EFFECTIVENESS OF MITIGATION SYSTEMS IN REDUCING HAZARDS OF HYDROGEN FLUORIDE LEAKS

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ABSTRACT

Hydrogen fluoride (HF) is used in the petroleum industry as a catalyst in the alkylation process for producing high octane gasoline components. Over the past several years, an increasing awareness of the hazards associated with an accidental release of HF has resulted in a review of the potential hazards associated with the acid. In a typical alkylation unit, a release of anhydrous HF will result in an airborne aerosol cloud that contains HF vapor and HF droplets. Experiments (Goldfish tests, aerosol release [Blewitt, et al., 1987a]) and accidents (Marathon vapor release [EPA, 1993]) indicate that the formation of an aerosol may be one of the single most important parameters that determines the size of the hazard zone.

Over the past several years, different mitigation systems have been designed to reduce the impact of an HF release. The systems have varied from active systems that are designed to reduce the duration of an acid release or absorb acid out of the released cloud, to passive systems that alter the nature of the acid itself. In this paper, three current and proposed mitigation systems will be reviewed. Each system will have advantages and disadvantages relative to the others. For each system, a release from a generic HF alkylation unit will be evaluated. The effect of the mitigation system on the rate at which acid reaches the atmosphere, as well as the downwind travel distance to a toxic endpoint, will be calculated. The three mitigation systems to be evaluated are:

- Rapid acid deinventory system
- Water spray system
- Acid additive

Several studies [Technica, 1990; Maher, Kaiser, and Alderman, 1994] have attempted to compare the risk of using HF as the alkylation acid to the risk associated with the use of sulfuric acid (H_2SO_4) as the alkylation acid. A key component to any risk analysis study is the accurate calculation of the source term. Considerably more information is now available for calculating the acid release rates. As a point of comparison, the release rates and dispersion distances for an equivalent release of H_2SO_4 will also be included in the analysis.

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This paper will be divided into three sections:

1. Advantages and disadvantages of each mitigation system.
2. Effect of each mitigation system on the release rate and airborne fraction of acid.
3. Effect of each mitigation system on the downwind dispersion distance of airborne acid.

ADVANTAGES AND DISADVANTAGES OF MITIGATION SYSTEMS

Each mitigation system listed above has the potential to reduce the potential hazard zone associated with an HF release. However, each system may also have limitations that should be considered before implementation.

Rapid Deinventory System

The primary aim of a rapid deinventory system is to reduce the amount of HF that might be released during an accident. Generally, the acid is transferred (dumped) to an empty storage vessel by the available system pressure or pumps. Depending on the size of the unit and the transfer mechanism and pipe diameters, the total time to transfer the acid will vary and may be on the order of twenty minutes.

The potential advantages of a deinventory system are:

- reduces the duration of a potential release by removing inventory.
- relatively simple operation.

The potential disadvantages of a deinventory system are:

- does not reduce the rate at which HF is released.
- does not reduce the fraction of HF released that remains airborne.
- as an active mitigation system, someone or something must activate the isolation valves that initiate the dump.
- during the recognition and response time, no acid is removed from the system except for the acid leaking into the atmosphere.
- if the deinventory rate is small relative to the leak rate, the benefit derived from the deinventory system may not be significant.
- as an active mitigation system, maintenance and reliability can be issues.
- availability—what if the initiating event that caused the release of HF from the alkylation unit also damaged the deinventorying equipment, thus rendering it inoperable?

Water Spray System

There are two principal benefits to a water spray system. For HF, the first benefit is derived from the ability of water to absorb HF, thus removing the HF from the released cloud. The second benefit comes from the enhanced turbulence generated by the water mixing with the released cloud. The increased turbulence adds air to the system, reducing the concentration of HF in the cloud. There are several water spray mitigation systems available: water curtains, fixed water monitors, portable water cannons, etc. Although the benefits are the same for each system, their efficiencies, response times, and reliability vary. For the purposes of this paper, only the fixed water curtain system is evaluated.

The potential advantages of a fixed water spray curtain are:

- absorption of HF by water, thus removing the acid from the vapor cloud.
- increased turbulence induced by introduction of the water curtain, lowering the HF concentration.

The potential disadvantages of a fixed water spray curtain are:

- does not reduce the rate at which HF is released.
- as an active mitigation system, someone or something must activate the water spray curtain before it becomes operational.
- during the recognition and response time, no acid is removed from the cloud.
- the efficiency of the curtain is dependent on many factors, such as hole size and location, release orientation, distance between HF release point and water curtain, and the ratio of water mass flow to HF mass release rate.
- availability—what if the initiating event that caused the release of HF from the alkylation unit also damaged the water spray curtain equipment, thus rendering it inoperable?

HF Additive to Reduce Volatility

There have been several efforts made [Muralidhar, et al., 1995; Melhem, Comey, and Gustafson, 1995] to identify a material(s) that, when added to the HF acid, would reduce the potential size of the hazard zone following a release. In general, a desirable additive would have the following characteristics:

- the additive increases the ratio of HF that falls to the ground versus the HF that remains airborne during a release.
- the additive dilutes the acid, reducing its concentration.
- the additive works to reduce the vapor pressure of the HF phase, thus making the HF/additive mixture less volatile.
- the additive does not affect the alkylation efficiencies.

The potential advantages of using an additive are:

- the additive reduces the amount of HF that remains airborne following a release when compared to the no-additive release.
- since the additive is mixed with the HF, the behavior of the acid upon release is immediate. There is no response time; the mitigation is built into the system.

The potential disadvantages of an additive are:

- having the HF/additive mixture on the ground creates liquid containment problems.
- effectiveness of the additive is partially defined by the release trajectory that defines the amount of time required for the HF/additive to reach grade.

EFFECT OF EACH MITIGATION SYSTEM ON THE RELEASE RATE AND AIRBORNE FRACTION OF ACID

In order to compare the effect of a mitigation system on the amount of acid that remains airborne or falls to the ground, a consistent set of initial conditions must be defined. For this example, a "typical" HF alkylation unit is presented in Figure 1. The total HF acid inventory is 15,000 gallons. For the purposes of comparing the different mitigation systems, the following parameters are set.

