APPENDIX F: Supplemental Risk Management Program Guidance for Wastewater Treatment Plants

# Appendix F: Supplemental Risk Management Program Guidance for Wastewater Treatment Plants

This appendix supplements the main body of the General Guidance to provide additional information for wastewater treatment plants (WWTPs), including publicly owned treatment works (POTWs) and other industrial treatment systems. It provides guidance on how to comply with part 68 with respect to chlorine, ammonia (anhydrous and aqueous), sulfur dioxide, and digester gas, the substances WWTPs usually use for treatment or produce as a result of treatment. We expect that any regulated substances present in your waste streams will be in concentrations too low to require compliance. If you have other processes that use regulated substances other than these, refer to the main body of the *General Guidance* (and any other applicable industry-specific appendix) for information on compliance with the rule for those processes. The appendix covers Risk Management Program elements in the same general order as those elements are addressed in the main document. However, note that the appendix does not address some generic RMP elements (e.g., Management System). For elements not addressed in this appendix, simply refer to the applicable guidance in the main document.

## F.1 General Applicability

The following list includes the chemicals regulated under part 68 and OSHA PSM that are commonly used at WWTPs, along with their associated threshold quantity:

Chemical	EPA Threshold Quantity	OSHA Threshold Quantity
Chlorine	2,500 pounds	1,500 pounds
Anhydrous Ammonia	10,000 pounds	10,000 pounds
Aqueous Ammonia	20,000 pounds	15,000 pounds
(concentration 20% or greater)	_	(>44%)
Anhydrous Sulfur Dioxide	5,000 pounds	1,000 pounds
	-	(Liquid)
Methane	10,000 pounds	10,000 pounds

For methane, the 10,000-pound threshold applies to the total weight of the flammable mixture of digester gases, not just the weight of methane or flammables in the mixture. However, if your WWTP uses methane (or a methane mixture) as fuel or sells it as fuel (as a retail facility), the amount of methane that you use or sell as fuel is not covered under part 68. For aqueous ammonia, the threshold applies only to the weight of ammonia in the mixture.

In general, regulated chemicals in a waste stream at a POTW will not exceed one percent of a mixture and thus will not be covered by part 68. If an industrial WWTP has more than 1 percent of a regulated substance in the waste stream, the quantity of

the substance in the waste stream will have to be determined and compared to the threshold quantity. Oxygen is not subject to either part 68 or OSHA PSM. Ozone is also not subject to part 68, although it is covered by OSHA PSM.

# F.2 Program Levels

Program levels for private WWTPs and industrial wastewater treatment processes are determined in the same manner as other covered processes (See Chapter 2 of the main document for more information). However, a POTW will determine its Program levels based, in part, on the state or territory in which it is located. If OSHA has delegated its programs to the state or territory in which your POTW is located, you are covered by OSHA standards under state law (it is a condition of gaining delegation that the state apply OSHA rules to state and local governments). If you are in one of the states or territories with a delegated OSHA program (listed in Exhibit F-2), your processes will be in Program 1, if eligible; otherwise, processes involving regulated toxics substances or digester gas production not used for fuel will be in Program 3 because they are subject to OSHA PSM.

Several states have not been granted delegation by federal OSHA (listed in Exhibit F-1). However, some of these states have enacted legislation or promulgated regulations that adopt the federal OSHA PSM standard and applied them to state and local governments. If you are in one of these states, your POTW process will be in either Program 1 or Program 3.

If you are in one of the states without a delegated OSHA program *and* the state has not incorporated the federal OSHA PSM standard by reference into state law or code, your processes will generally be in either Program 1 or Program 2. An exception to this would be in cases where a POTW in a Federal OSHA state is operated by contractor employees. Since the private contractors employees are subject to Federal OSHA regulations, these POTW processes will be subject to Program 1 or Program 3.

#### **Exhibit F-1: Federal OSHA States**

Alabama	Kansas	North Dakota
Arkansas	Louisiana	Ohio
Colorado	Maine	Oklahoma
Delaware	Massachusetts	Pennsylvania
DC	Missouri	Rhode Island
Florida	Mississippi	South Dakota
Georgia	Montana	Texas
Idaho	Nebraska	West Virginia
Illinois	New Hampshire	Wisconsin
	New Jersey	

# Exhibit F-2: States with Delegated OSHA Programs

Alaska	Maryland	South Carolina
Arizona	Michigan	Tennessee
California	Minnesota	Utah
Connecticut	Nevada	Vermont
Hawaii	New Mexico	Virginia
Indiana	New York	Virgin Islands
Iowa	North Carolina	Washington
Kentucky	Oregon	Wyoming
	Puerto Rico	

#### F.2.1 QUICK RULES FOR DETERMINING PROGRAM 1 ELIGIBILITY

#### **TOXIC GASES**

If you have a process containing more than a threshold quantity of chlorine, ammonia, or sulfur dioxide or any other regulated toxic gas that is not liquefied by refrigeration alone (i.e., you hold it as a gas or liquefied under pressure), the distance to the endpoint estimated for a worst-case release of the toxic gas will generally be several miles. As a result, the distance to endpoint is unlikely to be less than the distance to public receptors, unless the process is very remote. In some cases, however, toxic gases in processes in enclosed areas may be eligible for Program 1.

## **REFRIGERATED TOXIC GASES**

If you have a process containing anhydrous ammonia liquefied by refrigeration alone, and your worst-case release would take place into a diked area, the chances are good that the process may be eligible for Program 1, unless there are public receptors very close to the process. Even if you have many times the threshold quantity of ammonia, the process may still be eligible for Program 1. The worst-case analysis for a process containing chlorine liquefied by refrigeration is unlikely to show eligibility for Program 1, unless your site is extremely remote from the public or the release would occur within an enclosure.

#### **TOXIC LIQUIDS**

The distance to an endpoint for a worst-case release involving toxic liquids kept under ambient conditions may be smaller than the distance to public receptors in a number of cases. If public receptors are not found very close to the process (within <sup>1</sup>/<sub>2</sub> mile), the process may be eligible for Program 1. However, facilities on small acreage sites are highly unlikely to meet to be eligible for Program 1 if they are in a developed area. Remotely located facilities or processes found near the center of large (acreage) sites are more likely to be eligible.

#### WATER SOLUTIONS OF TOXIC SUBSTANCES

Processes containing water solutions of toxic substances (e.g., aqueous ammonia) at ambient temperatures may be eligible for Program 1 (depending in some cases on the concentration of the solution), if spills would be contained in diked areas and public receptors are not located close to the process (within ½ mile). As noted above, facilities on small acreage sites in developed areas are highly unlikely to be eligible for Program 1; remotely located facilities or processes found near the center of large acreage sites are more likely to be eligible.

#### **FLAMMABLE SUBSTANCES**

Many processes containing regulated flammable substances are likely to be eligible for Program 1, unless there are public receptors within a very short distance. If you have a process containing up to about 20,000 pounds (twice the threshold quantity) of methane, your process is likely to be eligible for Program 1 if you have no public receptors within about 400 yards (1,200 feet) of the process. If you have up to 100,000 pounds in a process (ten times the threshold quantity), the process may be eligible for Program 1 if there are no public receptors within about 700 yards (2,000 feet). In general, it would be worthwhile to conduct a worst-case analysis for any processes containing only flammables to determine Program 1 eligibility, unless you have public receptors very close to the process. Consequently, you may have to conduct more worst-case analyses if you want to qualify processes for Program 1; for Program 2 and 3 processes, you need analyze only one worst-case release scenario to cover all flammables. For Program 1, you must be able to demonstrate, through your worst-case analysis, that every process you claim is Program 1 meets the criteria.

Remember that the Program level designation for a process is based on the regulated substance that has the greatest distance to an endpoint. If your digesters are considered part of a process that includes chlorine, ammonia, or sulfur dioxide, the toxics will determine whether the process is eligible for Program 1 because the distances to an endpoint will be greater for the toxics.

## F.2.2 PROGRAM 3

Any covered process that is not eligible for Program 1 and is subject to OSHA PSM under federal or state law is subject to Program 3 requirements, which include risk management measures and requirements virtually identical to the OSHA PSM Standard. (The other criterion for Program 3 applicability (§ 68.10(d)(1)) does not apply to WWTPs.)

Private WWTPs are likely to be subject to OSHA PSM for processes containing more than a threshold quantity of chlorine, anhydrous ammonia, or sulfur dioxide. POTWs in states with delegated OSHA programs or in non-state-plan states that have adopted the PSM standard to cover state and local governments are subject to the PSM standard if they have more than a threshold quantity of these substances. OSHA's thresholds are generally lower than EPA's so it is possible that you may have a process that is subject to OSHA PSM and is not covered by part 68. For example, if you store a single, one-ton cylinder of chlorine, OSHA PSM will cover it because it has a 1,500 pound threshold for chlorine, but EPA's part 68 will not because its threshold quantity for chlorine is 2,500 pounds.

OSHA PSM covers aqueous ammonia at a concentration of greater than 44 percent (as opposed to EPA's 20 percent or greater); therefore, your aqueous ammonia process may not be subject to OSHA PSM.

# F.2.3 PROGRAM 2

Program 2 is considered a default program level because any covered process that is not eligible for Program 1 or assigned to Program 3 is, by default, subject to Program 2 requirements, including a streamlined accident prevention program. One or more processes at your facility are likely to be in Program 2 if:

- You are a publicly owned and operated facility in a state that does not have a delegated OSHA program, and the state has not incorporated the OSHA PSM standard by reference into state law or code.
- You use aqueous ammonia in solutions with greater than 20 percent concentration but less than 44 percent concentration.
- You use regulated acids in solution in activities.
- You store regulated liquid flammable substances in atmospheric storage tanks.

The last two of these conditions are unlikely to apply to WWTPs.

# F.3 Offsite Consequence Analysis

This section gives guidance on how to perform the OCA for the five regulated substances that are typically used or produced at WWTPs:

- Chlorine (toxic)
- Sulfur dioxide (toxic)
- Anhydrous ammonia (toxic)
- Aqueous ammonia (20 percent or greater, toxic)
- Methane (digester gas, flammable)

This chapter presents discussions and tables for the worst-case scenario for all five substances listed above, followed by discussions and tables for alternative scenarios for the six substances. Because many WWTPs store chlorine and sulfur dioxide in buildings, we have included methods for estimating the mitigating effects of buildings. The remaining sections provide guidance on defining offsite impacts, documentation, and the symbols used in the chapter. The guidance presented in this chapter is intended for users - that is, it does not contain any explanations of how the guidance was derived. Those readers who are interested in obtaining an explanation can obtain from EPA a document entitled *Technical Background Document for Offsite Consequence Analysis for Anhydrous Ammonia, Aqueous Ammonia, Chlorine and Sulfur Dioxide*.

## F.3.1 Worst-Case Release Scenarios

This subsection provides guidance on how to analyze worst-case scenarios for chlorine, sulfur dioxide, anhydrous ammonia, aqueous ammonia, and methane. For information on the general requirements of the regulations pertaining to worst-case scenarios, refer to chapter 4 of the main document.

The *toxic endpoints* are:

Ammonia: 0.14 mg/L (200 ppm) Chlorine: 0.0087 mg/L (3 ppm) Sulfur Dioxide: 0.0078 mg/L (3 ppm)

The regulations require you to use tables or models for atmospheric dispersion analysis that appropriately account for gas density. For the specific case of WWTPs, chlorine and sulfur dioxide are always dense gases (that is, denser than air). Anhydrous ammonia, if released from the liquid space of a container in which it is liquefied under pressure, forms a denser-than-air vapor cloud. Ammonia evaporating from a pool of aqueous ammonia is treated as neutrally buoyant (that is, it has about the same density as air).

#### CHLORINE

At WWTPs, chlorine is most likely to be present in 150-lb cylinders, in one-ton (2,000-lb) cylinders, in 17-ton tank trucks, or in 90-ton railcars. The worst-case scenario assumes that these quantities are completely released over a period of 10 minutes (e.g., a 150-lb worst case corresponds to a 15-lb/min rate of release). The predicted distances to the toxic endpoint for each of these scenarios is given in Exhibit F-3. These distances are for releases that are assumed to take place outdoors. See Section F.3.3 for a discussion on buildings.

Scenario	Release Rate (lbs/min)	Distance to Toxic Endpoint (miles	
		Rural	Urban
150-lb cylinder	15	0.8	0.4
1-ton cylinder	200	3.0	1.3
17-ton tank trucks	3,400	12	5.8
90-ton rail car	18,000	>25	14

## Exhibit F-3 Distances to Toxic Endpoints - Chlorine F Stability, Wind Speed 1.5 Meters per Second

If your facility does not fit into the standard pattern of 150-lb cylinders, one-ton cylinders, 17-ton tank trucks, or 90-ton railcars, you should use Figure F-1 or Exhibit F-4. Identify the chlorine vessel that contains the largest quantity of any in your facility and divide that mass by 10 to obtain the release rate in lb/min. Look for that release rate, or the rate nearest to it, in Exhibit F-4. Then read across to the rural or urban distances.

Alternatively, look along the bottom axis of Figure F-1, read up to the curve(s) and then across to the corresponding distances on the vertical axis. As noted above, the results presented in Exhibits F-3 and F-4 are for a release that is outside. Many of you will keep your chlorine vessels inside buildings. Some will even have specially designed, leak-tight buildings with chlorine or sulfur dioxide scrubbers. However, the intention of this section is to provide information on the worst-case scenario. There are times when you will be handling the cylinders outside. Nevertheless, in discussions with local agencies and local communities you may well want to explain how your facility is designed to prevent or mitigate worst-case scenarios.

