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ANALYSIS OF VAPOR BARRIER EXPERIMENTS TO EVALUATE THEIR EFFECTIVENESS AS A MEANS TO MITIGATE HF CLOUD CONCENTRATIONS

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ABSTRACT

Accidental release of Hydrogen Fluoride (HF) can result in initially dense, highly reactive and corrosive gas clouds. These clouds will typically contain a mixture of gases, aerosols and droplets which can be transported significant distances before lower hazard levels of HF concentration are reached. Previous related field and laboratory experiments have been analyzed to estimate the effectiveness of barrier devices. The experiments were examined to determine their relevance to Hydrogen Fluoride spill scenarios. Wind tunnel and field data were compared where possible to validate the laboratory experiments. Barrier influence on peak concentrations, cloud arrival time, peak concentration arrival time, and cloud departure time were determined. These data were used to develop entrainment models to incorporate into integral and depth averaged numerical models. The models were then run to examine barrier performance for a typical Hydrogen Fluoride spill for a wide range of vapor barrier heights, spill sizes, meteorological conditions and release configurations. Finally the results of the data analysis and numerical sensitivity study were interpreted and expressed in a form useful to evaluate the efficiency of vapor barrier mitigation devices.

INTRODUCTION

Recent disastrous accidents (e.g., Bohpal [1984], Chernobyl [1986], Kerr-McGee [1986]) have focused attention on the potential risks of large and small scale releases of flammable or toxic gases. Exxon Research and Engineering Company, in conjunction with and on behalf of an ad hoc Industry Cooperative Hydrogen Fluoride (HF) Mitigation and Assessment Group has funded this study to assess the effectiveness of vapor barriers in diluting and delaying heavier-than-air HF vapor clouds.

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HYDROGEN FLUORIDE GAS CHARACTERISTICS

Hydrogen fluoride is a colorless, corrosive toxic liquid or gas, depending on the temperature. The concentration that produces acute effects varies with the time of exposure. The American Industrial Hygiene Association recommends levels of ERPG1 = 5 ppm, ERPG2 = 20 ppm and ERPG3 = 50 ppm for the Emergency Response Planning Guidelines. The 1979 ACGIH has also established a Threshold Limit Value (TLV) of 3 ppm (2 mg/m3) for exposures of people in occupational settings.

HF can exist as unassociated HF or as an HF polymer, with association favored by low temperatures. A turbulent jet expands and entrains air, any liquid droplets entrained by the flashed HF vapor will vaporize thereby drastically reducing the cloud temperature. Air dilution will reduce the HF partial pressure thus favoring dissociation, but the temperature reduction resulting from liquid HF vaporization will favor HF association. Simultaneously, the rapid temperature drop due to entrained liquid HF vaporization will condense out moisture from the ambient air as frost or droplets. This condensed water will react with the HF forming a stable, maximum boiling water/HF azeotrope. The result is a persistent HF/water fog whose properties are changing significantly as it entrains air and is advected downwind.

Schotte (1987) developed equations for liquid HF releases to predict temperature changes, onset or disappearance of fog, amount of fog, fog density, and concentration of HF in the fog. Calculations for HF release conditions suggest that the initial source cloud consists of 80% - 90% liquid aerosol and initial cloud temperatures of 0 to 14 °C. The subsequent rise and fall of liquid aerosol fraction and cloud temperature are quite complex, but the effective cloud density decreases monotonically with increase in entrained air. It is this cloud density state relation which determines cloud spreading behavior and effects the turbulent mixing rates.

An ideal gas can be conceived with molecular weight of 20, a very cold source temperature, and a specified molar specific heat capacity that will have the same number of molecules per volume as an HF aerosol cloud. Careful selection of the ideal gas molar specific heat capacity permits the ideal gas to reproduce the density behaviors noted above.

Hydrogen Fluoride Spill Experience

Although accidental releases of Hydrogen Fluoride have occurred (Kerr-Mcgee spill in 1986), little information can be gleaned from post spill analysis about the cloud mixing process. Hence, in 1986 Amoco Oil Company and the Lawrence Livermore National Laboratory (LLNL) conducted a series of six experiments involving atmospheric releases of anhydrous hydrofluoric acid at the Department of Energy Liquefied Gaseous Fuels Test Facility. The purpose of these tests was to examine source characteristics, dispersal properties and water spray mitigation techniques. A description of the experimental design and limited results were presented in papers by (Blewitt et al., 1987a, 1987b).