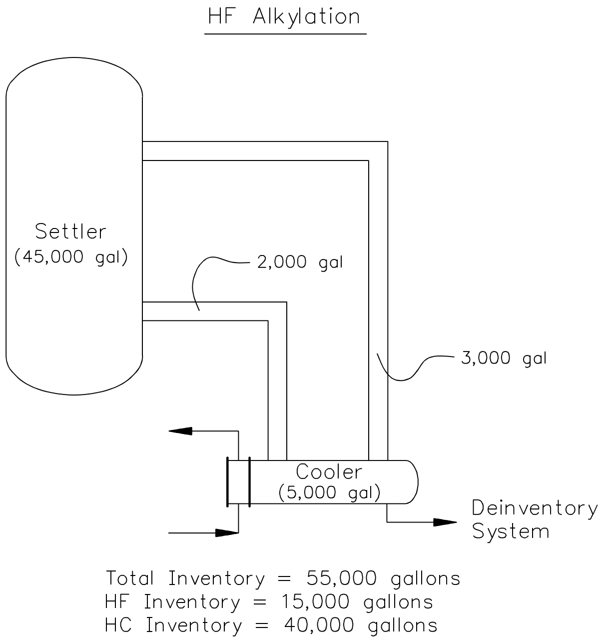

Figure 1

Hole size = 2 inches (5 cm) in diameter
Hole location = 4 feet (1.2 m) above grade, in acid cooler, horizontal release
Operating conditions = 100 psig (690 kPa gauge), 90°F (32.5°C)
Atmospheric conditions = 5 m/s winds, D stability, 70% relative humidity, 70°F (21°C) air temperature

This release description will allow the mitigation systems to be evaluated on the same basis; what is the hazard associated with an acid release from a two-inch hole?

Release Number 1 - Pure HF, No Mitigation Systems

Work conducted by Quest indicates that at 90°F, a very small fraction (~3%) of the HF released under the defined conditions would reach the ground. The total mass flow rate out of the two-inch hole in the settler is 85.4 lb/s (38.8 kg/s). The mass flow rate for each phase (HF vapor, HF liquid entrained as aerosol, and HF liquid raining out to the ground) is presented in Figure 2. For the first seventeen minutes, pure HF is released out of the two-inch hole. During this time, very little of the acid reaches the ground as the flashing process shatters the liquid into small drops that remain suspended as an aerosol cloud.

Release Number 2 - HF/HC, No Mitigation Systems

As the HF is released from the bottom of the acid cooler, the mixed layer of HF and hydrocarbon (HC) reaches the hole. This occurs approximately seventeen minutes after the release starts. For the purposes of

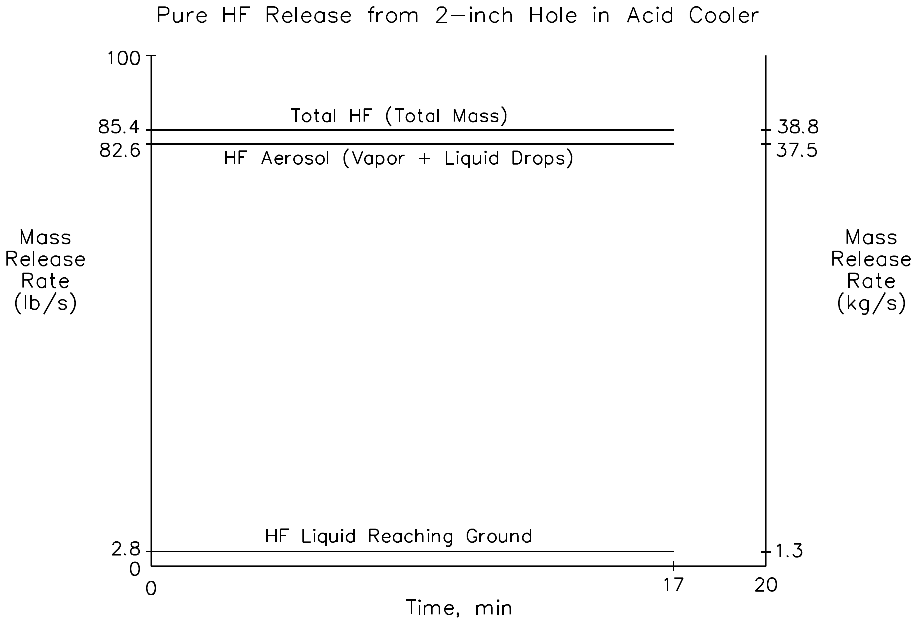

Figure 2

this example, the ratio of HF/HC is defined to be 50/50 by mass. Once the HF/HC mixture reaches the hole, several things happen:

- mass flow rate out of the hole drops since the density of the HF/HC mixture is less than that of HF.
- flashing of the more volatile HC intensifies the shattering process of the remaining liquid HF and HC.

Figure 3 presents the full release history from a two-inch hole in the acid cooler. During the first seventeen minutes, only HF is released. After seventeen minutes, the HF/HC interface reaches the hole, the total flow drops, but the flashing process puts all of the HF into the air as an aerosol cloud. As can be seen in Figure 3, the mass rate of HF entering the air is lower (36.8 lb/s) when the HF/HC mix is released than when the pure acid is released (82.6 lb/s). In essence, even though the HC aids in the shattering of the remaining liquid, it also acts to dilute the released acid.

Release Number 3 - Pure HF, Rapid Deinventory System

The effect of adding a rapid deinventory system to the alkylation unit is seen in Figure 4. The rapid deinventory system was designed to remove 2,000 gpm from the bottom of the acid cooler. A key element in assessing the effectiveness of any active mitigation system is the system's response time. That is, how long after the hole appears is the release detected, identified, and the deinventory system enabled? For the purposes of this paper, a one-minute response time was chosen.

Activating the deinventory system serves to reduce the duration of the total release. As can be seen in Figure 4, after about twenty-one minutes, the total inventory of the acid cooler, settler, and associated piping has been either dumped to an acid holding tank or released into the environment. It is also clear from comparing Figure 3 and Figure 4 that, for the release location chosen (bottom of the acid cooler), the deinventory system did reduce the period of time pure HF is released from seventeen to four minutes.