# Exhibit F-4 Distances to Toxic Endpoint - Chlorine F Stability, Wind Speed 1.5 Meters per Second

Release Rate	Distance to E	ndpoint (miles)
(lbs/min)	Rural	Urban
1	0.2	0.1
2	0.3	0.1
5	0.5	0.2
10	0.7	0.3
15	0.8	0.4
20	1.0	0.4
30	1.2	0.5
40	1.4	0.6
50	1.5	0.6
60	1.7	0.7
70	1.8	0.8
80	1.9	0.8
90	2.0	0.9
100	2.2	0.9
150	2.6	1.2
200	3.0	1.3
250	3.4	1.5
300	3.7	1.6
400	4.2	1.9
500	4.7	2.1
600	5.2	2.3
700	5.6	2.5

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
750	5.8	2.6
800	5.9	2.7
900	6.3	2.9
1,000	6.6	3.0
1,500	8.1	3.8
2,000	9.3	4.4
2,500	10	4.9
3,000	11	5.4
4,000	13	6.2
5,000	14	7.0
6,000	16	7.6
7,000	17	8.3
7,500	18	8.6
8,000	18	8.9
9,000	19	9.4
10,000	20	9.9
15,000	25	12
20,000	*	14
25,000	*	16
30,000	*	18
40,000	*	20
50,000	*	0

\* More than 25 miles (report distance as 25 miles)

These are results that you can simply quote when you submit your RMP.

#### SULFUR DIOXIDE

Sulfur dioxide, if present at a WWTP, is also likely to be in 150-lb cylinders, one-ton cylinders, 17-ton tank cars, or 90-ton railcars. The worst-case scenario assumes that these quantities are completely released over a period of 10 minutes. The predicted distances to the toxic endpoint for each of these scenarios is given in Exhibit F-5.

#### EXHIBIT F-5 Distances to Toxic Endpoint - Sulfur Dioxide F Stability, Wind Speed 1.5 Meters per Second

Scenario	Release Rate (lbs/min)	Distance to Toxic Endpoint (miles)	
		Rural	Urban
150-lb cylinder	15	0.7	0.3
1-ton cylinder	200	3.1	1.3
17-ton tank trucks	3,400	15	6.0
90-ton rail car	18,000	>25	15

These are results that you can simply quote when you submit your RMP. If your facility does not fit into the standard pattern of 150-lb cylinders, one-ton cylinders, or 90-ton railcars, you should use Figure F-2 or Exhibit F-6. Identify the sulfur dioxide vessel that contains the largest quantity of any in your facility. Divide that quantity by 10 to obtain the release rate in lb/min and look for that rate, or the rate nearest to it, on Exhibit F-6. Then read across to the rural or urban distances. Alternatively, use Figure F-2.

# EXHIBIT F-6 DISTANCES TO TOXIC ENDPOINT FOR SULFUR DIOXIDE F Stability, Wind Speed 1.5 Meters per Second

-

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural	Urban	
1	0.2	0.1	
2	0.2	0.1	
5	0.4	0.2	
10	0.6	0.2	
15	0.7	0.3	
20	0.9	0.4	
30	1.1	0.5	
40	1.3	0.5	
50	1.4	0.6	
60	1.6	0.7	
70	1.8	0.7	
80	1.9	0.8	
90	2.0	0.8	
100	2.1	0.9	
150	2.7	1.1	
200	3.1	1.3	
250	3.6	1.4	
300	3.9	1.6	
400	4.6	1.9	
500	5.2	2.1	
600	5.8	2.3	
700	6.3	2.5	

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
750	6.6	2.6
800	6.8	2.7
900	7.2	2.9
1,000	7.7	3.1
1,500	9.6	3.8
2,000	11	4.5
2,500	13	5.0
3,000	14	5.6
4,000	17	6.5
5,000	19	7.3
6,000	21	8.1
7,000	23	8.8
7,500	24	9.1
8,000	25	9.5
9,000	*	10
10,000	*	11
15,000	*	13
20,000	*	16
25,000	*	18
30,000	*	19
40,000	*	23
50.000	*	*

\* More than 25 miles (report distance as 25 miles)

#### **ANHYDROUS AMMONIA**

In WWTPs, anhydrous ammonia is generally stored as a liquid under pressure in vessels that are kept outdoors. These vessels are relatively large (e.g., 10,000 gallons or ~56,000 lb). Identify the quantity of ammonia in your storage vessel and divide by 10 to obtain the release rate in lb/min. Look for that release rate, or the release rate nearest to it, on Exhibit F-7. Then read across to the rural or urban distances. Alternatively, use Figure F-3.

The 10,000-gallon vessel mentioned above contains 56,000 lb when full. (You may take into account any administrative controls that limit the quantity of the ammonia in the vessel. For example, you will generally require that the vessel never be filled above 85 percent of its total volume to allow for the high coefficient of volumetric expansion of ammonia.) Assuming for the sake of the present example that 56,000 lb is the greatest quantity of ammonia that will ever be in the vessel, the release rate is 5,600 lb/min. The closest release rate on Exhibit F-7 is 6,000 lb/min. The corresponding rural distance is approximately 4.4 miles and the corresponding urban distance is approximately 2.8 miles.

## EXHIBIT F-7 DISTANCES TO TOXIC ENDPOINT FOR ANHYDROUS AMMONIA LIQUEFIED UNDER PRESSURE F Stability, Wind Speed 1.5 Meters per Second

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural	Urban	
1	0.1	<0.1*	
2	0.1	0.1	
5	0.1	0.1	
10	0.2	0.1	
15	0.2	0.2	
20	0.3	0.2	
30	0.3	0.2	
40	0.4	0.3	
50	0.4	0.3	
60	0.5	0.3	
70	0.5	0.3	
80	0.5	0.4	
90	0.6	0.4	
100	0.6	0.4	
150	0.7	0.5	
200	0.8	0.6	
250	0.9	0.6	
300	1.0	0.7	
400	1.2	0.8	
500	1.3	0.9	
600	1.4	0.9	
700	1.5	1.0	
750	1.6	1.0	
800	1.6	1.1	
900	1.7	1.2	

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural	Urban	
1,000	1.8	1.2	
1,500	2.2	1.5	
2,000	2.6	1.7	
2,500	2.9	1.9	
3,000	3.1	2.0	
4,000	3.6	2.3	
5,000	4.0	2.6	
6,000	4.4	2.8	
7,000	4.7	3.1	
7,500	4.9	3.2	
8,000	5.1	3.3	
9,000	5.4	3.4	
10,000	5.6	3.6	
15,000	6.9	4.4	
20,000	8.0	5.0	
25,000	8.9	5.6	
30,000	9.7	6.1	
40,000	11	7.0	
50,000	12	7.8	
75,000	15	9.5	
100,000	18	10	
150,000	22	13	
200,000	**	15	
250,000	**	17	
750.000	**	**	

\* More than 25 miles (report distance as 25 miles)

#### **AQUEOUS AMMONIA**

Some WWTPs keep aqueous ammonia in outside storage tanks at atmospheric pressure. The tanks usually stand in a diked area. Commercial grades of aqueous ammonia vary from less than 20 weight percent to about 30 weight percent. For ease of presentation, the ammonia is assumed to be in a 30 weight percent solution. Because this has the highest vapor pressure of any of the commercial grades used in wastewater treatment facilities, its use is conservative if you have aqueous ammonia in a less than 30 weight percent solution.

If there is a catastrophic failure, the aqueous ammonia will spill into the diked area.

You are allowed to consider the dike, which is a passive mitigation feature. However, if you have any reason to believe that the dike will not withstand the event that leads to the spill, or if your tank does not stand in a diked area, then you should assume, as required by the rule, that the spill spreads out until its depth is only 1 cm (0.39 inch). The first step is to calculate the rate of evaporation from the pool.

#### **UNDIKED AREA**

For an undiked area, the rate of release of ammonia from the pool (QR) (lb/min) is given by:

$$QR = 0.020QS \tag{1}$$

where QS is the total quantity (lb) of the spill of aqueous ammonia. For example, if there is a spillage of 80,000 lb, the rate of evaporation is  $0.02 \times 80,000 = 1,600$  lb/min. The present guidance assumes that this is the average rate of release over 10 minutes, after which the pool will be more dilute than it was initially and will be evaporating much less rapidly.

#### DIKED AREA

For a diked area, the rate of evaporation is:

$$QR = 0.036A_{\rm p} \tag{2}$$

where  $A_p$  is the diked area in square feet. For example, if the vessel stands in a diked area that is 40 feet x 40 feet = 1,600 ft<sup>2</sup>, the predicted rate of evaporation is 0.036 x 1,600 = 58 lb/min.

The maximum area of the pool that would be formed by the spilled liquid can be estimated as 0.55QS. If you have a diked area that is larger than the maximum area, use Equation 1 for an undiked area to estimate the release rate to air.

RATES OF RELEASE AT TEMPERATURES OTHER THAN 25 °C

The actual temperature of stored aqueous ammonia varies with the ambient temperature. The rule requires you to consider the release temperature to be the highest daily temperature observed during the last three years, or the operating temperature, whichever is highest. The ratio  $R_{vp}(T)$  represents the ratio of the partial pressure of ammonia at temperature T °C to the partial pressure at 25 °C.

Exhibit F-8 gives values of  $R_{vp}(T)$  for 30 percent aqueous ammonia in 1 °C increments from 15 °C to 40 °C (59 °F to 104 °F). The rates of evaporation in Equations 1 and 2 are proportional to the vapor pressure, so to obtain a rate of evaporation for a temperature T °C other than 25 °C, simply multiply the right-hand side of Equation 1 or 2 by the corresponding value of  $R_{vp}(T)$ . For example, for an undiked release of 80,000 lbs of ammonia at 35 °C, the calculation is (0.020)(80,000)(1.45) = 2,300 lbs/min.

The vapor pressure of ammonia at other temperatures can be obtained from the *Handbook of Chemistry and Physics*, CRC Press, 1998.

#### DISTANCES TO TOXIC ENDPOINT

Take the evaporation rate and look for that rate, or the rate nearest to it, on Exhibit F-9. Then read across to the rural or urban distances. For example, for the 58 lb/min release rate derived above, the closest release rate on Exhibit F-9 is 60 lb/min. The predicted rural distance is approximately 0.4 mile and the predicted urban distance is approximately 0.2 mile. Alternatively, use Figure F-4.

Temperature (°C)	Ratio R <sub>vp</sub> (T)	Temperature (°C)	Ratio R <sub>vp</sub> (T)
15	0.67	28	1.12
16	0.70	29	1.16
17	0.73	30	1.21
18	0.76	31	1.25
19	0.79	32	1.30
20	0.82	33	1.35
21	0.86	34	1.40
22	0.89	35	1.45
23	0.93	36	1.50
24	0.96	37	1.55
25	1.00	38	1.61
26	1.04	39	1.66
27	1.08	40	1.72

# Exhibit F-8 Ratio of Vapor Pressure of Ammonia in 30% Aqueous Ammonia (Ratio is Unity at 25 °C)

# EXHIBIT F-9 Distances to Toxic Endpoint for Aqueous Ammonia F Stability, Wind Speed 1.5 Meters per Second

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural	Urban	
1	0.1		
2	0.1	<0.1*	
5	0.1		
10	0.2	0.1	
15	0.2	0.1	
20	0.3	0.1	
30	0.3	0.1	
40	0.4	0.1	
50	0.4	0.1	
60	0.4	0.2	
70	0.5	0.2	
80	0.5	0.2	
90	0.5	0.2	
100	0.6	0.2	
150	0.7	0.2	
200	0.8	0.3	
250	0.8	0.3	
300	0.9	0.3	
400	1.1	0.4	
500	1.2	0.4	
600	1.3	0.4	
700	1.4	0.5	
750	1.4	0.5	
800	1.5	0.5	
900	1.5	0.6	

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural Urban		
1,000	1.6	0.6	
1,500	2.0	0.7	
2,000	2.2	0.8	
2,500	2.5	0.9	
3,000	2.7	1.0	
4,000	3.1	1.1	
5,000	3.4	1.2	
6,000	3.7	1.3	
7,000	4.0	1.4	
7,500	4.1	1.5	
8,000	4.2	1.5	
9,000	4.5	1.6	
10,000	4.7	1.7	
15,000	5.6	2.0	
20,000	6.5	2.4	
25,000	7.2	2.6	
30,000	7.8	2.8	
40,000	8.9	3.3	
50,000	9.8	3.6	
75,000	12	4.4	
100,000	14	5.0	
150,000	16	6.1	
200,000	19	7.0	
250,000	21	7.8	
750.000	**	13	

\*Report distance as 0.1 mile

\*\* More than 25 miles (report distance as 25 miles)

#### METHANE

Methane is present at some wastewater treatment facilities as a component of digester gas. Typical constituents of digester gas are 55 to 70 percent methane by volume, 25 to 30 percent carbon dioxide by volume, and small amounts of nitrogen and hydrogen. Modern facilities may well have processes containing more than 10,000 lb of digester gas at any one time (the entire quantity of the flammable mixture in a process must be compared with the threshold quantity (TQ) of 10,000 lb to determine whether the facility is covered; note that digester gas that is used as fuel is not covered). Proceed as follows:

1. Determine the density Dm of the methane in the digester at operating temperature T (°F), assuming that there is X volume percent of methane and 100 - X volume percent of carbon dioxide and other materials. You should determine X by analysis of your digester gas; if you do not know the percentage of methane, you may use 70 percent as a conservative assumption. If X varies over time, you should use the largest value of X that is seen in your facility.

$$\mathbf{D}_{\rm m} = 0.22 \; {\rm X}/(460 + {\rm T}) \tag{3}$$

As an example, if X = 65, and the operating temperature is 95 °F,  $\mathbf{D}_{m} = 0.026$  lb/ft3.

