 1. Input Data for HF and \( \text{NH}_3 \) Simulations |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| H\(_2\)O/Gas  |
| Mass Rate*   | Water Flow Rate (kg/s) | Nozzle Type** | Water Pressure psig (kPa) | Mean Drop Size (\( \mu \)m) | Air Temperature \( ^\circ \text{C} \) | Wind Speed (m/s) |
| Ratio*        | 6.6             | 1.6             | TF10FCN        | 23 (158)         | 315             | 92 (33)         | 3.3             |
| 13.4          | 3.4             | 3.4             | TF12FCN        | 43 (296)         | 287             | 90 (32)         | 3.1             |
| 28.1          | 6.4             | 6.4             | TF16FCN        | 56.9 (386)       | 326             | 87 (31)         | 3.4             |
| 56.4          | 12.6            | 12.6            | TF20FCN        | 92 (634)         | 318             | 90 (32)         | 3.3             |

* Gas denotes either HG or \( \text{NH}_3 \). The gas-flow rate is approximately constant while the water flow rates vary. The gas plume enters the spray envelope with a uniform concentration of about 4 wt. %.

** Beta Fog Nozzle Inc., full cone nozzles, pointing downward.
Figure 1. Mitigation modeling regimes.

Figure 2. Comparison of model estimates of HF and NH₃ mitigation.

Figure 3. Conceptual design of water curtain around a unit handling a hazardous heavy gas.

Figure 4. Simulation of HF mitigation.
9.5 kg/s release at grate, sprayed by a two-tier water curtain, inward nozzles, total water flow 12,000 gal/min (757 L/s), wind speed 5 m/s; predicted HF removal effectiveness = 90%.
[such as 25 ft (7.6 m) and 45 ft (13.7 m)] with nozzles pointing horizontally toward the release. Two different types of spray nozzles producing drops of different size were tested. HF releases at two elevations and flow rates were considered to bracket the range of potential releases. At grade (that is, 1 m above the ground), the release rate was 9.5 kg/s and at a 10 m elevation the release flow rate was 8.2 kg/s. The water-flow rate in the entire water curtain system was 12,000 gal/min (757 L/s). The lateral spread and the concentration of the plume as it intersects the spray were determined from fluid modeling tests. According to the HGSPRAY5 simulations, the two-tier horizontal configuration removed HF somewhat more effectively than the up-and-down configuration for the specific release heights. Effectiveness of HF removal ranged from 70% for strong wind speeds (such as 12 m/s) to 92% for light wind speeds (such as 5 m/s). The corresponding effectiveness of the up-and-down system was lower, because a part of the plume was escaping at the top. Figures 4 and 5 show example simulations of this mitigation performance evaluation; the different shade contours show HF concentrations, the arrows show gas-phase velocities and the dotted lines the outer drop trajectories produced by the sprays.

**Case B: Fire water monitors**

HGSPRAY5 is capable of modeling a release of HF anywhere between fire water monitors. A release can be introduced within the computational space either as a point release of a specified flow rate, or as a line release of a specified concentration profile. However, two-dimensional approximations of the monitor configuration need be developed. Therefore, the application of this model to describing the flow fields induced by fire water monitors spraying from various positions requires considerable simplification of complex three-dimensional fields and poses significant constraints in its application. Reasonable estimates of spray effectiveness can be obtained when the water is applied on a symmetrical pattern. One sample case, involving 12 monitors in various positions around a process/storage

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**Figure 5. Simulations of HF mitigation.**
Release at 10 ft (3 m) off the ground, 9.5 kg/s, sprayed by a two-tier water curtain, downward nozzles, total water flow 12,000 gal/min (757 L/s), predicted HF removal.

**Figure 6. Simulations of HF mitigation.**
8.3 kg/s release at grade; sprayed by 11 upwind and downwind monitors, total water flow 11,000 gal/min (694 L/s), wind speed 7 m/s; predicted HF removal effectiveness = 80%.
unit, was approximated with 5 "composite" monitors at upwind and downwind positions. In the simulations, upstream monitors at the same elevation and same distance from the release point were grouped into a single composite monitor, and, similarly, downstream monitors were grouped at an antidiometrical downstream position. The composite monitors carry the sum of the flow rates of their components, and the same drop velocities and drop-size distribution as that of a single monitor. The velocity and concentration fields of this simulation are shown in Figure 6.

**Alternative Means of Mitigation**

Application of water to an ammonia leak is an effective means of mitigation. However, supplying, handling, and disposing of large water volumes can be a challenge. In cold climates, water sprays might not work at all, unless the pipes and nozzles are heated. At low temperatures, water drops crystallize and ammonia absorption is detrimentally reduced. Disposal of the alkaline water might require a separate sewer system, neutralization pits, and collection ponds, which can add substantially to the cost of the water spray system.