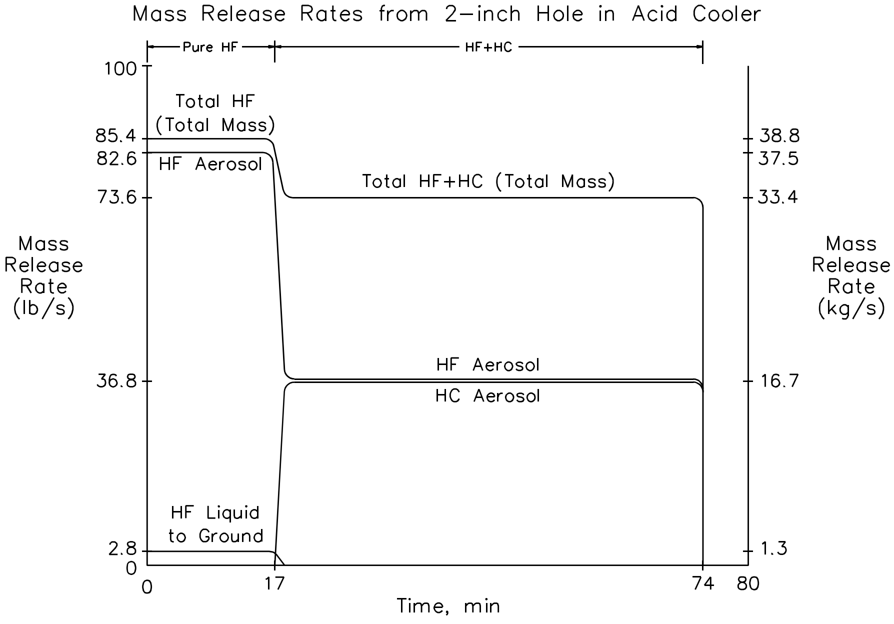

Figure 3

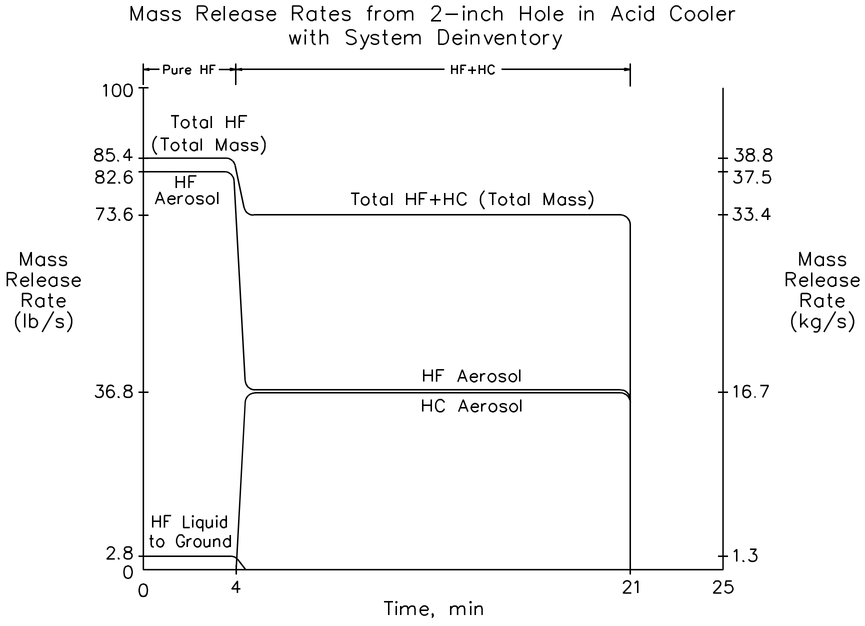

Figure 4

Release Number 4 - Pure HF, Water Spray System

A considerable amount of work has been carried out in an effort to determine the effectiveness of introducing water sprays into an HF cloud. Research has shown that when the water contacts the HF, it is absorbed into the water droplets that fall to the ground. Under controlled conditions (enclosed wind tunnels) with high water to HF ratios (50:1 water/HF mass ratio) [Fthenakis, Blewitt, and Hague, 1995], removal efficiencies of 80% can be obtained for pure HF releases from a one and three-fourths inch hole.

As in the case for the rapid deinventory system, a concern for the water spray curtain system is the system response time. An additional concern is the determination of HF removal efficiencies for outdoor, uncontrolled conditions. The initial outdoor HF/water curtain tests were performed in 1986 [Blewitt, et al., 1987b], with HF mass flow rates on the order of 33 gpm (equal to a release from a hole about one-half inch in diameter). These tests, which used a water/HF mass ratio of twenty-three, removed approximately 50% of the HF from the aerosol cloud. For these cases, the water spray curtain was 100 ft downwind of the release point.

In this example, we will assume a 50% acid removal efficiency for a water curtain that is activated one minute after the start of the release. Figure 5 shows a plot of the acid release history and where the acid ends up after the water curtain is activated.

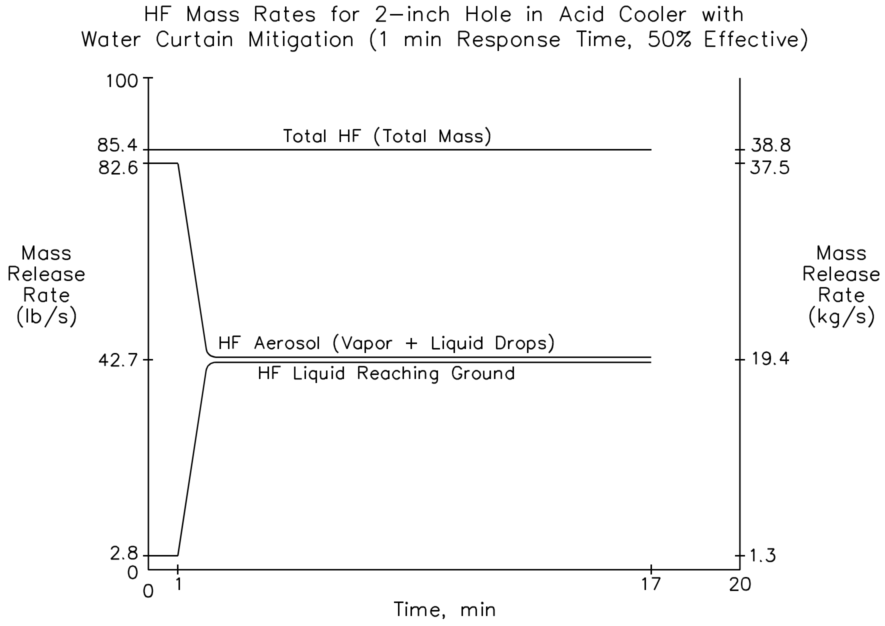

Figure 5

Release Number 5 - HF/Additive Release

Two industry research groups have been actively investigating whether a compound(s) can be mixed with the HF that will reduce its tendency to form an aerosol upon release from an alkylation unit. The two groups (Mobil/Phillips and Texaco/UOP) have independently come up with different additives. Although the additives are different, the purpose of each is similar. Each additive reduces the acid concentration in the unit by dilution, as well as lowering the volatility of the acid phase.