2. Calculate the total volume V ( $ft^3$ ) occupied by digester gas in one digester (the largest). Associated pipework can be neglected.

$$\mathbf{V} = \mathbf{B}\mathbf{r}^{2}\mathbf{H} \tag{4}$$

Here, r is the digester radius and H is the maximum digester head space. As an example, if H = 8 ft and r = 40 ft, then V =  $\mathbf{B}r^2H = (3.14)(40)^2(8) \cdot 40,200 \text{ ft}^3$ .

3. Calculate the quantity Q of methane contained in V:

$$\mathbf{Q} = \mathbf{D}_{\mathrm{m}} \mathbf{V} \tag{5}$$

In the current example, Q = (0.026)(40,200) = 1,045 lb

Note that this quantity of methane itself, as well as the total quantity of digester gas, is less than the 10,000-lb TQ for flammable materials. This is because the total amount of digester gas (i.e., not just methane) in a process is used to determine whether that process is covered by the regulation (assuming the digester gas is not being used as fuel). It may be the case that no single digester contains more than the TQ of digester gas, but you still will be covered if there are several digesters in your process and the total quantity of digester gas in all of the digesters together exceeds the threshold. However, you are required to consider only the quantity of methane in a single vessel when calculating the results of a worst-case vapor cloud explosion.

4. Use the TNT-equivalency model to calculate the distance D (miles) to the 1 psi overpressure endpoint:

$$\mathbf{D} = 0.0082 \ (\mathbf{Q})^{1/3} \tag{6}$$

Equation 6 has been customized for methane. In the present example,  $D = 0.0082(1,045)^{1/3} = 0.08$  mile. Alternatively, you can use Exhibit F-10 to estimate the distance to the endpoint for a range of quantities of methane.

## EXHIBIT F-10 Distance to Overpressure Endpoint of 1.0 PSI for Vapor Cloud Explosions of Methane Based on TNT Equivalent Method, 10 Percent Yield Factor

Quantity in Cloud (pounds)	Distance to Endpoint (miles)	Quantity in Cloud (pounds)	Distance to Endpoint (miles)
500	0.07	50,000	0.3
2,000	0.1	100,000	0.4
5,000	0.1	200,000	0.5
10,000	0.2	500,000	0.7
20,000	0.2	1,000,000	0.8

Some facilities have an intermediate storage vessel for digester gas, at a pressure that may be typically 45-50 psig. You should use the quantity of methane in such a vessel in Equation 6 or Exhibit F-10 if it contains the largest quantity of digester gas on site.

# F.3.2 Alternative Release Scenarios

This subsection provides guidance on how to choose and model alternative scenarios for chlorine, sulfur dioxide, anhydrous ammonia, aqueous ammonia, and methane. For information on the general requirements of the regulations pertaining to alternative release scenarios, refer to chapter 4 of the main document.

A number of scenarios other than those listed in the rule may be worth considering for WTTPs. Many WWTPs have single-stage, pass-through chemical scrubbers to neutralize compounds such as sulfur dioxide. Failure of the neutralizing solution's recirculation pump and continued operation of the blower fan could not only allow a release, but also exacerbate it by mechanically evacuating the substance from the room.

Accidents reported to EPA involving chlorine systems have been caused by "rust holes," failure of a diaphragm, leak during hookup to a tank, a packing nut leak, faulty cylinders, removal of a valve in error, faulty valves, leaking gaskets, and a blown pressure gauge. Similar accidents involving sulfur dioxide systems have been reported. In addition, natural events, such as floods, tornados, earthquakes, and hurricanes could cause several releases to occur simultaneously. You may want to consider these types of scenarios when you select your alternative release scenarios.

#### CHLORINE

## FLASHING LIQUID RELEASES

Many of the potential alternative scenarios could involve the release of liquid chlorine from a small hole. The liquid chlorine flashes immediately to vapor and fine liquid droplets and is carried downwind.

The rate of release of a liquid through an hole is given by Bernoulli's formula for liquid releases (see section F.3.4). Using chemical-specific data for chlorine, the formula becomes:

$$QR = 3,140 \times A_{\rm h} \tag{8}$$

where:

$A_h =$	the area of the hole ( $in^2$ - for example, the area of a hole of diameter 1 inch is 0.785 in <sup>2</sup> )
3,140 =	factor applicable to chlorine liquefied under a pressure of 98.5 psig (see Section F.3.4)

Note that this is the formula for the release of a pure liquid and would apply to a breach in the wall of a vessel or to the rupture of a very short pipe. For long pipes, there is a pressure drop between the vessel and the hole, and there will be flashing in the pipe and a reduced rate of release. Therefore, Equation 8 may be conservative.

If there is a small leak from the liquid space of a large storage vessel, the reservoir can essentially be considered as infinite, and the chlorine will be steadily emitted at a constant rate for a relatively long period. Such leaks may occur because of a gasket failure, a pump seal leak, or a corrosion hole, for example. You can use Equation 8 and the estimated area of the hole to calculate the release rate (QR).

To predict the distance to the toxic endpoint, take the calculated value of QR and identify the closest value on Exhibit F-11 (150 lb/min). Read off the corresponding distance, in this case, 0.6 mile for a rural site and 0.2 mile for an urban site. Alternatively, use Figure F-5.

Exhibit F-12 provides release rate estimates for releases of liquid chlorine through holes of diameter 1/16 inch to 5 inches and the distances to the endpoint corresponding to these release rates. You can use this table instead of Equation 8 and Exhibit F-11 to estimate the distance to the endpoint.

# EXHIBIT F-11 Distances to Toxic Endpoint for Chlorine D Stability, Wind Speed 3 Meters per Second

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural	Urban	
1	<0.1*		
2	0.1	< 0.1*	
5	0.1		
10	0.2	0.1	
15	0.2	0.1	
20	0.2	0.1	
30	0.3	0.1	
40	0.3	0.1	
50	0.3	0.1	
60	0.4	0.2	
70	0.4	0.2	
80	0.4	0.2	
90	0.4	0.2	
100	0.5	0.2	
150	0.6	0.2	
200	0.6	0.3	
250	0.7	0.3	
300	0.8	0.3	
400	0.8	0.4	
500	1.0	0.4	
600	1.0	0.4	
700	1.1	0.4	

Release Rate	Distance to Endpoint (miles)		
(lbs/min)	Rural	Urban	
750	1.2	0.4	
800	1.2	0.5	
900	1.2	0.5	
1,000	1.3	0.5	
1,500	1.6	0.6	
2,000	1.8	0.6	
2,500	2.0	0.7	
3,000	2.2	0.8	
4,000	2.5	0.8	
5,000	2.8	0.9	
7,500	3.4	1.2	
10,000	3.9	1.3	
15,000	4.6	1.6	
20,000	5.3	1.8	
25,000	5.9	2.0	
30,000	6.4	2.1	
40,000	7.3	2.4	
50,000	8.1	2.7	
75,000	9.8	3.2	
100,000	11	3.6	
150,000	13	4.2	
200,000	15	4.8	

\* Report distance as 0.1 mile

## EXHIBIT F-12 Release Rates and Distance to the Endpoint for Liquid Chlorine Releases D Stability, Wind Speed 3 Meters per Second

Hole Diameter	Release Rate	Distance (miles)	
(inches)	(lb/min)	Rural	Urban
1/16	10	0.2	0.1
3/16	87	0.4	0.2
1/4	150	0.6	0.2
5/16	240	0.7	0.3
1/2	620	1.0	0.4
1	2,500	2.0	0.7
2	9,900	3.9	1.3
3	22,200	5.3	1.8
4	39,500	7.3	2.4
5	61,700	8.1	2.7

#### TWO-PHASE RELEASES

In case of a release from a long pipe carrying liquid chlorine  $(L/d_h >> 1)$ , where L is the length of the pipe between the reservoir of chlorine and the atmosphere and  $d_h$  is the diameter of the pipe), there can be flashing in the discharge pipe, resulting in a two-phase mixture emerging to the atmosphere. In this case, the rate of release in lb/min for chlorine is given by:

$$QR = 1,100 \times A_{\rm h} \times F \tag{9}$$

where:

1,100 =	chemical-specific factor applicable to chlorine at 25 °C (see
	Section F.3.4)
$A_h =$	hole area $(in^2)$ = area of pipe opening
$\mathbf{F} =$	frictional loss factor (dimensionless) with values as follows:
	$\underline{F}$ $\underline{L/d}_{h}$
	1 10
	0.85 50
	0.75 100
	0.65 200
	0.55 400

Exhibit F-13 presents release rates for a range of pipe diameters and length-diameter ratios for two-phase releases of chlorine from a pipe. You can read the release rate from the exhibit or calculate the release rate from Equation 9, then find the distance to the endpoint corresponding to the release rate by referring to Exhibit F-11.

EXHIBIT F-13 Release Rates for Two-Phase Releases from Pipes Carrying Liquid Chlorine

Pipe	Pipe Length/Diameter (L/d <sub>h</sub> )				
Diameter (inches)	10 (F=1) 50 (F=0.85) 100 (F=0.75) 200 (F=0.65) 400 (F=0.55				
	Chlorine Release Rate (lbs/min)				
1/4	54	46	40	35	30
5/16	84	72	63	55	46
1/2	220	180	160	140	120
3/4	490	410	360	320	270
1	860	730	650	560	480
2	3,500	2,900	2,600	2,200	1,900
3	7,800	6,600	5,800	5,100	4,300

#### **VAPOR RELEASES**

For a choked release of vapor (i.e., emerging at the speed of sound from the hole, which will invariably be the case for chlorine at atmospheric temperatures), the release rate for chlorine is given by:

$$QR = 190 \times A_{\rm h} \tag{10}$$

where:

190 = chemical-specific factor for chlorine at a tank pressure of 113 psia and temperature 25 °C (see Section F.3.4)

 $A_h =$  hole area (in<sup>2</sup>)

You can use Equation 10 to estimate the release rate of chlorine from a hole in the vapor space of a tank. For example, such a hole could result from shearing off a valve at the top of a tank. The distance to the endpoint can be estimated from the release rate, using Exhibit F-11 or Figure F-5.

As an alternative to Equation 10, for releases from holes ranging from 1/16-inch to 5 inches in diameter, you can read the release rate and the corresponding distance from Exhibit F-14.

## EXHIBIT F-14 Release Rates and Distance to the Endpoint for Chlorine Vapor Releases D Stability, Wind Speed 3 Meters per Second

Hole	Release Rate	Distance (miles)	
Diameter (inches)	(lbs/min)	Rural	Urban
1/16	0.6	0.1	0.1
3/16	5	0.1	0.1
1/4	9	0.2	0.1
5/16	15	0.2	0.1
1/2	37	0.3	0.1
1	150	0.6	0.2
2	600	1.0	0.4
3	1,300	1.6	0.6
4	2,400	2.0	0.7
5	3,700	2.5	0.8

Note that the release rate estimated by the method above is conservative. As the release proceeds, chlorine continuously evaporates from the liquid surface in the cylinder. This causes the liquid to cool, the vapor pressure to decrease, and the rate of release to decline. However, the equations for calculating this effect are rather complex and not included in this guidance.

#### **OTHER CHLORINE SCENARIOS**

If you wish to do so, you can simply quote any of the results above, if they are applicable to your site, when you submit your Risk Management Plan. However, you may also choose to develop other scenarios, using Equations 8, 9, or 10, and Exhibit F-11 or Figure F-5.

#### **DURATION OF RELEASE**

You may calculate the maximum duration by dividing the quantity in the tank or the quantity that would be released from a pipe by the release rate. You may use 60 minutes as a default value for maximum release duration. If you know, and can substantiate, how long it is likely to take to stop the release, you may use that time as the release duration.

## SULFUR DIOXIDE

#### FLASHING LIQUID RELEASES

Sulfur dioxide is similar to chlorine in the way that it would be released, so Bernoulli's formula is applicable. Using Bernoulli's formula, incorporating chemicalspecific data for sulfur dioxide, you can estimate the release rate from a hole in the liquid space of a tank from the following equation:

$$QR = 2,020 \times A_{\rm h} \tag{11}$$

where:

$A_h =$	the area of the hole (in <sup>2</sup> )
2,020 =	factor applicable to sulfur dioxide liquefied under a pressure of 43 psig (see Section F.3.4)

After you have estimated the release rate, you can find the predicted distance to the toxic endpoint for sulfur dioxide from Exhibit F-16 or Figure F-6. Alternatively, you can use Exhibit F-15. This exhibit gives release rates and distances to the endpoint for flashing liquid releases through holes of diameter 1/16 inch to 5 inches.

EXHIBIT F-15
Release Rates and Distance to the Endpoint for Liquid Sulfur Dioxide Releases
D Stability, Wind Speed 3 Meters per Second

Hole Diameter	Release Rate	Distance	e (miles)
(inches)	(lb/min)	Rural	Urban
1/16	6	0.1	0.1
3/16	56	0.4	0.2
1/4	99	0.5	0.2
5/16	160	0.6	0.2
1/2	400	0.9	0.4
1	1,600	1.9	0.6
2	6,300	3.3	1.1
3	14,300	5.6	1.7
4	25,300	7.3	2.1
5	39,600	9.2	2.6

## TWO PHASE RELEASES

A break in a long pipe (whose length is much greater than its diameter) carrying liquid sulfur dioxide can result in the release of a two-phase mixture, as discussed above for chlorine. The release rate can be estimated from the following equation:

$$QR = 252 \times A_{\rm h} \times F \tag{12}$$

where:

252 = chemical-specific factor applicable to sulfur dioxide at 25 °C (see Section F.3.4)

 $A_h =$  hole area (in<sup>2</sup>) = area of pipe opening

F = frictional loss factor (dimensionless) with values as shown in the section on chlorine

You can estimate the release rate from Equation 12, then find the distance to the endpoint corresponding to the release rate by referring to Exhibit F-11. You also can find the release rate for a range of pipe diameters and  $L/d_h$  values in Exhibit F-17.