These tests were designated the "Goldfish" test series by LLNL. The first three tests were unmitigated releases (i.e. no water sprays); whereas the next three tests considered the mitigating influence of water sprays. Goldfish Trials 1, 2, and 3 have been used to validate the numerical entrainment models. Goldfish Trial 1 was also chosen to be the reference case against which sensitivity calculations were performed for the mitigating effects of water sprays and vapor fences operating at various locations, wind speeds, spray strengths and barrier heights.

APPLICABLE DATA BASES

Puttock, Blackmore and Colenbrander (1982) identified over 22 field experiment programs on dense gas emissions. Subsequently, further field measurements have been performed on the release of Freon-air mixtures at Thorney Island, the release of hydrocarbon fuels at Maplin Sands, and the release of hydrocarbon fuels, ammonia, rocket fuels, and even HF at the DOE Liquefied Gaseous Fuels Test Facility at Frenchman's Flats, Nevada. A number of these experiments have also been simulated in fluid modeling facilities (Meroney, 1986a). Meroney et al. (1988) recently examined eleven data sets from field and laboratory experiments dealing with the influence of vapor barrier fences and water spray curtains on the dispersion of dense gas clouds. Tests were paired into sets of data which reflected the dilution of the cloud with and without the barriers present. Peak concentration ratios, cloud arrival time ratios, peak arrival time ratios, and departure time ratios were calculated for each test pair.

PREDICTION OF HF DILUTION

When the flow situation is steady and diffusion in one direction is weak with respect to advection, it is possible to integrate over a plume cross-section and calculate plume width, average height, and cross-section averaged velocities, concentrations, temperatures, and humidity. Such a "box" type model is numerically very fast since the conservation equations reduce to a set of coupled ordinary differential equations. Alternatively when vapor generation is transient, and there are opportunities for upwind flow, a set of coupled partial differential equations of only two dimensions and time can be created by integrating the conservation equations over just the depth. Such a "shallow layer" or "slab" type model provides information about time- and space-dependent cloud widths, heights, and depth-averaged velocities, concentrations, temperatures, and humidities.

A box model (DENS62: Meroney and Lohmeyer, 1984; Meroney, 1983; and Andriev et al., 1983) and a slab model (SPRAY23: Meroney and Lohmeyer, 1984, and Meroney, 1984a and 1984b) have been adapted to consider HF dilution by water sprays and vapor barrier fences.

Entrainment Models for Vapor Barriers and Water Spray Curtains

Both numerical models normally use the concept of an entrainment velocity, w^Ye^X, across the upper cloud surface to mix the cloud with ambient air. The entrainment velocity is a semi-empirical function of boundary-layer and cloud variables such that,

$$w_e = f(U_g,\ u_*,\ w_*,\ Ri_*),$$

where U_g = plume frontal velocity, u_* = friction velocity, w_* = convective velocity, Ri_* = local Richardson number.

Reductions in HF cloud concentrations can occur through chemical reaction between the cloud and water spray. HF reacts with the liquid water and leaves the cloud as the water deposits on the ground. Laboratory and field tests described by Blewitt et al. (1987c) measured HF removal ranging from 9 to 80%.

Britter (1982) reviewed a number of special hydraulic effects expected from stratified fluids in the presence of surface obstacles or sloping terrain. Later Rottman et al. (1985) considered the Thorney Island Phase II trials.

Essentially the cloud may behave like a moving layer of liquid traveling either as a rapid (supercritical) or tranquil (subcritical) flow, where $Fr > 1$ or $Fr < 1$, respectively passing over a surface obstruction. When the flow is rapid the obstacle may block and reflect the cloud upwind; increase upwind depth and accelerate the cloud over the obstacle; and then sometimes mix aggressively in a hydraulic jump. Calculations suggested that with low ambient winds the gas cloud would not pass over a fence if the height of the fence is more than 2.5 times the height of the approaching gravity current. When the approach flow is tranquil and the cloud height is greater than the fence height, then the cloud upper surface may dip down briefly as it passes over the obstacle.

Rottman et al. (1985) also concluded that when a rapid flow passes through a porous fence the cloud may accelerate and the cloud height will decrease. This could lead to earlier arrival times downwind of the fence.

The following simple model is proposed to described the increased entrainment resulting from a vapor barrier fence:

$$(w_e)_{fence} = C_D U(H)(1 - P)(1 - (x - x_f)/(30H)),$$

where x is distance downwind of the source, x_f is fence location, and the relation is not used downwind of x_f. This model was used in the numerical models to compare with selected field and model data.

Comparison of Numerical Models with Goldfish Trials Data

Blewitt, Yohn, and Ermak (1987b) compared the box model SLAB developed by Ermak et al. (1985) and the slab model DEGADIS developed by Havens and Spicer (1985) against Goldfish Trials No. 1, 2, and 3. A transient version of SLAB predicted experimental data within a factor of two.