Unlike the deinventory and water spray systems, the additive is a passive mitigation system. Since the additive is dissolved in the acid, the mitigation effects of the additive are seen immediately. By reducing the volatility of the acid phase, the ability of the acid to form an airborne aerosol is reduced.

For the purposes of this example, a mixture of 50% HF and 50% additive will be used. Figure 6 shows the rate at which the HF/additive is released from a two-inch hole and where the material ends up. As can be seen in Figure 6, during the first seventeen minutes of the release, only the acid phase (HF/additive) is released. During this time, 46.4 lb/s of acid is released (one-half of the total mass release rate). Of this 46.4 lb/s, 27.6 lb/s rains out onto the ground with the additive. This 27.6 lb/s represents 60% of the total acid released. The remaining acid, 18.8 lb/s, remains in the air as a vapor. This vapor is generated primarily as the HF evaporates from the HF/additive droplets as they fall to the ground. Thus, none of the HF remains airborne as an aerosol.

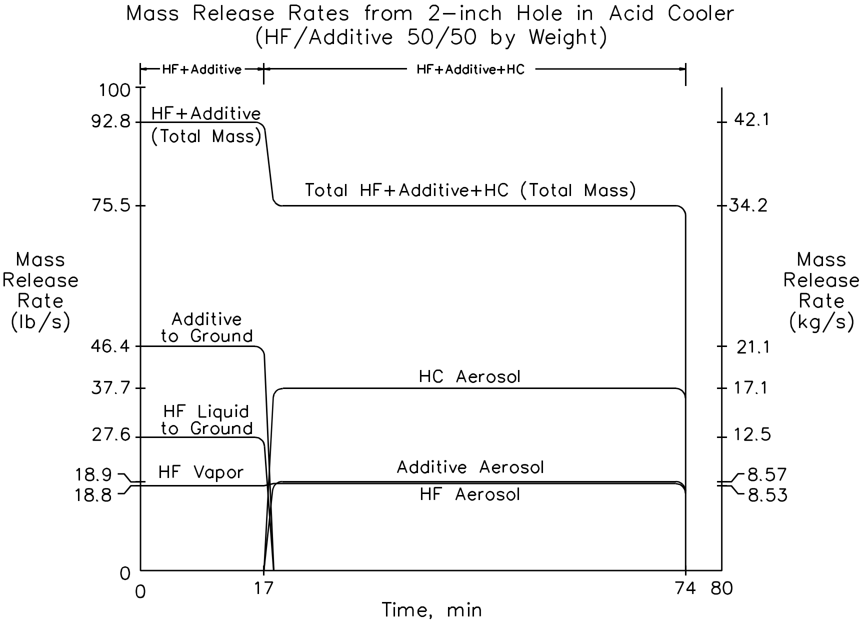

Figure 6

When the first seventeen minutes of the HF/additive release (Figure 6) are compared to the first seventeen minutes of a pure HF release (Figure 2), it can be seen that the amount of HF that remains in the air is significantly reduced (18.8 lb/s from 82.6 lb/s). In addition, when HF is released with the additive, the HF remaining airborne is a vapor, not an aerosol.

Release Number 6 - HF/Additive/HC Release

When the HF/additive/HC interface reaches the hole (approximately seventeen minutes after the start of the release), the behavior of the release changes. This behavior is shown in Figure 6. The energy supplied by the HC flashing (now 50% of the mass released) causes the entire stream to shatter into small drops. Thus, all of the acid, additive, and hydrocarbon become an aerosol upon release. As it turns out, the total mass rate of HF being released in the HF/additive/HC phase is 18.9 lb/s, essentially the same as the HF mass rate when the HF/additive was released. The difference is in the form of the release. With the addition of the HC to the stream, all of the HF is in the vapor phase or in the HF/additive liquid drops.

SULFURIC ACID ALKYLATION SYSTEMS

In order to compare the behavior of acid releases in HF and H_2SO_4 alkylation systems, a comparable H_2SO_4 alkylation unit must be defined. For this example, a “typical” H_2SO_4 alkylation unit is presented in Figure 7. The total H_2SO_4 acid inventory is 36,000 gallons.

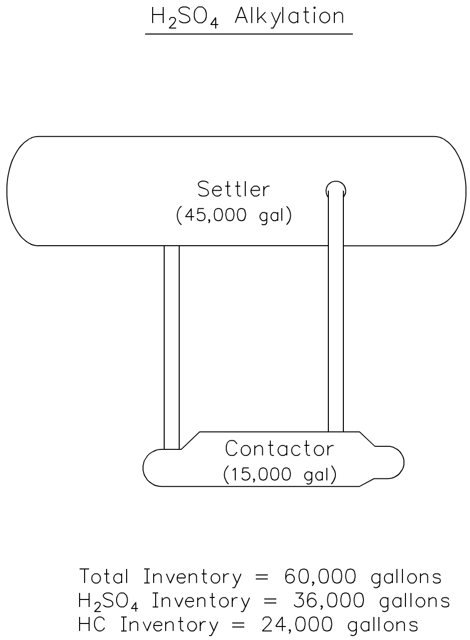

Figure 7

For the purpose of comparing the HF and H_2SO_4 acid hazards from alkylation units, the following parameters for the H_2SO_4 releases were set:

Hole size = 2 inches (5 cm) in diameter
Hole location = 4 feet (1.2 m) above grade, in acid contactor, horizontal release
Operating conditions = 60 psig (415 kPa gauge), 60°F (16°C)
Atmospheric conditions = 5 m/s winds, D stability, 70% relative humidity, 70°F (21°C) temperature

This release description will allow the H_2SO_4 units to be evaluated on the same basis as the HF units; what is the hazard associated with an acid release from a two-inch hole?