# Exhibit F-16 Distances to Toxic Endpoint for Sulfur Dioxide D Stability, Wind Speed 3.0 Meters per Second

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
1	< 0.1*	
2	0.1	<0.1*
5	0.1	
10	0.2	0.1
15	0.2	0.1
20	0.2	0.1
30	0.2	0.1
40	0.3	0.1
50	0.3	0.1
60	0.4	0.2
70	0.4	0.2
80	0.4	0.2
90	0.4	0.2
100	0.5	0.2
150	0.6	0.2
200	0.6	0.2
250	0.7	0.3
300	0.8	0.3
400	0.9	0.4
500	1.0	0.4
600	1.1	0.4
700	1.2	0.4

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
750	1.3	0.5
800	1.3	0.5
900	1.4	0.5
1,000	1.5	0.5
1,500	1.9	0.6
2,000	2.2	0.7
2,500	2.3	0.8
3,000	2.7	0.8
4,000	3.1	1.0
5,000	3.3	1.1
7,500	4.0	1.3
10,000	4.6	1.4
15,000	5.6	1.7
20,000	6.5	1.9
25,000	7.3	2.1
30,000	8.0	2.3
40,000	9.2	2.6
50,000	10	2.9
75,000	13	3.5
100,000	14	4.0
150,000	18	4.7
200,000	20	5.4

\* Report distance as 0.1 mile

#### **EXHIBIT F-17**

## Release Rates for Two-Phase Releases from Pipes Carrying Liquid Sulfur Dioxide

Pipe	Pipe Length/Diameter (L/d <sub>h</sub> )				
Diameter (inches)	10 (F=1)	50 (F=0.85)	100 (F=0.75)	200 (F=0.65)	400 (F=0.55)
	Sulfur Dioxide Release Rate (lb/min)				
1/4	12	11	9	8	7
5/16	19	16	14	13	11
1/2	49	42	37	32	27
3/4	110	95	83	72	61
1	200	170	150	130	110
2	800	670	600	520	440
3	1,800	1,500	1,300	1,200	980

## **VAPOR RELEASES**

For a choked release of sulfur dioxide vapor, the release rate is given:

$$QR = 91 \times A_{\rm h} \tag{13}$$

where:

91 = chemical-specific factor for sulfur dioxide at a tank pressure of 58 psia and temperature 25 °C (see Section F.3.4)

 $A_h =$  hole area (in<sup>2</sup>)

The distance to the endpoint can be estimated from the release rate, using Exhibit F-16 or Figure F-6.

As an alternative to Equation 13 and Exhibit F-16, for releases from holes ranging from 1/4 inch to 5 inches in diameter, you can read the release rate and the corresponding distance from Exhibit F-18.

## EXHIBIT F-18 Release Rates and Distance to Endpoint for Sulfur Dioxide Vapor Releases D Stability, Wind Speed 3 Meters per Second

Hole Diameter	Release Rate	Distance	e (miles)
(inches)	(lb/min)	Rural	Urban
1/4	4	0.1	0.1
5/16	7	0.1	0.1
1/2	18	0.2	0.1
1	71	0.4	0.2
2	280	0.8	0.3
3	640	1.1	0.4
4	1,100	1.5	0.5
5	1,800	2.2	0.7

#### **OTHER SULFUR DIOXIDE SCENARIOS**

If you wish to do so, you can simply quote any of the results above, if they are applicable to your site, when you submit your Risk Management Plan. However, you may also choose to develop other scenarios, using Equations 11, 12, or 13, and Exhibit F-16 or Figure F-6.

#### **ANHYDROUS AMMONIA**

#### FLASHING LIQUID RELEASES

Like chlorine and sulfur dioxide, ammonia will be liquefied under pressure in its own storage vessel. Bernoulli's equation is applicable for flashing liquid releases (see Section F.3.4). The equation for ammonia liquefied under a pressure of 130 psig is:

$$QR = 2,380 \times A_{\rm h} \tag{14}$$

where:

 $A_h =$  hole area (in<sup>2</sup>)

2,380 = chemical-specific factor for ammonia liquefied under pressure.

After you have estimated the release rate, you can find the predicted distance to the toxic endpoint for ammonia from Exhibit F-20 or Figure F-7.

Alternatively, you can use Exhibit F-19. This exhibit gives release rates and distances to the endpoint for flashing liquid releases through holes of diameter 1/16 inch to 5 inches.

## EXHIBIT F-19 Release Rates and Distance to the Endpoint for Liquid Ammonia Releases D Stability, Wind Speed 3 Meters per Second

Hole Diameter	Release Rate	Distance	e (miles)
(inches)	(lb/min)	Rural	Urban
1/16	7	0.1	0.1
3/16	66	0.2	0.1
1/4	120	0.2	0.1
5/16	180	0.4	0.2
1/2	470	0.4	0.2
1	1,900	0.8	0.3
2	7,500	1.6	0.5
3	16,800	2.2	0.7
4	30,000	3.1	1.0
5	46,800	3.9	1.2

# EXHIBIT F-20 DISTANCES TO TOXIC ENDPOINT FOR ANHYDROUS AMMONIA D Stability, Wind Speed 3 Meters per Second

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
<10	<0.1*	
10	0.1	
15	0.1	
20	0.1	
30	0.1	
40	0.1	<0.1*
50	0.1	
60	0.2	0.1
70	0.2	0.1
80	0.2	0.1
90	0.2	0.1
100	0.2	0.1
150	0.2	0.1
200	0.3	0.1
250	0.3	0.1
300	0.3	0.1
400	0.4	0.2
500	0.4	0.2
600	0.5	0.2
700	0.5	0.2
750	0.5	0.2
800	0.5	0.2

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
900	0.6	0.2
1,000	0.6	0.2
1,500	0.7	0.3
2,000	0.8	0.3
2,500	0.9	0.3
3,000	1.0	0.4
4,000	1.2	0.4
5,000	1.3	0.5
7,500	1.6	0.5
10,000	1.8	0.6
15,000	2.2	0.7
20,000	2.5	0.8
25,000	2.8	0.9
30,000	3.1	1.0
40,000	3.5	1.1
50,000	3.9	1.2
75,000	4.8	1.4
100,000	5.4	1.6
150,000	6.6	1.9
200,000	7.6	2.1
250,000	8.4	2.3

\* Report distance as 0.1 mile

#### **AQUEOUS AMMONIA**

Alternative scenario spills of aqueous ammonia are going to be similar to worst-case scenario spills in that there will be a leak of some kind and the liquid will either spread across a diked area or spread out until its depth is only 1 cm (0.39 inch). The principal difference will be in the amount spilled.

The calculation of the rate of spillage is again performed using Bernoulli's formula see Section F.3.4). The density of 30 percent aqueous ammonia is 57.33 lb/ft3, so the equation becomes:

$$QR_{\rm L} = 153 \times A_{\rm h} \times ({\rm h})^{0.5} \tag{15}$$

where:

 $QR_L$  = rate of spillage of ammonia solution onto the ground (lbs/min), not the rate of evaporation

$$A_h =$$
 hole area (in<sup>2</sup>)  
h = static head

For example, for a <sup>1</sup>/<sub>2</sub>-inch diameter opening with a static head h of 10 ft:

$$QR_{I} = 153 \times \mathbf{B} \times (\frac{1}{2} \times \frac{1}{2})^{2} \times (10)^{\frac{1}{2}} = 153 \times 3.142 \times \frac{1}{16} \times 3.16 = 95 \text{ lb/min}$$

This is the rate of spillage of the total solution of water plus ammonia as a liquid onto the ground.

If you know, and can document, how long it will take to stop the release, you should estimate the total quantity of solution spilled to the ground (QS) by multiplying the estimated rate of liquid spillage by the estimated duration of the release (in minutes).

Then you can estimate the release rate to air (QR) as the evaporation rate of ammonia from the pool. For an undiked area (pool depth 1 cm):

$$QR = 0.025QS$$
 (16)

For a diked pool (pool depth greater than 1 cm) of area A<sub>p</sub> square feet:

$$QR = 0.046A_{\rm p} \tag{17}$$

The maximum area of the pool that would be formed by the spilled liquid is 0.55QS.

If you have a diked area that is larger than the maximum area, use the equation for an undiked area to estimate the release rate to air.

It is possible that you may estimate a rate of evaporation of ammonia from the pool that exceeds the spill rate of the liquid solution, particularly if the liquid spill rate is small and the spill of the liquid may last for a fairly long time. In such a case, under the assumptions used in this estimation method, no pool would be formed. Instead of the evaporation rate, in this case, you should use the liquid spill rate  $(QR_L)$  as the release rate to air.

You also can determine how far the pool will spread until the rate of spillage is matched by the rate of evaporation of ammonia. For aqueous ammonia at 77 °F (25 °C), the rate of evaporation is 0.046  $A_p$  (from Equation 17).

The area that will cause the rate of evaporation to exactly balance the rate of spillage is given by:

$$A_{p} = QR/0.046 = 22QR_{L}$$
(18)

In the example given above,  $QR_L = 95$  lb/min, so  $A_p = 2,100$  ft<sup>2</sup>. This value should be compared with the available diked area and the <u>smaller</u> of the two values chosen. Thus, if the diked area happens to be 50 ft x 50 ft = 2,500 ft<sup>2</sup>, the area chosen for subsequent calculation is  $A_p = 2,100$  ft<sup>2</sup> and QR = 95 lb/min. (If the diked area happened to be smaller — say 20 ft x 20 ft = 400 ft<sup>2</sup> — then the spilled ammonia would cover the diked area, and, using Equation 17, the rate of evaporation QR would be (0.046)(400) = 18 lb/min.)

To predict the distance to the toxic endpoint in typical weather conditions, take the value of QR calculated above and identify the closest value on Exhibit F-21. Read off the corresponding distance. For the 95 lb/min case, the result is 0.2 mile for a rural site and 0.1 mile for an urban site. Alternatively, use Figure F-8.

# EXHIBIT F-21 Distance to Toxic Endpoint for Aqueous Ammonia D Stability, Wind Speed 3 Meters per Second

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural	Urban
<8	< 0.1*	
8	0.1	
10	0.1	
15	0.1	
20	0.1	
30	0.1	<0.1*
40	0.1	
50	0.2	0.1
60	0.2	0.1
70	0.2	0.1
80	0.2	0.1
90	0.2	0.1
100	0.2	0.1
150	0.3	0.1
200	0.3	0.1
250	0.4	0.2
300	0.4	0.2
400	0.4	0.2
500	0.5	0.2
600	0.6	0.2
700	0.6	0.2
750	0.6	0.2

Release Rate	Distance to Endpoint (miles)	
(lbs/min)	Rural Urban	
800	0.7	0.2
900	0.7	0.3
1,000	0.8	0.3
1,500	1.0	0.4
2,000	1.2	0.4
2,500	1.2	0.4
3,000	1.5	0.5
4,000	1.8	0.6
5,000	2.0	0.7
7,500	2.2	0.7
10,000	2.5	0.8
15,000	3.1	1.0
20,000	3.6	1.2
25,000	4.1	1.3
30,000	4.4	1.4
40,000	5.1	1.6
50,000	5.8	1.8
75,000	7.1	2.2
100,000	8.2	2.5
150,000	10	3.1
200,000	12	3.5

\* Report distance as 0.1 mile
## METHANE

Consider the case of methane released from a digester. Assuming that the full contents of a digester were released over a few minutes (say 10 minutes), in the example given in Section 4.1, the release rate would be 105 lb/min (total quantity of methane in the digester, 1,053 lb). The LFL for methane is 33 mg/L. Conservatively taking digester gas/methane as a neutrally buoyant gas (it will actually rise from the ground), you need to use Exhibit F-22 (for a rural site) or Exhibit F-23 (for an urban site) to estimate the distance to the LFL. From Exhibit F-22, the predicted distance for a release rate of 105 lb/min is 0.1 mile at a rural site and, from Exhibit F-23, it is 0.1 mile at an urban site.

It is unlikely that a BLEVE would occur. They are not known to take place in low pressure containment such as that of a digester. A pool fire does not need to be considered, because the methane is not liquefied.