**Dry Powders.** In cold climates, mitigation of releases might be accomplished with dry powders. This option has been tested in laboratory scale for HF. Dry powders, such as metal carbonates, oxides, or hydroxides, have the intrinsic advantage of low weight to HF ratio. For instance, stoichiometrically, 1 kg of titanium dioxide can react with 1 kg of HF. The laboratory studies showed that, with low multiples of stoichiometric ratio (contained) HF clouds can be mitigated with very high efficiency. Several dry powder systems are commercially used for firefighting, but they are not large enough to handle powder rates of several tons per minute, the size required for a large HF or NH₃ leak.

**Process Changes.** Other options, intended to reduce the amount of airborne material produced by a release, include reduced operating pressure, temperature, and inventory of the unit, and additives to suppress volatilization. For HF, specifically, proprietary additives have been developed that can change the physical properties of the gas so that a lower percentage of the leaking material remains airborne. The liquid fraction spilled on the ground can be collected in a dike and treated.

**Foams.** Spills of refrigerated ammonia on the ground may vaporize rather slowly and allow for foam coverage to reduce the evaporation. Application of foams to reduce the vaporization from anhydrous ammonia spills was shown to be both effective and economical (Norman and Swihart, 1991).

**Hybrid Systems,** combining features from different approaches, have not been investigated to any substantial extent at this time. During the ICHMAP studies, vapor barriers were evaluated. A box-shaped, open-top enclosure around the alkylation unit showed significant delay for cloud arrival time (near distance) and a reduction of peak concentrations. Such a vapor barrier combined with water sprays might provide an acceptable mitigation system. However, industry concerns regarding hydrocarbon accumulation within the barrier and the potential for explosion, together with reduced accessibility, have kept interest at a low point.

**Other Considerations**

**Fire concerns**

Anhydrous ammonia is flammable in air in the range of 16%-25% by volume; its ignition temperature is 1,123 K. Although this high temperature and narrow ignition range is difficult to attain in outdoor releases, explosions have occurred. Water fog application will help mitigate the ammonia vapor concentration and reduce the explosion hazard.

**Induced vaporization**

Caution should be used to avoid directing water into the ammonia liquid itself since this will cause rapid and vigorous boiling and vaporization of the cold liquid, thereby making the situation more dangerous by increasing the amount of vapor released.

**Protective personal apparatus**

In case of manned response to NH₃ release, heavy chemical protective clothing for the head, hand, body
and feet should be worn to totally protect the responder against both corrosive vapors and the freezing action of the liquid, along with properly fitted self-contained breathing apparatus to protect against the vapors.

**Liquid waste management**

The application of water fog to ammonia vapor and aerosol creates a fallout of aqueous solution which, unless properly contained, can contaminate water supplies and streams with excess nitrogen levels and higher than normal pH levels. This liquid needs to be contained and neutralized.

**Conclusion**

The capability of water sprays in mitigating releases of highly water soluble gases (that is, HF, NH₃) has been demonstrated in large-scale field experiments. The performance of these systems in the field can be evaluated using the model HGSPRAY5. The model is capable of predicting the performance of water-spray systems (both water curtain or monitor configurations), in mitigating water-soluble gases via absorption and dilution, and in reducing the concentration of flammable vapors via dilution.

**Literature Cited**


Schatz K.W., and V.M. Fthenakis, “Mitigation of Hydrogen Fluoride Aerosols by Dry Powders,” *J.
DISCUSSION

Y. Nishikawa, Mitsubishi Chemical Corp.: Do you require any special strainers ahead of the sprays to remove dust or particles from the water?

Fthenakis: Yes. There are screens on the lines that would take care of any particles. The system would be wet in most locations all the way to the nozzle, and there would be screens that would filter any particles. The nozzles have a rather large orifice, about a 1/4 in., they have been tested many times, and they never have experienced any plugging problems.

W. Delboy, DuPont: Can you tell me what the Texas city site does with the water once it’s sprayed on the ground? Do they have any collection or treatment of the water?

Fthenakis: Definitely. The whole unit is paved and is drained to a collection basin where the water can be neutralized. All of these units have a collection system.

Delboy: How often do they test the system?

Fthenakis: In the beginning it was tested several times. I don’t think they have a program to test it more than once a year now. In the beginning it was a manual operation, but now it is on automatic operation connected to three different types of detection systems. The first is visual, the second utilizes IR, and the third utilizes hydrogen fluoride probes.