Release Number 7 - H_2SO_4/HC Release

A release from a two-inch hole in the bottom of the contactor results in an emulsion of H_2SO_4 and hydrocarbon being released. Upon release to the atmosphere, the H_2SO_4/HC emulsion behaves differently than the HF/HC mixture. The emulsion is composed of 15% by mass hydrocarbon and operates at lower temperature. Thus, the fraction of the total stream that could flash is smaller than that in the HF/HC stream. In addition, the emulsion has a high viscosity that retards the hydrocarbon vapor bubbles from shattering the liquid stream. These phenomena result in very little of the H_2SO_4 acid remaining airborne. This behavior is presented in Figure 8. From Figure 8, it can be seen that it takes about twenty-seven minutes for the emulsion in the

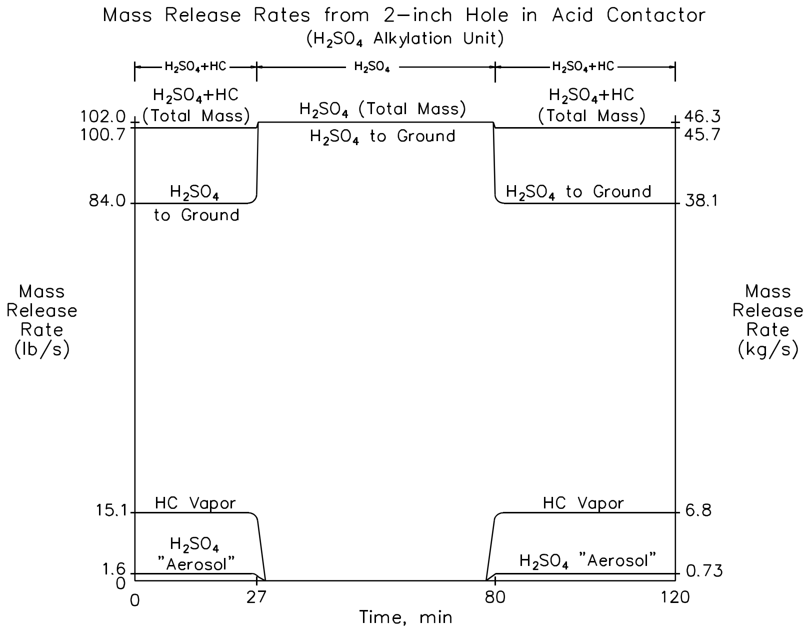

Figure 8

contactor to be released. These results are documented in work performed for the Petroleum Energy Research Foundation [Johnson, 1994].

According to the test data, a small amount of H_2SO_4 was not captured in the immediate vicinity of the release. The primary reason for this was due to the capture array being too small. During some of the tests, it was observed that some of the drops missed the capture pans either on the side or over the end of the array.

The 1.6 lb/s (2% of the total acid rate) that was not directly captured is believed to have been suspended as a film on the hydrocarbon bubbles that evolved out of the emulsion in the capture pan. The acid would then remain suspended on the hydrocarbon bubble until the bubble burst. Upon bursting, most of the liquid H_2SO_4 drops would fall to the ground.

Release Number 8 - H_2SO_4 Release

When the emulsion in the contactor has been driven out of the two-inch hole, the pure acid layer from the settler is then released. During this period of time, about fifty-three minutes in this example, all of the H_2SO_4 released falls to the ground. This results in a local hazard due to the liquid acid, but not a significant vapor cloud hazard. Once the pure acid layer has been released out of the contactor, the emulsion that was pumped to the settler now is driven from the hole. For this example, the composition of the emulsion was assumed to be the same as that in the contactor. This behavior is shown in Figure 8.

SUMMARY OF ACID RELEASE RATES

A summary of the acid release rates for the eight scenarios described above is given in Table 1 and presented graphically in Figure 9. As can be seen from Figure 9, the release of pure HF results in the greatest mass flow rate of acid that remains airborne (82.6 lb/s). The two active mitigation systems, rapid deinventory and

Table 1
Acid Release Rates from Alkylation Units

Released Material [Mitigation System]	Operating Temperature (°F)	Operating Pressure (psig)	Hole Diameter (inches)	Total Mass Release Rate (lb/s)	Total Acid Release Rate (lb/s)	Acid Rate to Grade [Rainout] (lb/s)	Acid Rate Airborne (lb/s)
HF [No mitigation]	90	100	**2.0**	85.4	85.4	2.8	**82.6**
HF/HC (50/50 by mass) [No mitigation]	90	100	**2.0**	73.6	36.8	0.0	**36.8**
HF [**Water curtain**, 50% effective, 1 minute response time]	90	100	**2.0**	85.4	85.4	2.8/**42.7**[1]	82.6/**42.7**[2]
HF [**Deinventory system**, 1 minute response time]	90	100	**2.0**	85.4	85.4	2.8	**82.6**
HF/**ADDITIVE** (50/50 by mass) [Additive to reduce volatility]	90	100	**2.0**	92.8	46.4	27.6	**18.8**
HF/ADDITIVE/HC (25/25/50 by mass) [Additive to reduce volatility]	90	100	**2.0**	75.5	18.9	0.0	**18.9**
H_2SO_4/HC (85/15 by mass) [No mitigation]	60	60	**2.0**	100.7	77.9	76.3[3]	**1.6**[4]
H_2SO_4 (93% acid) [No mitigation]	60	60	**2.0**	102.0	94.9	94.9[3]	**0.0**[4]

[1] Rainout rate ' before water curtain activated/**after water curtain activated**
[2] Airborne rate ' before water curtain activated/**after water curtain activated**
[3] Rainout rate ' rate of acid to fall within 100 ft of release point
[4] Airborne rate ' rate of acid remaining airborne past 100 ft of release point

Release conditions:
RH = 70%, T_{air} = 70°F, z_r = 0.007 m
Two-inch diameter hole
Elevation = 4 ft
Orientation = horizontal