## EXHIBIT F-22 Neutrally Buoyant Plume Distances to Lower Flammability Limit (LFL) Rural Conditions, D Stability, Wind Speed 3.0 Meters per Second

Release Rate (lbs/min)	Distance to Endpoint (miles)
0 - 1,980	0.1
1,980 - 7,260	0.2
7,260 - 17,490	0.3
17,490 - 28,380	0.4
28,380 - 42,900	0.5
42,900 - 56,100	0.6
56,100 - 72,600	0.7
72,600 - 89,100	0.8
89,100 - 108,900	0.9

Release Rate (lbs/min)	Distance to Endpoint (miles)
108,900 - 128,700	1.0
128,700 - 148,500	1.1
148,500 - 171,600	1.2
171,600 - 191,400	1.3
191,400 - 224,400	1.4
224,400 - 270,600	1.6
270,600 - 320,100	1.8
320,100 - 363,000	2.0
363,000 - 429,000	2.2

## EXHIBIT F-23 Neutrally Buoyant Plume Distances to Lower Flammability Limit (LFL) Urban Conditions, D Stability, Wind Speed 3.0 Meters per Second

Release Rate (lbs/min)	Distance to Endpoint (miles)
0 - 4,950	0.1
4,950 - 23,430	0.2
23,430 - 49,500	0.3
49,500 - 85,800	0.4
85,800 - 132,000	0.5
132,000 - 181,500	0.6
181,500 - 240,900	0.7

Release Rate (lbs/min)	Distance to Endpoint (miles)
240,900 - 303,600	0.8
303,600 - 363,000	0.9
363,000 - 462,000	1.0
462,000 - 594,000	1.2
594,000 - 858,000	1.4
858,000 - 1,023,000	1.6
1,023,000 - 1,254,000	1.8

## F.3.3 BUILDINGS

In many WWTPs, chlorine and sulfur dioxide cylinders or other vessels are kept indoors. Unless your cylinders are delivered directly into the building (i.e., they are not unloaded outdoors and moved inside later), you should not consider buildings in your worst-case scenario, even though they are passive mitigation systems, because there will be some time when the vessels are outdoors. If your cylinders are delivered indoors or if your largest vessel is indoors, you may want to analyze the mitigating effects of the building when you do your worst-case analysis. You may also want to consider alternative scenarios that consider buildings as mitigation systems. Some buildings are strong, leak-tight buildings that are designed to contain the release of the contents of a one-ton cylinder or other vessel. Some of them contain scrubbers that activate upon release of chlorine or sulfur dioxide; if these scrubbers function as designed, they can ensure that any release to the external atmosphere would be small. (Scrubbers are active mitigation features that cannot be considered to work for a worst-case scenario.) At the other end of the spectrum, some buildings are intended to do no more than keep the rain off.

## MITIGATION OF RELEASES OF ANHYDROUS AMMONIA, CHLORINE, OR SULFUR DIOXIDE INTO BUILDINGS

EPA's *RMP Offsite Consequence Analysis Guidance* provides a simple building release-rate- multiplicative factor of 55 percent for toxic gases in both worst-case and

alternative scenarios (i.e., the predicted rate of release is 55 percent of that for the same accident if it should occur outdoors).

Example: Assume that there is a liquid chlorine release through a 5/16-inch opening as described in the discussion of chlorine alternative scenarios (see Exhibit F-12). This release takes place indoors and, per the discussion above, is reduced to 55 percent of the release rate of 240 lb/min, i.e., to 130 lb/min. From Exhibit F-11, the predicted distance to the toxic endpoint is 0.6 mile for a rural site and 0.2 mile for an urban site, compared to 0.7 mile (rural) and 0.3 mile (urban) for an outdoor release.

The *RMP Offsite Consequence Analysis Guidance* also provides factors for toxic liquids of 10 percent for worst-case scenarios and 5 percent for alternative scenarios. These factors may be used for releases of aqueous ammonia that take place inside buildings.

The following discussion provides a more sophisticated approach for considering effects of building mitigation for worst-case (if appropriate) and alternative scenarios involving release of gases and mixtures of gases and entrained liquid. Analysis of release scenarios inside buildings involves consideration of the structure of the building, liquid rain-out, and release containment issues. The procedure addressing these issues which is recommended for developing release rate estimates for both worst-case (if appropriate) and alternative scenarios is presented in Figure F-9.

The release into the building is assumed to occur over a 10-minute period. For the worst-case scenario, the quantity released into the building equals the total quantity in the largest vessel or pipeline. For alternative scenarios, you must estimate the total quantity of ammonia, chlorine, or sulfur dioxide released from the equipment over a 10-minute period. This 10-minute assumption is made to keep this guidance simple.

Calculations of the likely rise in pressure show that, for a release distributed over 10 minutes, building failure is unlikely to occur unless you have a very large vessel in a very small room. However, if the ratio of room volume to quantity in the vessel is < 0.1 ft<sup>3</sup>/lb for ammonia and < 0.05 ft<sup>3</sup>/lb for chlorine or sulfur dioxide, you should look at the possibility that the room will fail by windows blowing out or doors blowing open.

If the release is indoors directed towards a door or window that is potentially open, the release rate to the outside is the total quantity, uniformly distributed over 10 minutes. If the release is indoors and not directed towards a door or window, mitigation of the release by scrubbing, rain-out, or ventilation dilution may occur. If there is a scrubber, the release of material to the environment may be low. If there is no scrubber, the ventilation rate  $N_v$ , expressed as room volumes exchanged per hour, is identified, and the room volume per unit quantity of either ammonia, chlorine, or sulfur dioxide vapor released to the room (**1**) and the quantity airborne in the room (**Q**<sub>a</sub>) are calculated for either a vapor or a vapor/liquid release.

For vapor releases, the amount of vapor released into the room is clearly Q, so  $\mathbf{1} = V/Q$ . For a flashing liquid release, 20 percent of the release typically flashes to vapor, so  $\mathbf{1} = V/(0.2Q)$ . The quantity airborne in the room is the total quantity released from the equipment to the room in 10 minutes for vapor releases and fourteenths of the total quantity released from the equipment to the room in 10 minutes for vapor/liquid releases. The basis for this four-tenths assumption is that, in a room, a flashing liquid jet will encounter obstacles that will cause 60 percent of the release to collect as a relatively slowly evaporating pool on the ground. The release over the initial ten minutes leads to predictions of higher concentrations downwind than does the slowly evaporating pool; therefore, you can consider only the release rate of the airborne material (0.4Q/10) and ignore the evaporating pool in estimating the distance to the toxic endpoint.

Given the values of  $N_v$  and **1**, the building mitigation factor (FR<sub>10</sub>) is identified for 10-minute releases of ammonia in Exhibit F-24, and for 10-minute releases of either chlorine or sulfur dioxide in Exhibit F-25, respectively. The release rate to the environment is the total quantity airborne in the room, reduced by the building mitigation factor, distributed uniformly over 10 minutes.

Example: A 25-ton (50,000 lb) chlorine storage vessel is in a room of dimensions 40 feet x 40 feet x 30 feet = 48,000 ft<sup>3</sup>. There is a worst-case release, so that the 50,000 lb is released into the building over a period of 10 minutes. The release is not adjacent to a potentially open door or window. Because it is a worst-case scenario, the scrubber (if there is one) is not operating. The ventilation rate  $N_v = 4$ . The release is a mixture of vapor and liquid droplets, so that  $\mathbf{1} = V/(0.2Q) = 48,000/10,000 = 4.8$  ft<sup>3</sup>/lb, and the airborne quantity  $Q_a = 0.4Q = 20,000$  lb. From Exhibit F-24, with  $N_v = 4$  and  $\mathbf{1} = 4.8$  (the closest entries on Exhibit F-25 are  $N_v = 5$  and  $\mathbf{1} = 4.0$ ), FR<sub>10</sub> = 0.46.

Therefore, the predicted worst-case scenario release rate from the building is:

 $0.46 \times ((0.4 \times 50,000)/10) = 920$  lb/min

Compare this value with 5,000 lb/min from an open-air release. From Exhibit F-4, the predicted distance for a 920 lb/min release at a rural site is 6.3 miles and, at an urban site, is 2.9 miles. By comparison, the 5,000 lb/min release would lead to corresponding distances of 15 miles and 7 miles, respectively.

Example: Take a chlorine alternative scenario for a flashing liquid release through a 1/4-inch hole (see Section F.3.2). Exhibit F-13 shows a release rate of 150 lbs/min for this release. Assume this release takes place in a building with no scrubber for 10 minutes at a release rate of 150 lb/min for a total release of 1,500 lb. Assume that the building has dimensions of 50 feet x 25 feet x 20 feet = 25,000 ft<sup>3</sup>. The release is a flashing liquid and, therefore, consists of a mixture of vapor and liquid.  $Q_a$ , the quantity that becomes airborne, is (0.4)(1,500) = 600 lb. The quantity of vapor is (0.2)(1,500) = 300 lb. Then  $\mathbf{1} = 25,000/300 = 83$ . 80. You will have to determine N<sub>y</sub> from the characteristics of your building. For this example, assume that the

building is being ventilated with  $N_v = 5$ . From Exhibit F-25,  $FR_{10} = 0.32$ , so that the rate of release to the external atmosphere is (0.1)(0.32)(600) = 19 lb/min. From Exhibit F-11, the predicted distance to the endpoint is 0.2 mile for a rural site and 0.1 mile for an urban site. For the original release rate of 150 lb/min, the distances to the endpoint are 0.6 mile for a rural site and 0.2 mile for an urban site.

## **EXHIBIT F-24** TEN-MINUTE BUILDING RELEASE ATTENUATION FACTORS FOR PROLONGED **RELEASES OF ANHYDROUS AMMONIA**

1	N <sub>v</sub>	FR <sub>10</sub>
(քէ <sup>3</sup> /Љ)	( <b>br</b> <sup>-1</sup> )	(dim)
150.0	(m)	$(\mathbf{u}\mathbf{n}\mathbf{n})$
130.0	0	0.07
	1	0.08
	<u> </u>	0.52
	10	0.51
	20	0.71
	30	0.80
	40	0.85
100.0		
100.0	0	0.11
	1	0.11
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85
50.0	0	0.20
	1	0.20
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85
25.0	0	0.35
	1	0.35
	5	0.35
	10	0.51
	20	0.71
	30	0.80
	40	0.85

1	N <sub>v</sub>	FR <sub>10</sub>
	- 1.	
(ft³/lb)	(hr <sup>-1</sup> )	(dim)
10.0	0	0.61
	1	0.61
	5	0.61
	10	0.61
	20	0.71
	30	0.80
	40	0.85
5.0	0	0.79
	1	0.79
	5	0.79
	10	0.79
	20	0.79
	30	0.80
	40	0.85
1.0	0	0.96
	1	0.96
	5	0.96
	10	0.96
	20	0.96
	30	0.96
	40	0.96
0.5	0	0.98
	1	0.98
	5	0.98
	10	0.98
	20	0.98
	30	0.98
	40	0.98

## **EXHIBIT F-25** TEN-MINUTE BUILDING RELEASE ATTENUATION FACTORS FOR PROLONGED **RELEASES OF CHLORINE AND SULFUR DIOXIDE**

4	NT	ED
Ĩ	1N <sub>v</sub>	<b>г к</b> <sub>10</sub>
(ft³/lb)	( <b>hr</b> <sup>-1</sup> )	(dim)
160.0	0	0.02
	1	0.08
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85
80.0	0	0.03
	1	0.08
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85
32.0	0	0.08
	1	0.08
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85
16.0	0	0.15
	1	0.15
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85

1	N <sub>v</sub>	FR <sub>10</sub>
(ft³/lb)	( <b>hr</b> <sup>-1</sup> )	(dim)
8.0	0	0.28
	1	0.28
	5	0.32
	10	0.51
	20	0.71
	30	0.80
	40	0.85
4.0	0	0.46
	1	0.46
	5	0.46
	10	0.51
	20	0.71
	30	0.80
	40	0.85
0.8	0	0.85
	1	0.86
	5	0.86
	10	0.86
	20	0.86
	30	0.86
	40	0.86
0.32	0	0.94
	1	0.94
	5	0.94
	10	0.94
	20	0.94
	30	0.94
	40	0.94



Figure F-1 Worst-Case Scenario – Estimated Distances to Toxic Endpoint for Chlorine Atmospheric Stability Class F with Wind Speed 1.5 m/s

100.00 50.0 -rural urban 1 1 1 1 1 1 Model Limit 20.0 10.00 Distance To Toxic Endpoint (miles) 5.0 ТП Ш ÷ΤΤ 2.0 1.00 tt. 0.5 **Ŧ**## 0.2 0.10 0.05 0.02 0.01 -5 500 2 20 50 200 2000 5000 20000 50000 10 100 1000 10000 100000 1 Rate of Release (lbs/min)

Figure F-2 Worst-Case Scenario – Estimated Distances to Toxic Endpoint for Sulfur Dioxide Atmospheric Stability Class F with Wind Speed 1.5 m/s



Figure F-3 Worst-Case Scenario – Estimated Distances to Toxic Endpoint for Anhydrous Ammonia Atmospheric Stability Class F with Wind Speed 1.5 m/s

10.00 ++5 2 Distance To Toxic Endpoint (miles) 1.00 0.5 ••• ı rural urban 0.2 0.10 **d**t: 0.05 П 0.02 0.01 -20 50 200 2000 2 5 500 5000 20000 50000 10 10000 100000 100 1000 1 Rate of Release (lbs/min)

Figure F-4 Worst-Case Scenario – Estimated Distances to Toxic Endpoint for Aqueous Ammonia Atmospheric Stability Class F with Wind Speed 1.5 m/s

Figure F-5 Alternative Release Scenario – Estimated Distances to Toxic Endpoint for Chlorine Atmospheric Stability Class D with Wind Speed 3 m/s



10.00 5 2 Distance To Toxic Endpoint (miles) 1.00 П ++++. . Ħ ТП 0.5 **1** 0.2 0.10 ++++Ħ 0.05 Ш Π 0.02 0.01 20 50 2000 200 500 5000 2000 5000 2 5 1000 10 100 10000 100000 1

Figure F-6 Alternative Release Scenario – Estimated Distances to Toxic Endpoint for Sulfur Dioxide Atmospheric Stability Class D with Wind Speed 3 m/s

Rate Of Release (lbs/min)

Figure F-7 Alternative Release Scenario – Estimated Distances to Toxic Endpoint for Anhydrous Ammonia Atmospheric Stability Class D with Wind Speed 3 m/s



10.00 5 П 2 Distance To Toxic Endpoint (miles) 1.00 0.5 HT Π RURAL URBAN 0.2 0.10 0.05  $\square$ Ш 0.02 0.01 50000 100000 5 20 50 200 500 2000 5000 20000 2 10 1000 10000 100 1

Figure F-8 Alternative Release Scenario – Estimated Distances to Toxic Endpoint for Aqueous Ammonia Atmospheric Stability Class D with Wind Speed 3 m/s

Rate Of Release (lbs/min)

Figure F-9 Guidance on Effectiveness of Building Enclosures for Alternative Release Scenarios



## F.3.4 Equations

## AMMONIA PARTIAL PRESSURE

The ratio  $R_{vp}(T)$  of the partial pressure of ammonia at temperature T °C to the partial pressure at 25 °C is given by the empirical formula:

 $R_{vn}(T) = \exp[10.438 - 717.4/(T + 273.4) - 2132.5/(T + 240.25)]$ 

### **DENSITY OF METHANE IN DIGESTER**

 $\mathbf{D}_{\rm m} = (X/100)(0.0409)(537/(460+T)) = 0.22 \ X/(460+T)$ 

where 0.0409 lb/ft<sup>3</sup> is the density of pure methane at 77 °F (25 °C) and the factor 537/(460+T) represents how the density changes with temperature, assuming that methane obeys the perfect gas law. The effect of the small operating pressure in compressing the gas has been ignored.