DENS62 (Meroney, 1988) predictions of Goldfish Trials No. 1, 2 and 3 were calculated using an ideal gas with molecular weight equal to 20, source temperatures of 20, 20, and 10 °K, respectively, and molar specific heat capacities of 0.83, 0.83 and 0.9 times that of air, respectively. As noted above these values are necessary to reproduce the HF density behavior predicted by the Schotte equations. Figure 1 compares the centerline concentration decay of the HF plume with measured values and the SLAB predictions by Blewitt et al. (1987b).

Calibration of the Vapor Barrier Fence Entrainment Model

Data from the pre-Falcon model tests performed by Neff and Meroney (1986) were used to calibrate the vapor barrier fence entrainment model. Run No. 2 (9.4 m fence, no vortex generator, enclosure alone) was selected to compare with Run No. 10 (no enclosure). Figure 2 compares the results of calculations by FENC62 when the coefficient CD = 0.1. Variations in virtual distance between 60 and 44 m, and variations in the entrainment coefficient over a two-fold range did not significantly improve agreement. Best agreement occurred for Trial No. 10 data when the initial source width without a fence was set to 44 meters. A small dike existed about the model water spray pond, which may have inhibited lateral spread at the source.

Calibration of the Vapor Removal Model

Deposition measurements suggested that the water sprays removed 10-25%, 44%, and 47% of the HF during Goldfish Trials 4, 5, and 6, respectively. The water spray systems were designed to produce small droplets to enhance chemical reactions, rather than strong dilution. DENS65 was used to predict cloud concentrations with the reduction mode on but water spray entrainment set to zero. Figures 3 compares program predictions of cloud concentrations against measured values for Goldfish Trial No. 6.

SENSITIVITY STUDY

The effects of fence location were determined to be similar to that of water spray curtain location. Fences are more effective in terms of initial dilution, when they are placed nearer the source. Fence dilution effects did not persist beyond 1000 m, when the fence was placed less than 400 m downwind of the source.

Effects of Fence Height

The fence entrainment model permits the entrainment velocity to increase with fence height velocity. Since wind profiles increase with height, then the dilution rate should increase with fence height. The FENC62 model assumes that a logarithmic velocity profile exists, such that wind speed is determined by surface roughness and friction velocity. Figure 4 displays a set of curves for fence heights ranging from 3 to 12 meters. The entrainment velocity does not turn off abruptly like the water spray model, but decreases linearly out to a distance of 30 fence heights. The resulting displacement of the concentration profile is cusp shaped rather than triangular, and the dilution effect is small after about 200 fence heights. The effect of fence height on cloud height is displayed in Figure 5. The cloud height approaches the cloud height in the absence of a barrier after 1000 meters or about 200 fence heights.

Effects of Wind Speed

Increased wind speeds result in larger entrainment rates, but this is compensated by the tendency for the plume to pass through the fence wake more quickly. Given a constant fence height of 3 meters located 100 meters downwind of the source for a range of wind speeds varying from 1 to 8 m/sec, the increased entrainment and shortened time in the wake balance out to produce no net change in dilution rate. Plume height also remains constant. These calculations agree with other experiences in building aerodynamics, where it is found that perturbation of gas plumes by obstacles seems to be velocity independent. Concentrations decay at higher wind speeds inversely with the speed, but this is an independent effect of source dilution by the ambient wind, not an effect of a fence.

Cloud height downwind of an obstacle is expected to be independent of wind speed, since a sharp edged geometry will produce similar streamline patterns over a range of velocities. Model results suggest that the perturbation produced by a fence is constant, but the model fails to allow for a constant height wake region.

Water Spray Effects on HF Reduction

Water spray curtain tests were performed during the Goldfish Trials No. 4, 5, and 6. These tests included chemical reactions between the HF and the water spray and subsequent deposition of the HF on the ground. Goldfish Trial No. 1 conditions are used below to examine the effect of various spray placement and water spray reduction and entrainment rate alternatives.

SPRAY65 and SPRAY 23 were used to predict the joint effects of water spray dilution and deposition on an HF cloud. Figure 6 displays the effect of placing a single spray which produces 80% deposition at 100m followed by a second spray of similar strength at 300 m. Notice that spray deposition produces a parallel shift of the concentration decay curve. A second spray produces a second shift of equivalent width. The decrease in concentration persists at all subsequent downstream distances.

Figure 7 depicts the effect of joint dilution and depletion. In this case it is assumed that $(w_e)_{spray}$ = 6 m/sec and HF reduction is again 80%. Reductions in plume concentration produced by the water spray alone do not persist, but combined dilution and reduction produce large local reductions and concentration followed by a shift in the concentration curve downward.