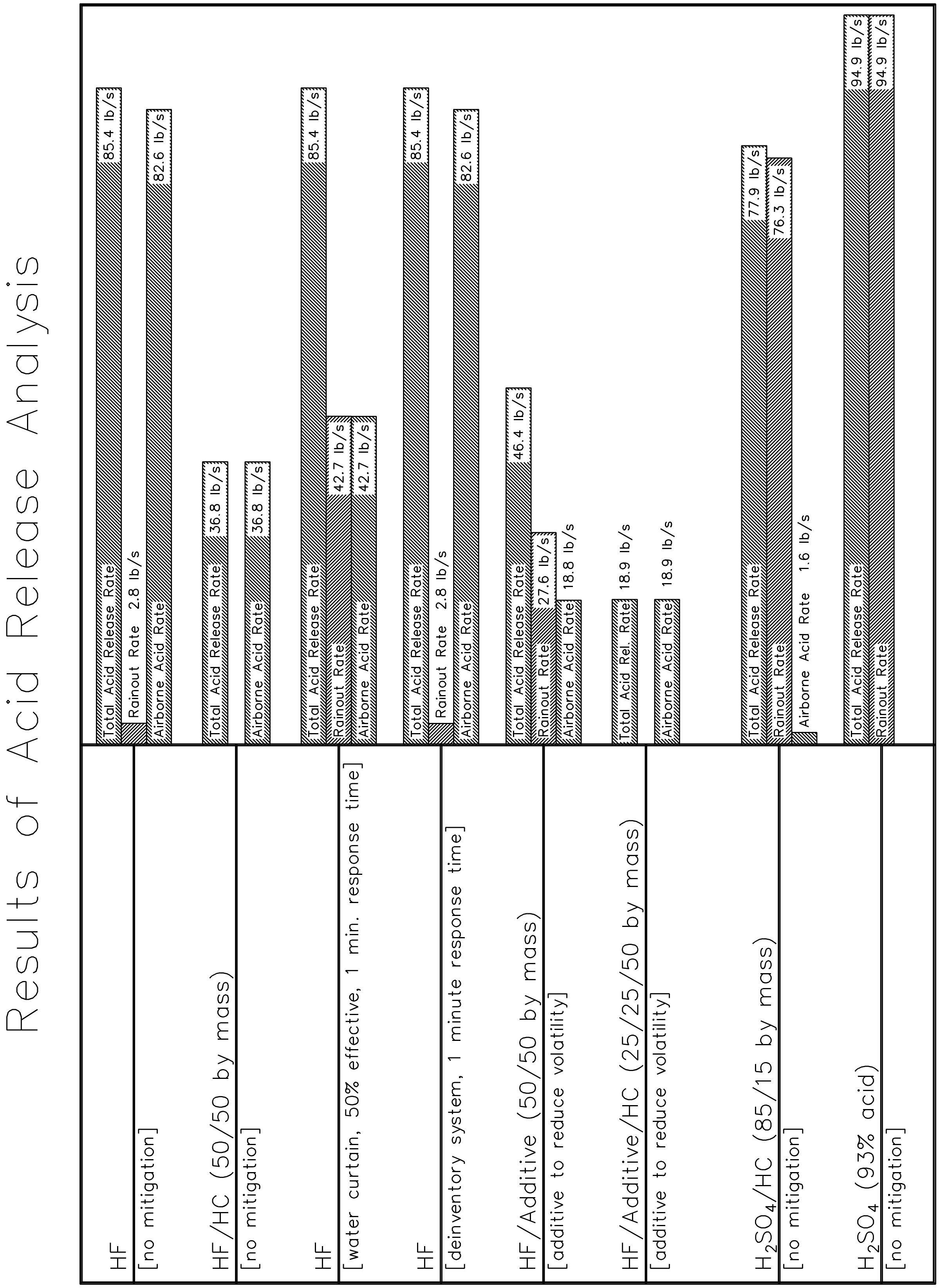
Results of Acid Release Analysis
HF
[no mitigation]
Total Acid Release Rate 85.4 lb/s
Rainout Rate 2.8 lb/s
Airborne Acid Rate 82.6 lb/s
HF/HC (50/50 by mass)
[no mitigation]
Total Acid Release Rate 36.8 lb/s
Airborne Acid Rate 36.8 lb/s
HF
[water curtain, 50% effective, 1 min. response time]
Total Acid Release Rate 85.4 lb/s
Rainout Rate 42.7 lb/s
Airborne Acid Rate 42.7 lb/s
HF
[deinventory system, 1 minute response time]
Total Acid Release Rate 85.4 lb/s
Rainout Rate 2.8 lb/s
Airborne Acid Rate 82.6 lb/s
HF/Additive (50/50 by mass)
[additive to reduce volatility]
Total Acid Release Rate 46.4 lb/s
Rainout Rate 27.6 lb/s
Airborne Acid Rate 18.8 lb/s
HF/Additive/HC (25/25/50 by mass)
[additive to reduce volatility]
Total Acid Rel Rate 18.9 lb/s
Airborne Acid Rate 18.9 lb/s
H_2SO_4/HC (85/15 by mass)
[no mitigation]
Total Acid Release Rate 77.9 lb/s
Rainout Rate 76.3 lb/s
Airborne Acid Rate 1.6 lb/s
H_2SO_4 (93% acid)
[no mitigation]
Total Acid Release Rate 94.9 lb/s
Rainout Rate 94.9 lb/s

Figure 9

water spray, yield the same high flow rate until the systems are activated. Upon activation, the acid rate remaining airborne is lowered (water spray) or the duration of the release is shortened (rapid deinventory). In all cases where the acid is diluted, either with additive or hydrocarbon, the rate of acid remaining airborne is lowered.

DISPERSION ANALYSIS

The definitions of the airborne mass rates for the acid, hydrocarbon, and additive for each of the releases evaluated above provide the initial conditions for dispersion calculations. In order to compare the hazards associated with each of the releases, dispersion calculations were performed until the acid concentration diluted below Emergency Response Planning Guideline Level 3 (ERPG-3). ERPG-3 is defined as a concentration level that could be tolerated by nearly all individuals for up to one hour without experiencing or developing life-threatening health effects. The ERPG-3 level for HF is 50 ppm, while the ERPG-3 level for H_2SO_4 is 30 mg/m^3 (measured as a mist, but equivalent to 7.5 ppm if converted to gaseous form).

For this example, we are concerned with the acid cloud that is immediately formed following the release. In some cases, this is an aerosol cloud; in other cases, the acid is released as a vapor. In all cases, the acid is released with some velocity associated with its storage under pressure. For the immediately airborne clouds, a momentum jet model (based on the work of Ooms) within the QuestFOCUS suite of models was used. This model has been modified to incorporate aerosol thermodynamics and has been reviewed by independent third parties [Hanna, Strimaitis, and Chang, 1991; TRC, 1991].

Dispersion calculations for any acid evolving off a liquid pool resulting from a release were not made for this study.