### ALTERNATIVE RELEASE EQUATIONS

### **BERNOULLI'S FORMULA**

The rate of release of a liquid through an hole is given by Bernoulli's formula for predicting the rate of release QR (lb/min) of liquid from a vessel:

$$m = A_h C_d (\mathbf{D}_{[2g} \mathbf{D}_{[(H_L - H_h) + 2(P_0 - P_a)])^2})$$

where:

m = Discharge rate (kilograms per second)

 $A_{h}$  = Opening area (square meters)

 $C_d$  = Discharge coefficient (unitless)

g = Gravitational constant (9.8 meters per second squared)

**D** = Liquid density (kilograms per cubic meter)

 $P_0 =$  Storage pressure (Pascals)

 $P_a$  = Ambient pressure (Pascals)

 $H_L$  = Liquid height above bottom of container (meters)

 $H_h$  = Height of opening (meters)

To create the equations in the text, this equation was converted to English units.

#### GASES LIQUEFIED UNDER PRESSURE

For gases liquefied under high pressure, the term containing the liquid height in Bernoulli's formula can be neglected. The equation for the release rate for gases liquefied under pressure becomes:

$$QR = 32.07 \times Ah \times D_{L} \times (P_{g}/D_{L})^{0.5}$$

To derive the chemical specific factors presented in the text for gases liquefied under their vapor pressure at 25 °C, the following data were substituted into the equation:

Liquefied Gas	Liquid Density ( <b>D</b> ), lbs/ft <sup>3</sup>	<u>Tank Vapor Pressure (P<sub>g</sub>), psig</u>
Chlorine	97.5	98.5
Sulfur dioxide	91.3	43.3
Ammonia	42.5	130

#### LIQUID AT AMBIENT PRESSURE

For liquids stored at ambient pressure, the difference between storage pressure and ambient pressure is zero, and the pressure term drops out of the equation above. The equation can be rewritten and converted to English units as follows:

$$QR = 132.2 \times A_{h} \times 6.4516 \times 10^{-4} \times (h)^{0.5} \times 0.5521 \times 0.8 \times (2 \times 9.8)^{0.5} \times \mathbf{D} \times 16.018$$

where:

QR = Release rate (pounds per minute)

132.2 = Conversion factor for kilograms per second to pounds per minute

 $A_{h}$  = Hole area (square inches)

 $6.4516 \times 10^{-4}$  = Conversion factor for square inches to square meters (HA)

0.5521= Conversion factor for square root of feet to square root of meters (h)

0.8 = Discharge coefficient (0.8)

9.8 = Gravitational constant (meters per second squared)

 $\mathbf{D}_{\rm L}$  = Liquid density (pounds per cubic foot)

16.018 = Conversion factor for pounds per cubic foot to kilograms per cubic meter

For ammonia solutions, the factor presented in the text was derived assuming a density of 57.33 lb/ft<sup>3</sup>.

### **TWO-PHASE RELEASE**

For long pipes  $(L/d_h >> 1)$ , where L is the length of the pipe between the reservoir of chlorine and the atmosphere and  $d_h$  is the pipe diameter), there can be flashing in the discharge pipe, and a two-phase mixture emerges to the atmosphere. In this case, the rate of release in lb/min is given by:

 $QR = 9,490(A_h)(F)(h_L)/[v_{lg}([T + 460]C_{pl})^{\frac{1}{2}}]$ 

where those symbols not already defined are:

F a frictional loss factor, which is dimensionless and takes on a value of 1 for  $L/d_h = 10, 0.85$  for  $L/d_h = 50, 0.75$  for  $L/d_h = 100, 0.65$  for  $L/d_h = 200$ , and 0.55 for  $L/d_h = 400$ 

h<sub>L</sub> the latent heat of vaporization (Btu/lb)

 $v_{lg}$  the difference in specific volume between the gas and liquid (lb/ft<sup>3</sup>)

T the reservoir temperature (°F), and

C<sub>pl</sub> the liquid heat capacity (Btu/lb/°F)

For chlorine,  $h_L$  is 124 Btu/lb,  $v_{lg}$  = 0.68 lb/ft³, T = 77 °F (25 °C), and  $C_{pl}$  = 0.222 Btu/lb/°F

For sulfur dioxide,  $v_{lg} = 1.55 \text{ ft}^3/\text{lb}$ ,  $h_L = 80 \text{ Btu/lb}$ ,  $C_{pl} = 0.34 \text{ Btu/lb}/^{\circ}\text{F}$ 

#### VAPOR RELEASES

For a gas release under choked flow conditions (i.e., emerging at the speed of sound from the hole, the maximum flow rate), the following equation can be used to estimate the release rate:

$$m = C_d A_h(\mathbf{p}_0 \mathbf{D}_0[2/(\mathbf{(+1)})^{(\mathbf{(+1)/(\mathbf{(-1)})})^{0.5}})$$

where:

m = Discharge rate (kg/s)

 $C_d = Discharge coefficient$ 

 $A_h = Opening area (m2)$ 

 $\mathbf{I} = \mathbf{R}$ atio of specific heats

 $p_0 = Tank pressure (Pascals)$ 

 $\mathbf{D}_0 = \text{Density (kg/m3)}$ 

Density  $(\mathbf{D}_0)$  can be rewritten as a function of pressure and molecular weight, based on the ideal gas law:

$$\mathbf{D}_0 = (\mathbf{p}_0 \times \mathbf{MW})/\mathbf{R} \mathbf{T}_t$$

where:

MW = Molecular weight (kilograms per kilomole)

R = Gas constant (8,314 Joules per degree-kilomole)

 $T_t = Tank$  temperature (K)

The choked flow equation can be rewritten and converted to English units as follows:

 $\begin{array}{l} QR = 132.2 \times A_h \times 6.4516 \times 10^{-4} \times P_a \times 6895 \times \\ 0.8 (\textbf{(}[2/(\textbf{(+1)}]^{(\textbf{(+1)/(\textbf{(-1)})})0.5} \times (MW/8314 \times T_l)^{0.5} \end{array} \end{array}$ 

where:

0.8 = Discharge coefficient

132.2 =Conversion factor for lbs/min to kg/s

6,895 =Conversion factor for psi to Pascals (p0)

 $6.4516 \times 10^{-4}$  = Conversion factor for square inches to square meters (A<sub>h</sub>)

 $P_a = Absolute pressure in the reservoir/tank (psia)$ 

 $A_h =$  Hole area (inches)

To derive the chemical-specific factors for gas releases presented in the text, the temperature  $(T_t)$  was assumed to be 298 K, and the following chemical-specific data were substituted into the choked flow equation:

<u>Gas</u>	Molecular Wt (MW)	Tank Press. (P <sub>a</sub> ) (psia)	Ratio of Specific Heats (()
Chlorine	70.91	113	1.32
Sulfur dioxide	64.07	58	1.26

## LOG-LOG TABLE EQUATIONS

This section presents formulas for estimating the distance to the endpoint from the rate of release for each of the toxic substances addressed in this appendix. The formulas are given in the form:

 $D = a (QR)^b$ 

where:

D = distance to the endpoint (miles)

a and b = chemical-specific factors

QR = release rate (lbs/min)

The formulas for each chemical were developed based on the best straight-line fits to the log-log graphs of release rate versus distance (Figures F-1 to F-8). The formulas are easy to use with a scientific calculator and may be used instead of the distance tables or figures. Since the equations are best fits to the curves on Figures F-1 to F-8, they may not give exactly the same predictions as appear in the corresponding exhibits.

#### CHLORINE

## WORST CASE

The guidance on Figure F-1 is essentially in the form of a straight line on a log-log plot:

 $D = 0.2273(QR)^{0.4879}$  for a rural site, and

 $D = 0.0878(QR)^{0.5134}$  for an urban site

### ALTERNATIVE

Figure F-5 is roughly a straight line on a log-log plot:

 $D = 0.053(QR)^{0.4647}$  for a rural site, and

 $D = 0.026(QR)^{0.4263}$  for an urban site.

## SULFUR DIOXIDE

#### WORST CASE

The guidance on Figure F-2 is essentially in the form of a straight line on a log-log plot:

 $D = 0.165(QR)^{0.5562}$  for a rural site, and

 $D = 0.0726(QR)^{0.5419}$  for an urban site.

#### ALTERNATIVE

The curves on Figure F-6 are approximately straight lines on a log-log plot:

 $D = 0.047(QR)^{0.4961}$  for a rural site, and

 $D = 0.025(QR)^{0.4407}$  for an urban site.

### **ANHYDROUS AMMONIA**

#### WORST CASE

The guidance on Figure F-3 is essentially in the form of a straight line on a log-log plot:

 $D = 0.0607(QR)^{0.4923}$  for a rural site, and

 $D = 0.0443(QR)^{0.4782}$  for an urban site.

## ALTERNATIVE

The curves on Figure F-7 are approximately straight lines on a log-log plot:

 $D = 0.0222(QR)^{0.4780}$  at a rural site, and

 $D = 0.0130(QR)^{0.4164}$  at an urban site.

#### **AQUEOUS AMMONIA**

### WORST CASE

The guidance on Figure F-4 is essentially in the form of a straight line on a log-log plot:

 $D = 0.0667(QR)^{0.4617}$  for a rural site, and

 $D = 0.0221(QR)^{0.4712}$  for an urban site.

#### ALTERNATIVE

The curves on Figure F-8 are roughly straight lines on a log-log plot:

 $D = 0.02(QR)^{0.5174}$  for a rural site, and

 $D = 0.0107(QR)^{0.4748}$  for an urban site.

## F.3.5 Limitations of Results

The guidance in this appendix is summarized in the form of various tables and plots giving the predicted distance to the toxic endpoint as a function of the rate of release. There are upper and lower limits on the validity of these tables and plots—the models used are not valid beyond 25 miles, nor at less than 0.06 mile (100 m ~ 300 feet). It should be noted that the guidance presented in this chapter in the form of plots and tables yield estimates that are among many possible. There is, in fact, a wide range of uncertainty, partly due to the still incomplete theoretical understanding of the atmospheric dispersion of large-scale accidental releases of hazardous vapors in the industrial environment, partly due to the need to specify the values of a number of parameters, the values of which may not be well known, and partly because there are relatively few large-scale experimental data sets with which to "tune" the models, especially for the conditions applicable to the worst-case scenario. Therefore, for any given rate of release of a specific material, such as chlorine, there may be a wide variety of predictions by analysts using different models, or using the same model with different input parameters. The potential range of uncertainty is addressed in the Technical Background Document for Offsite Consequence Analysis for Anhydrous Ammonia, Aqueous Ammonia, Chlorine and Sulfur Dioxide.

An attempt has been made to develop guidance in the mid-range of possibilities, with the hope that the most extreme conservatisms have been removed, but which is still modestly conservative. As a general (and much simplified) rule, you should not be surprised if, for worst-case scenarios, other analysts and models produce estimates that may be up to a factor of three higher or a factor of three lower than those presented here.

The estimates in the distance tables in the exhibits and all other estimates in this appendix for regulated toxic chemicals are based upon the methods described in the Technical Background Document. That method consisted of performing a range of sensitivity studies and then choosing guidance that lies within that range.

There are a number of caveats of which you should be aware.

The results given in the exhibits and figures are not in any absolute sense the "right" or "correct" ones. On the contrary, the Technical Background Document contains estimates from many sources. The intention there is to establish a range of uncertainties that might be regarded as reasonable by practitioners in the field of atmospheric dispersion modeling, and then to locate a reasonable guidance curve

(such as Figure F-1) within that range of uncertainty. In this way, it is hoped that the following objectives will be achieved:

- The facts that the results are uncertain and that there is no uniquely "right" result are not disguised.
- Nevertheless, there is a reasonable solution that is easy to use, and users of this guidance do not have to understand its derivation.

As noted above, the further downwind, the more likely it is that you are beyond the range of applicability of any atmospheric dispersion model. That is why, for the 90-ton railcar release of chlorine, the result is stated as "> 25 miles." For such a large release of chlorine, few models will estimate less than this distance, and some will estimate considerably more. There is no way to avoid the conclusion that the distance to the toxic endpoint for a worst-case release from a 90-ton chlorine railcar is very large, even though the current state of the models does not allow us to say exactly how far "large" is. Note that the discussion in this paragraph applies to railcars that are in the open air.

For the 150-lb and one-ton cylinder cases, the results are uncertain to within perhaps a factor of 5-10. The Technical Background Document shows that, under certain modeling assumptions, the distances could be perhaps a factor of three larger than those stated above or a factor of three smaller. You will also almost certainly be able to find a computer model that can be run to produce even smaller estimated distances. If you opt to do that, you will have to produce justification that the modeling is reasonable if you are audited by an implementing agency. [Note, however, that you are not obliged to use the guidance presented here; you can use whatever model you want provided that you have a solid scientific basis for doing so]. The fact that these large uncertainties exist explains why it is so difficult to develop a single guidance curve that everyone accepts. Many different choices for the guidance could fit comfortably within the range of uncertainties.