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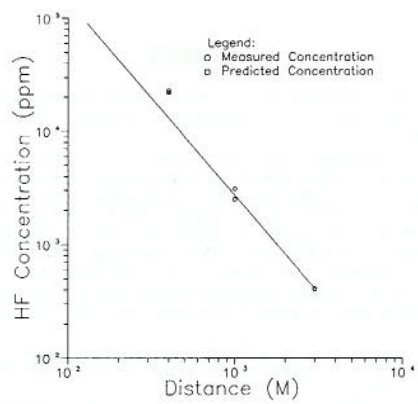

Figure 1 Comparison of observed, SLAB and DENS62 predicted plume centerline concentrations for Goldfish Test No. 1

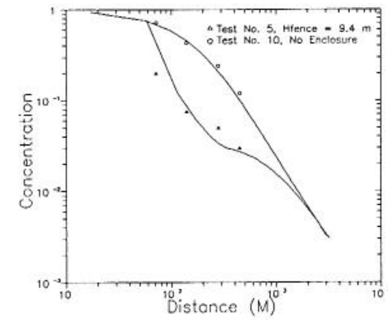

Figure 2 Comparison of observed and FENC62 predicted plume centerline concentrations for Pre Falcon Tests No. 5 and 10. Q_L = 40 m^3/sec, U = 3.5 m/sec, T_S = 111 oK, T_{amb} = 300 ^oK.

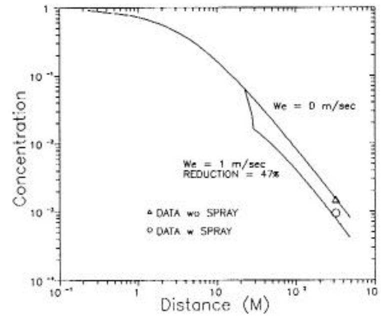

Figure 3 Comparison of observed and SPRAY 65 predicted plume centerline concentrations for Goldfish Test No. 6. Q_L = 33 gallons/min, U = 5.4 m/sec.

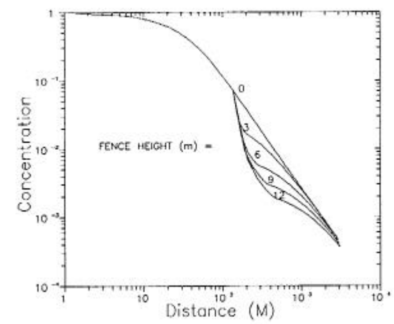

Figure 4 FENC62 predicted plume centerline concentrations for Goldfish Test No. 1, Fence heights = 0, 3, 6, 9, and 12 m/sec at X = 100 m.

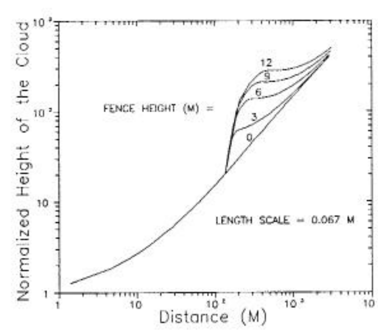

Figure 5 FENC62 predicted plume heights for Goldfish Test No. 1, Fence Heights = 0, 3, 6, 9, and 12 m at X = 100 m.

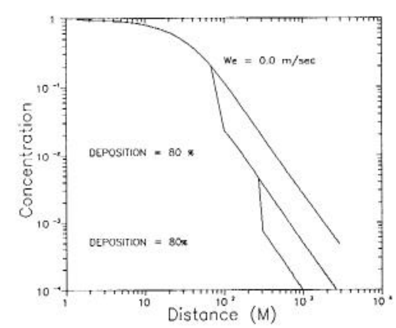

Figure 6 SPRAY65 predicted plume centerline concentrations for Goldfish Test No. 1, 80% HF removal by water spray at X = 100 m and X = 300 m.

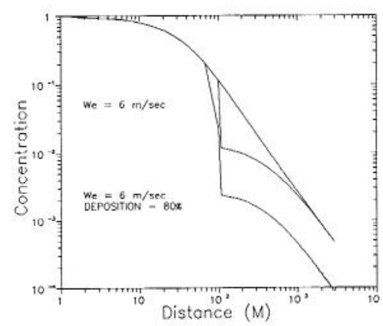

Figure 7 SPRAY65 predicted plume centerline concentrations for Goldfish Test No. 1, 80% HF removal and W_e = 1 m/sec by a water spray at X = 100 m.