DISPERSION ANALYSIS RESULTS

A summary of the results of the dispersion analysis is presented in Table 2 and Figure 10. For each of the eight releases studied, the calculations were performed under assumed “average” and “worst-case” weather conditions. For this study, average was defined as 5 m/s winds and Pasquill D (neutral) atmospheric stability. The worst-case conditions were defined as low winds, 1.5 m/s, and Pasquill F (extremely stable). As can be seen from Table 1, the distances to ERPG-3 for HF range from 5.2 miles (8.3 km) to 2.2 miles (3.5 km) under worst-case conditions when various mitigation options and compositions are available. Under more moderate or average conditions, the distances to ERPG-3 for HF range from 1.5 miles (2.4 km) to 0.75 miles (1.2 km).

None of the H_2SO_4 releases produced downwind dispersion distances greater than about 300 ft (95 m) from the release point. This is due primarily to the inability of the release to form a significant cloud with H_2SO_4 in it.

SUMMARY

The benefits and limitations of three different HF acid mitigation systems were reviewed. In order to compare the effectiveness of the systems under real world conditions, calculations were made for a release from a two-inch hole located at the bottom of the alkylation unit (acid cooler). The mitigated and unmitigated results for releases containing HF were then compared to a similar release from an H_2SO_4 alkylation unit.

The results of the analysis can be summarized as follows.

Table 2
Acid Dispersion Analysis from Alkylation Units

Released Material **[Mitigation System]**	**Acid Rate Airborne (lb/s)**	**Dispersion Distances (ft) to HF Concentration Level**	
		5.0 m/s; D Stability	**1.5 m/s; F Stability**
		50 ppm (ERPG-3)	**50 ppm (ERPG-3)**
HF [No mitigation]	**82.6**	**7,950**	27,400
HF/HC (50/50 by mass) [No mitigation]	**36.8**	**5,100**	16,800
HF [**Water curtain**, 50% effective, 1 minute response time]	82.6/**42.7**[1]	**5,300**[2]	15,400[2]
HF [**Deinventory system**, 1 minute response time]	**82.6**	**7,950**	27,400
HF/**ADDITIVE** (50/50 by mass) [Additive to reduce volatility]	**18.8**	**3,950**	11,700
HF/ADDITIVE/HC (25/25/50 by mass) [Additive to reduce volatility]	**18.9**	**4,260**	14,100
		Dispersion Distance (ft) to H_2SO_4 Concentration Level	
		7.5 ppm (ERPG-3)	**7.5 ppm (ERPG-3)**
H_2SO_4/HC (85/15 by mass) [No mitigation]	1.6[3]	260	305
H_2SO_4 (93% acid) [No mitigation]	0.0[3]	<100[4]	<100[4]

[1] Airborne rate ' before water curtain activated/**after water curtain activated**
[2] Hazard distance calculated for acid rate remaining airborne **after** water curtain is turned on
[3] Airborne rate ' rate of acid remaining airborne past 100 ft of release point
[4] All acid rains out within 100 ft of release point

Release conditions:
RH = 70%, T_{air} = 70°F, z_r = 0.007 m
Two-inch diameter hole
Elevation = 4 ft, Orientation = horizontal

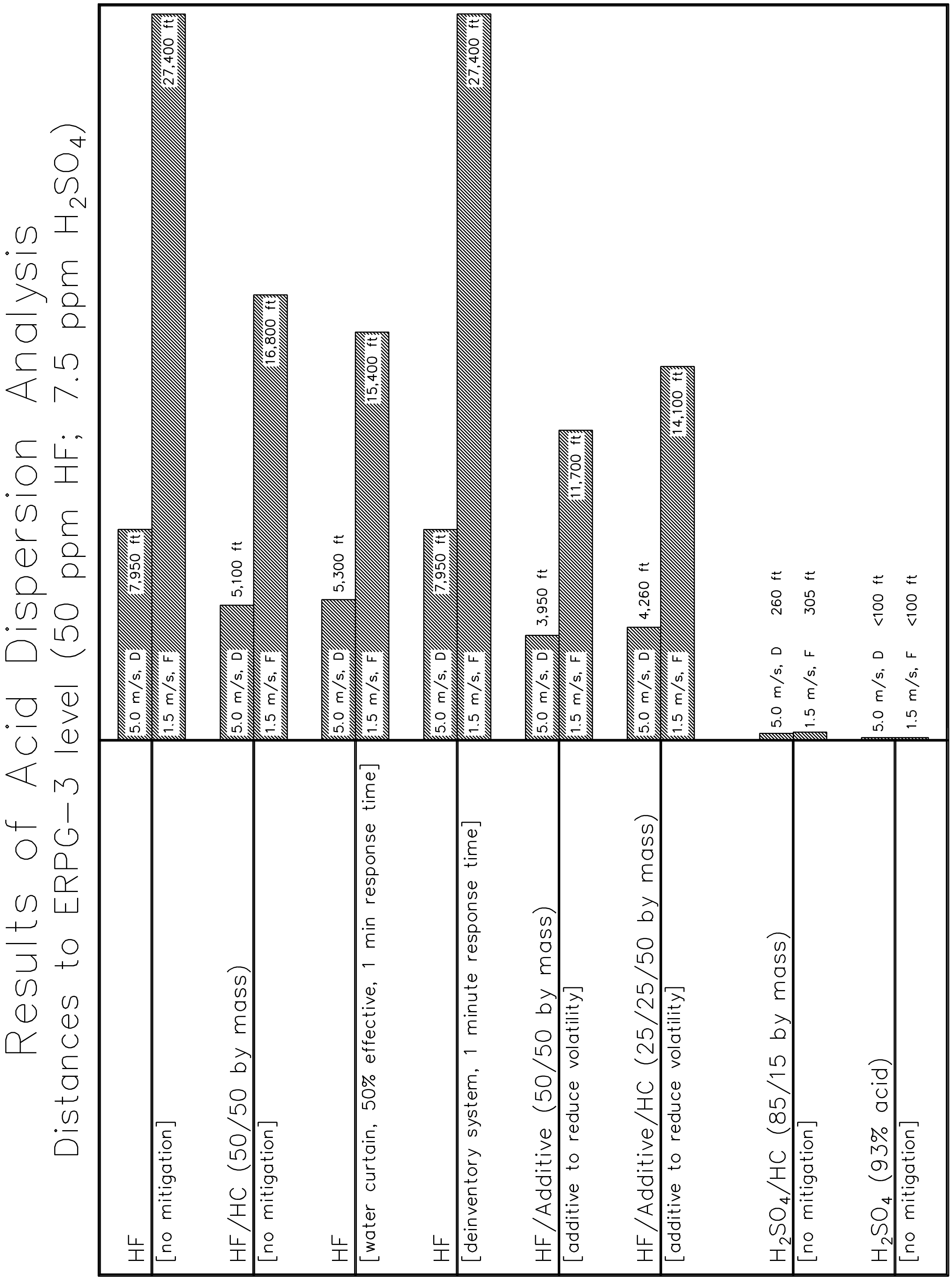
Results of Acid Dispersion Analysis
Distances to ERPG−3 level (50 ppm HF; 7.5 ppm H_2SO_4)
HF
[no mitigation]
5.0 m/s, D 7,950 ft
1.5 m/s, F 27,400 ft
HF/HC (50/50 by mass)
[no mitigation]
5.0 m/s, D 5,100 ft
1.5 m/s, F 16,800 ft
HF
[water curtain, 50% effective, 1 min response time]
5.0 m/s, D 5,300 ft
1.5 m/s, F 15,400 ft
HF
[deinventory system, 1 minute response time]
5.0 m/s, D 7,950 ft
1.5 m/s, F 27,400 ft
HF/Additive (50/50 by mass)
[additive to reduce volatility]
5.0 m/s, D 3,950 ft
1.5 m/s, F 11,700 ft
HF/Additive/HC (25/25/50 by mass)
[additive to reduce volatility]
5.0 m/s, D 4,260 ft
1.5 m/s, F 14,100 ft
H_2SO_4/HC (85/15 by mass)
[no mitigation]
5.0 m/s, D 260 ft
1.5 m/s, F 305 ft
H_2SO_4 (93% acid)
[no mitigation]
5.0 m/s, D <100 ft
1.5 m/s, F <100 ft