## F.4 Supplemental Accident Prevention Program Information

This section provides additional information specific to WWTPs on implementation of selected prevention program elements, to supplement the information provided in the main document.

## F.4.1 Safety Information

#### **MAXIMUM INVENTORY**

You must document the maximum intended inventory of any vessel in which you store or process a regulated substance above its threshold quantity. The U1A certificates on all vessels constructed under the ASME Boiler and Pressure Vessel Code are kept on file by the National Board. The nominal nameplate capacity can also be found on the permanently attached nameplate for your storage tank. The nameplate will also have the National Board Number for your vessel, which is the key to retrieving your U1A form from the Board. These nameplates may be located on one of the hemispherical heads, the manway, or the manway cover. The nominal capacity will usually be the water capacity, and you may want to convert it to pounds.

If you use transportation containers (railcars or tank trucks) as storage vessels, you can obtain the capacity from the required DOT nameplate, identification plate, or specification plate or from the owner of the containers. Smaller shipping containers are also marked. If you are not sure of the capacity of the vessel, you can obtain this information from the manufacturer of the vessel or tank.

The Chlorine Institute recommends that chlorine tanks not be filled beyond 95 percent at a maximum temperature of 122 degrees F. OSHA regulations limit liquid volumes of unrefrigerated anhydrous ammonia to the following:

Type of Container	Percent by Weight	Percent by Volume
Aboveground - Uninsulated	56%	82%
Aboveground - Uninsulated*		87.5%
Aboveground - Insulated	57%	83.5%
Underground - Uninsulated	58%	85%

\*Aboveground uninsulated containers may be charged to 87.5 percent by volume if the temperature of the anhydrous ammonia being charged is determined to be not lower than 30 degrees F or if the charging container is stopped at the first indication of frost or ice formation on its outside surface and is not resumed until such frost or ice has disappeared. (29 CFR 1910.111(b)(11)) Aqueous ammonia may be held in various concentrations; your supplier can provide the density and weight. You can use this information, with your tank capacity, to estimate the quantity of ammonia being stored.

The Compressed Gas Association provides the following recommendations for filling sulfur dioxide tanks at varying temperatures (CGA pamphlet G-3):

Temperature of Liquid SO <sub>2</sub> in Tank °F	Maximum Safe Volume Liquid SO <sub>2</sub> in % of Full Volume at 125% Filling Density
30	86
40	87
50	88
60	89
70	90
80	91
90	92
100	93

## F.4.2 Hazard Review

Some sample checklists for chemicals at wastewater treatment facilities are provided in section F.5 of this appendix, including:

- Exhibit F-26 General Conditions, Operation and Maintenance
- Exhibit F-27 Human Factors
- Exhibit F-28 Checklists for Chlorine and Sulfur Dioxide
- Exhibit F-29 Checklist for Anhydrous Ammonia Systems
- Exhibit F-30 Checklist for Aqueous Ammonia Systems

The examples of What-If questions in Exhibits F-31 through F-35 are derived from a variety of sources, including:

 "Guidelines for Hazard Evaluation Procedures - Second Edition with Worked Examples," published by the Center for Chemical Process Safety (CCPS), New York, 1992

WWTP	-63-	Appendix F

- Information collected from various wastewater treatment facilities during the development of this guidance.
- Information from industry associations such as the Chlorine Institute, the International Institute of Ammonia Refrigeration (IIAR), and the American Water Works Association (AWWA).

## **F.4.3 Additional References**

The Chlorine Institute (http://www.cl2.com) publishes information on safe use and handling of chlorine, including:

- ---- Chlorine Vaporizing Systems (Pamphlet # 9).
- Cylinder and Ton Container Procedures for Chlorine Packaging (Pamphlet # 17).
- Maintenance Instructions for Chlorine Institute Standard Safety Valves, Type 1-1/2 JQ (# 39).
- Maintenance Instructions for Chlorine Institute Standard Angle Valve (#40).
- Maintenance Instructions for Chlorine Institute Standard Safety Valve, Type 4JQ (#41).
- Maintenance Instructions for Chlorine Institute Standard Excess Flow Valves (#42).

The Compressed Gas Association publishes information on safe use and handling of compressed gases, including:

- *Anhydrous Ammonia* on properties, storage, handling, and use of anhydrous ammonia (Publication ID # G-2).
- ANSI K61.1, American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia (Publication ID # G-2.1).
- *Sulfur Dioxide* on properties, storage, handling, and use of sulfur dioxide (Publication ID # G-3).

The Water Environment Federation provides several training programs on wastewater treatment operation and maintenance (the programs also include general procedures) including the following:

- *Basic Course for Wastewater Treatment Plant Operators*, Instructor Set Order No. E0100GB, Student Workbook Order No. E0110GB.
- Intermediate Course for Wastewater Treatment Plant Operators, Instructor Set Order No. E0295GB, Student Workbook Order No. E0296GB.
- Chlorination Skill Training Course, Order No. E0312GB. Self Instruction Course.

The Water Environment Federation also publishes:

- Operation and Maintenance of Municipal Wastewater Treatment Plants (MOP-11).

The Water Environment Federation is located at 601 Wythe Street, Alexandria, VA 22134, and can be contacted at (800) 666-0206 or (703) 684-2452.

In addition, the following may be useful:

 NFPA-820, Standard for Fire Protection in Wastewater Treatment and Collection Facilities.

# F.5 Hazard Review Checklists, What If Questions, and HAZOP Procedures

Exhibit F-26
<b>General Conditions, Operation and Maintenance</b>
(For any WWTP)

General Conditions, Operation and Maintenance	Yes/No/NA	Comments
Are work areas clean?		
Are adequate warning signs posted?		
Is ambient temperature normally comfortable		
Is lighting sufficient for all operations?		
Are the right tools provided and used?		
Is personal protective equipment (PPE) provided and adequate?		
Are containers and tanks protected from vehicular traffic?		
Are all flammable and combustible materials kept away from containers, tanks, and feed lines?		
Are containers, tanks, and feed line areas kept free of any objects that can fall on them (e.g., ladders, shelves?)		
Are leak detectors with local and remote audible and visible alarms present, operable, and tested?		
Are windsocks provided in a visible location?		
Are emergency repair kits available for each type of supply present?		
Are appropriate emergency supplies and equipment present, including PPE and self-contained breathing apparatus (SCBA)?		
Are emergency numbers posted in an appropriate spot?		
Are equipment, containers, and railcars inspected daily?		
Are written operating procedures available to the operators?		
Are preventative maintenance, inspections, and testing performed as recommended by the manufacturer and industry groups and documented?		

## Exhibit F-27 Human Factors (General)

Human Factors	Yes/No/NA	Comments
Have operators been trained on the written operating procedures and the use of PPE in normal operations (or for operators on the job before June 21, 1999, have you certified that they have the required knowledge, skills, and ability to do their duties safely)?		
Do the operators follow the written operating procedures?		
Do the operators understand the applicable operating limits on temperature, pressure, flow, and level?		
Do the operators understand the consequences of deviations above or below applicable operating limits?		
Have operators been trained on the correct response to alarms and conditions that exceed the operating limits of the system?		
Are operators provided with enough information to diagnose alarms?		
Are controls accessible and easily understood?		
Are labels adequate on instruments and controls?		
Are all major components, valves, and piping clearly and unambiguously labeled?		
Are all components mentioned in the procedures adequately labeled?		
Are safe work practices, such as lockout/tagout, hot work, and line opening procedures followed?		
Are personnel trained in the emergency response plan and the use of emergency kits, PPE, and SCBAs?		
Are contractors used at the facility?		
Are contractors trained to work as safely as your own employees?		
Do you have programs to monitor that contractors are working safely?		

## Exhibit F-28 Checklists for Chlorine and Sulfur Dioxide

Chlorine and Sulfur Dioxide - Siting	Yes/No/NA	Comments
Are storage, use, and transfer areas not located uphill from adjacent operations?		
Are storage, use, and transfer areas located away from sewer openings and other underground structures?		
Do storage, use, and transfer areas have easy access for emergency response?		
Are storage, use, and transfer areas free of combustible or incompatible materials and isolated from hydrocarbons in accordance with NFPA Standard No. 49, Hazardous Chemicals Data?		
Are storage, use and transfer areas downwind of or separated from most operations and support areas and ventilation intakes based on prevailing wind direction?		
Are storage, use, and transfer areas isolated from sources of corrosion, fire, and explosion and protected from vehicle impact?		
Are storage, use, and transfer areas located away from residences and facility boundaries?		
If cylinders are stored outside, are they protected from impact by vehicular traffic?		
Chlorine and Sulfur Dioxide - Hazard Recognition	Yes/No/NA	Comments
Are material safety data sheets (MSDSs) readily available to those operating and maintaining the system?		
Do employees understand that there are certain materials with which Cl <sub>2</sub> (SO <sub>2</sub> ) must not be mixed?		
Do employees understand the toxicity, mobility, and ability of Cl <sub>2</sub> (SO <sub>2</sub> ) to sustain combustion?		
Do employees understand the consequences of confining liquid Cl <sub>2</sub> (SO <sub>2</sub> ) without a thermal expansion device?		
Do employees understand the effect of moisture on the corrosive potential of $Cl_2(SO_2)$ ?		

An	nendix	F
πp	penuix	1

WWTP

Do employees understand the effects of fire and elevated temperature on the pressure of confined chlorine (SO <sub>2</sub> ) and the potential for release?		
Chlorine and Sulfur Dioxide - Container Shipment Unloading	Yes/No/NA	Comments
Is the truck inspected for wheel chocks, proper position, and condition of crane?		
Are adequate warning signs posted? Are there "stops"?		
Is the shipment inspected for leakage, general condition, currency of hydrostatic test, and valve protective housing before accepting?		
Are containers placed in the 6 o'clock/12 o'clock position for storage to reduce the chance of a liquid leak through the valve?		
Chlorine and Sulfur Dioxide - Bulk Shipment Unloading	Yes/No/NA	Comments
Do procedures call for hand brakes to be set and wheels chocked before unloading?		
Do procedures call for safety systems to be inspected prior to making connections for unloading or between storage tanks and transfer or distribution systems?		
For railcars, are derails to protect the open end located at least 50 feet from the car being protected?		
Are railcars staged at dead-end tracks and guarded against damage from other railcars and motor vehicles?		
Are caution signs placed at each derail and as appropriate in the vicinity of Cl <sub>2</sub> (SO <sub>2</sub> ) storage, use, and transfer areas?		
Does the transfer operation incorporate an emergency shutoff system?		
Is a suitable operating platform provided at the transfer station for easy access and rapid escape?		
Is padding air for railcars from a dedicated, flow-limited, dry (to - 40 EF or below), and oil-free source?		
Is tank car attended as long as the car is connected, in accordance with DOT regulations?		
Building and Housing Cl2 (SO2) Systems	Yes/No/NA	Comments
Does the building conform with local building and fire codes and NFPA-820?		

Appendix F

Is the building constructed of non-combustible materials?		
Is continuous leak detection, using area Cl <sub>2</sub> (SO <sub>2</sub> ) monitors, provided in storage and process areas?		
If flammable materials are stored or used in the same building, are they separated from the Cl <sub>2</sub> (SO <sub>2</sub> ) areas by a fire wall?		
Are two or more exits provided from each Cl <sub>2</sub> (SO <sub>2</sub> ) storage and process area and building?		
Is the ventilation system appropriately designed for indoor operations (and scrubbing, if required) by local codes in effect at the time of construction or major modification?		
Are the exhaust ducts near floor level and the intake elevated?		
Can the exhaust fan be remotely started and stopped?		
If Cl <sub>2</sub> and SO2 are stored in the same building, are storage rooms separated as required?		
Chlorine and Sulfur Dioxide - Piping and Appurtenances	Yes/No/NA	Comments
Do piping specifications meet Cl <sub>2</sub> (SO <sub>2</sub> ) requirements for the service?		
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer?		
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer? Are piping systems properly supported, adequately sloped to allow drainage, and with a minimum of low spots?		
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer? Are piping systems properly supported, adequately sloped to allow drainage, and with a minimum of low spots? Is all piping protected from all risks of excessive fire or heat?		
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer? Are piping systems properly supported, adequately sloped to allow drainage, and with a minimum of low spots? Is all piping protected from all risks of excessive fire or heat? Is an appropriate liquid expansion device or vapor pressure relief provided on every line segment or device that can be isolated?		
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer? Are piping systems properly supported, adequately sloped to allow drainage, and with a minimum of low spots? Is all piping protected from all risks of excessive fire or heat? Is an appropriate liquid expansion device or vapor pressure relief provided on every line segment or device that can be isolated? Chlorine and Sulfur Dioxide - Design Stage Review of New/Modified Process	Yes/No/NA	Comments
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer? Are piping systems properly supported, adequately sloped to allow drainage, and with a minimum of low spots? Is all piping protected from all risks of excessive fire or heat? Is an appropriate liquid expansion device or vapor pressure relief provided on every line segment or device that can be isolated? Chlorine and Sulfur Dioxide - Design Stage Review of New/Modified Process Is the system designed to operate at lowest practical temperatures and pressures?	Yes/No/NA	Comments
Do you require suppliers to provide documentation that all piping and appurtenances are certified "for chlorine service" or "for sulfur dioxide service" by the manufacturer? Are piping systems properly supported, adequately sloped to allow drainage, and with a minimum of low spots? Is all piping protected from all risks of excessive fire or heat? Is an appropriate liquid expansion device or vapor pressure relief provided on every line segment or device that can be isolated? <b>Chlorine and Sulfur Dioxide - Design Stage Review of</b> <u>New/Modified Process</u> Is the system designed to operate at lowest practical temperatures and pressures? If Cl <sub>2</sub> (SO <sub>2</sub> ) demand is low enough, is the system designed to feed gaseous chlorine (SO <sub>2</sub> ) from the storage container, rather than liquid?	Yes/No/NA	Comments

Appendix F	-70-	WWTP
Are low-pressure alarms and Cl <sub>2</sub> (SO <sub>2</sub> ) feed lines?	d automatic shutoff valves provided on	
Are vent-controlled spill co sloped toward sumps for sta	llection sumps provided and floors tionary tanks and railcars?	
Are vaporizers provided with downstream pressure reducing temperature control system on low vaporizer temperature continuously manned control	th automatic gas line shutoff valve, ing valve, gas flow control valve, and interlocks to shut down gas flow re, and appropriate alarms in a ol room?	
Do vaporizers have a limiter	d heat input capacity?	
Are curbs, sumps, and dikin potential spills provided for	g that minimize the surface of stationary tanks and railcars?	