Figure 10

Rapid Deinventory System

The addition of a rapid deinventory system shortens the duration of the overall release. In particular, the duration of a pure acid release is shortened. For the example two-inch hole, the pure acid release duration was reduced from twenty-one to four minutes. The dispersion analysis to the ERPG-3 endpoint would not show a significant difference between a twenty-one and four minute release. However, if these results were incorporated into a risk analysis, the use of a probit relation to quantify the dose received at a downwind location would show a significant reduction in risk due to the addition of a rapid deinventory system.

Issues that would determine the effectiveness of a rapid deinventory system were identified as:

- Deinventory rate - the slower the rate, the less effective the system.
- Leak size versus deinventory rate - the smaller the leak, the longer the deinventory time. In general, this is a fair trade-off since the smaller leaks have smaller impacts.
- Response time - the longer it takes to detect a release and activate the system, the less effective the deinventory system becomes.
- Since the system is an active mitigation system, availability, reliability, and maintenance are always a concern.

Water Spray System

The effectiveness of any water spray mitigation system is subject to many parameters. Unlike the rapid deinventory system, the effectiveness of a water curtain is determined by whether the water contacts the HF. Whether the water contacts the HF and how effective the contact is (water/HF ratios) determine the water mitigation effectiveness. The parameters that determine the effectiveness of a water spray curtain were identified as:

- Location of the leak - some HF alkylation designs have elevated inventories of HF. If a release were to occur in an elevated piece of equipment, the release could be above the water curtain, thus rendering the water spray mitigation useless.
- Size of the leak - laboratory tests have focused on small-scale releases. Field tests have been limited to releases smaller than an equivalent one-half inch hole. If a large release were to occur, will the momentum of the release “blow through” the curtain? The answer to this question is not known at present. Clearly, the distance from the leak to the water curtain is an important factor in this analysis. The distance is also important in sizing the overall system. As the separation distance between the unit and the water curtain becomes larger, more water is required.
- Variable efficiencies - the size, location, and water/HF ratios all contribute to determining the effectiveness of a water curtain. It would be expected that, if the leak is contacted by water, the removal efficiency may be dependent on the size of the leak. Therefore, there is no single “efficiency” for a given water spray curtain. The efficiency must be determined for each combination of leak size, leak location, and curtain location.
- Response time - the longer it takes to detect a release and activate the system, the less effective the overall water spray curtain becomes.
- Since the system is an active mitigation system, availability, reliability, and maintenance are always a concern.

Acid Additive

The use of an additive to the HF has two effects on the overall behavior of an acid leak. First, the additive reduces the volatility of the acid phase; second, the additive dilutes the acid. The result of these two effects is to release acid at a lower rate than a pure acid release (dilution) and for the acid that is released, a greater percentage falls to the ground (reduced volatility) and does not enter the atmosphere immediately.

The dilution rate is determined by how much additive is added to the acid phase. For the example cases run, a 50/50 mix by weight of acid/additive was used. Thus, the concentration of acid leaving any leak is approximately one-half (by mass) of that without an additive. The ability of the additive to reduce the volatility of the acid phase results in 60% of the acid released falling to the ground. Thus, when the dilution effects and reduced volatility effects are combined, the result is that, for equal sized holes (e.g., two-inch), the rate of airborne HF is reduced from 82.6 lb/s (pure HF) to 18.8 lb/s, a 77% reduction.

When the HF/additive is mixed with the available HC, the internal energy of the HC forces the released stream to shatter and all the material (HF, additive, and HC) is released as an airborne aerosol. When the releases with and without additive are compared, the airborne HF rate is reduced from 36.8 lb/s (HF in HF/HC) to 18.9 lb/s, a 50% reduction. In this case, the reduction is due purely to dilution.

For an acid additive mitigation system, issues that should be considered are:

- Additive/HF ratio - the greater the additive fraction, the greater the dilution, the greater the benefit.
- Alkylation operability - will the addition of an acid additive change the operability or throughput of the alkylation unit?
- Passive mitigation - unlike the deinventory or water curtain mitigation systems, the additive is always present in the acid phase. Therefore, should a release occur, the mitigation effect is instantaneous and not conditional on operator or system reaction time.

CONCLUSIONS

The use of any HF acid mitigation system has the potential to reduce the impact of an acid release from an alkylation unit. This study has shown how the different mitigation systems currently suggested for use (rapid deinventory, water spray curtains, and acid additives) can affect the airborne acid release rates and thus the extent of an HF vapor cloud. The issues that determine the effectiveness of the mitigation systems were outlined and a release from a two-inch hole was evaluated to demonstrate the differences.

Comparisons between releases for HF, both mitigated and unmitigated, and H_2SO_4 were also made. In all cases, the rate of HF that would remain airborne following a release would be larger than the rate of H_2SO_4 remaining airborne.

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