# Exhibit F-29 Checklist for Anhydrous Ammonia Systems

Anhydrous Ammonia - Basic Rules	Yes/No/NA	Comments
Does the storage tank have a permanently attached nameplate?		
Are container(s) at least 50 feet from wells or other sources of potable water supply?		
Are container(s) painted white or other light reflecting colors and maintained in good condition?		
Is the area free of readily ignitable materials?		
Are all main operating valves on tanks identified to show liquid or vapor service?		
Anhydrous Ammonia - Appurtenances	Yes/No/NA	Comments
Are all appurtenances designed for maximum working pressure and suitable for ammonia service?		
Do all connections to containers have shut-off valves as close to container as practicable (except safety relief devices and gauging devices)?		
Are the excess flow and/or back pressure check valves located inside of the container or at a point outside as close as practicable to where line enters container?		
Are excess flow valves plainly and permanently marked with name of manufacturer, catalog number, and rated capacity?		
Anhydrous Ammonia - Piping	Yes/No/NA	Comments
Are piping and tubing suitable for ammonia service?		
Are provisions made for expansion, contraction, jarring, vibration and settling?		
Is all exposed piping protected from physical damage from vehicles and other undue strain (2,000 lb. pull)?		
Anhydrous Ammonia - Hoses	Yes/No/NA	Comments
Does the hose conform to TFI-RMA specifications for anhydrous ammonia?		
Is it 350 psig working, 1750 psig - burst?		

WWTP

Is it marked every 5 feet with "Anhydrous Ammonia, xxx psig (maximum working pressure), manufacturer's name or trademark, year of manufacture?		
Anhydrous Ammonia - Safety Relief Devices	Yes/No/NA	Comments
Are safety relief valves installed?		
Are they vented upward and unobstructed to the atmosphere?		
Do they have a Rain/Dust Cap?		
Are shut-off valves not installed between safety relief valve and container?		
Are safety relief valves marked with "NH3" or "AA", psig valve is set to start-to-discharge, CFM flow at full open, manufacturer's name, and catalog number?		
Is flow capacity restricted on upstream or downstream side?		
Are hydrostatic relief valve installed between each pair of valves in liquid piping or hose?		
Anhydrous Ammonia - Safety	Yes/No/NA	Comments
Are there two suitable full face masks with ammonia canisters as approved by the Bureau of Mines? Are self-contained breathing air apparatus required in concentrated atmospheres?		
Is an easily accessible shower or a 50 gallon drum of water available?		
Anhydrous Ammonia - Transfer of Liquid	Yes/No/NA	Comments
Are pump(s) designed for ammonia service and at least 250 psig working pressure?		
Does P.D. pump have relief valve installed?		
Is a 0-400 psi pressure gauge installed on pump discharge?		
Are loading/unloading lines fitted with back flow check or excess flow valves?		
Are caution sign(s) posted when rail car(s) are loading/unloading?		
Are containers equipped with an approved liquid level gauging device (except those filed by weight)?		
WWTP

Appendix F

Anhydrous Ammonia - Stationary Tank	Yes/No/NA	Comments
Are non-refrigerated container(s) designed for a minimum 250 (265 in CA) psig pressure?		
Are all liquid and vapor connections to container(s) except safety relief valves, liquid gauging and pressure gauge connections fitted with orifices not larger than No. 54 drill size equipped with excess-flow valves?		
Are storage containers fitted with a 0-400 psi ammonia gauge?		
Are they equipped with vapor return valves(s)?		
Are containers marked on at least two sides with "Anhydrous Ammonia" or "Caution - Ammonia" in contrasting colors and minimum 4 inch high letters?		
Is a sign displayed stating name, address and phone number of nearest representative, agent or owner?		
Are containers installed on substantial concrete, masonry or structural steel supports?		
Are ammonia systems protected from possible damage by moving vehicles?		

# Exhibit F-30 Checklist for Aqueous Ammonia Systems

Anhydrous Ammonia - Basic Rules	Yes/No/NA	Comments
Are storage tank(s) painted white or other light reflecting colors and maintained in good order?		
Is storage area free of readily ignitable materials?		
Are storage tank(s) kept away from wells or other sources of potable water supply?		
Are storage tank(s) located with ample working space all around?		
Are storage tank(s) properly vented and away from areas where operators are likely to be?		
Does receiving system include a vapor return?		
Is storage capacity adequate to receive full volume of delivery vehicle?		
Are storage tank(s) secured against overturn by wind, earthquake and/or floatation?		
Are tank bottom(s) protected from external corrosion?		
Is aqua ammonia system protected from possible damage from moving vehicles?		
Are storage tank(s) labeled as to content?		
Are all appurtenances suitable for aqua ammonia service?		
Are all storage tank(s) fitted with liquid level gauges?		
Are liquid level gauge(s) adequately protected from physical damage?		
If tubing is used, is it fitted with a fail closed valve?		
Are all storage tank(s) fitted with overfill fittings or high level alarms?		
Are tank(s) fitted with pressure/vacuum valves?		
Is an ammonia gas scrubber system used?		
Are piping and hose materials suitable for aqua ammonia service?		

Appendix F

Is piping free of strain and provision made for expansion, contraction, jarring, vibration and settling?	
Is all exposed piping protected from physical damage from moving vehicles and other undue strain?	
Are hoses securely clamped to hose barbs?	
Are hoses inspected and renewed periodically to avoid breakage?	
Are pump(s) designed for aqua ammonia service?	
Are pump(s) fitted with splash guard around seals?	
Are pump(s) fitted with coupling guard(s)?	
Do pump(s) have local start/stop stations?	
Are two (2) suitable full face masks with ammonia canisters as approved by the Bureau of Mines available? Is a self-contained breathing air apparatus required in concentrated atmospheres?	
Is an easily accessible quick acting shower with bubble fountain or 250-gallon drum of clean water available?	
Is an extra pair of chemical splash proof goggles and/or full face shields available?	
Is an extra set of ammonia resistant gloves, boots, coat and apron available?	
Are fire extinguishers and a first aid kit available?	
Are handlers/operators wearing their goggles and gloves when working with aqua ammonia?	
Are safety and first aid information posted?	
Are emergency phone numbers and individuals to contact posted?	

# Exhibit F-31 Sample What-If Analysis Procedure

Analysis Procedure. The steps in a What-If/Checklist analysis are as follows:

- 1. Select the team (personnel experienced in the process)
- 2. Assemble information (piping and instrumentation drawings (P&IDs), process flow diagrams (PFDs), operating procedures, equipment drawings, etc.)
- 3. Develop a list of What-If questions (use the ones in Exhibits F-32 through F-35 if you want)
- 4. Assemble your team in a room where each team member can view the information
- 5. Ask each What-If question in turn and determine:
  - **9** What can cause the deviation from design intent that is expressed by the question?
  - **g** What adverse consequences might follow ?
  - **g** What are the existing design and procedural safeguards?
  - **g** Are these safeguards adequate?
  - **g** If these safeguards are not adequate, what additional safeguards does the team recommend?
- 6. As the discussion proceeds, record the answers to these questions in tabular format. Exhibit F-36 provides an example.
- 7. Do not restrict yourself to the list of questions that you developed before the project started. The team is free to ask additional questions at any time.
- 8. When you have finished the What-If questions, proceed to examine the checklist. The purpose of this checklist is to ensure that the team has not forgotten anything. While you are reviewing the checklist, other What-If questions may occur to you.
- 9. Make sure that you follow up all recommendations and action items that arise from the hazards evaluation.

## MOVEMENT OF 1-TON CL2 (SO2) CYLINDERS

What if the cylinder is dropped from the lifting apparatus?

What if the truck rolls forward or backward?

What if a cylinder rolls and drops from the truck?

What if the cylinder swings while being lifted?

What if the Cl2 (SO2) container is not empty when removed from service?

What if the automatic container switchover system fails?

What if a Cl2 (SO2) cylinder is delivered instead of SO2 (Cl2)

What if the cylinder is not in good condition?

## TON CYLINDERS ON TRUNNION, INCL. PIGTAILS, (SUBHEADER LINES) TO MAIN HEADER LINES

What if pigtails rupture while connected on-line?

What if pigtail connections open or leak when pressure is applied?

What if something is dropped onto cylinder or connection?

What if cracks develop in the ton cylinder flexible connection?

What if liquid Cl2 (SO2) is withdrawn through the vapor lines from the ton cylinder?

What if the cylinder valve cannot be closed during an emergency?

What if there are pinholes or small leaks at the fusible plugs?

What if ton cylinder ends change shape from concave to convex?

What if liquid is trapped between two closed valves and the temperature rises?

What if there is a fire near the cylinders?

What if the operator leaves the valve open and disconnects the pigtail?

What if water enters the system?

#### CL2 (SO2) HEADERS IN THE CHLORINATION (SULFONATION) ROOM

What if the pressure relief valve sticks open?

What if a valve leaks?

What if there is inadequate flow in the gas line (e.g., filter clogged)?

## **EVAPORATORS**

What if there is overpressure in the evaporator?

What if there is high temperature in the evaporator?

What if there is low temperature in the evaporator?

What if rupture disks leak?

What if the vacuum regulator valve fails?

What if there is a gas pressure gauge leak?

What if the vacuum regulator check unit fails?

What if there is liquid Cl2 (SO2) carryover to the vacuum regulating valve downstream of the evaporator?

#### **CHLORINATION (SULFONATION) AND PIPES TO INJECTORS**

What if there are leaks in the chlorinator (sulfinator) unit?

What if there is rupture of the pipe from the chlorinator to the injector?

What if there is backflow of water into the Cl2 (SO2) line?

What if the water pump is not working?

#### GENERAL

What if there is a power failure?

What if Cl2 (SO2) is released during maintenance?

What if a Cl2 (SO2) leak is not detected?

What if there is moisture in the Cl2 (SO2) system?

#### **S**CRUBBERS

What if the system loses scrubber draft?

What if the system loses scrubber solution?

What if the manual vent to the scrubber is opened during operation?

What if the leak tightness of the building is compromised during emergency operation of the scrubbers?

## **TANK TRUCKS**

What if the liquid hose leaks or ruptures?

What if the vapor return hose leaks or ruptures?

What if the truck moves?

What if the mass of Cl2 (SO2) in the truck exceeds the capacity of the tank?

What if the Cl2 tank truck is connected to an SO2 vessel (or vice versa)?

What if there is something other than Cl2 (or SO2) in the truck?

What if there is a fire under or near the truck?

What if the truck collides with pipework or a building housing Cl2 (SO2) storage vessels?

### RAILCARS

What if the liquid hose leaks or ruptures?

What if the padding air is moist?

What if the padding air hose ruptures?

What if the railcar moves?

What if the relief valve lifts below the set pressure?

What if there is a fire under or near the truck?

What if there is a fire on or near the railcar?

# Exhibit F-33 What-If Questions for Ammonia Systems

## STORAGE VESSEL

What if the vessel is overfilled?

What if there is fire under or near the vessel?

What if the relief valve fails to lift on demand?

What if the relief valve opens below its set pressure?

What if the deluge system fails to work on demand?

## TANK TRUCK UNLOADING

What if the liquid unloading hose partially ruptures?

What if the liquid unloading hose completely ruptures?

What if the tank truck moves?

What if the tank truck drives away before the hose is disconnected?

What if the vapor return hose partially or completely ruptures?

What if valves are not completely closed before disconnecting the hoses?

What if the tank truck contains something other than ammonia?

What if the ammonia in the tank truck contains excess oxygen?

## Exhibit F-34 What-If Questions for Digester Systems

What if something falls onto a digester cover?

What if relief valves on a digester open?

What if an intermediate digester gas storage vessel fails?

What if air is introduced into the gas collection system?

What if the flare fails to operate?

What if the gas collection header leaks or ruptures or becomes blocked?

What if a digester gas compressor fails catastrophically?

What if there is a digester gas leak into a building (digester building, compressor room, boiler room)?

What if the digester gas pressure exceeds the cover pressure rating?

What if the floating digester gas cover jams or tilts?

# Exhibit F-35 General What-If Questions

What if the ambient temperature is abnormally high?
What if the ambient temperature is abnormally low?
What if there is a hurricane?
What if there is a tornado?
What if there is flooding?
What if there is a heavy snowfall?
What if there is an earthquake?
What if there is a tidal wave?
What if there is a failure of electric power?

# Exhibit F-36 Example What-If Checklist Log Sheet

Company / Facility: Process Unit: PHA Date: Leader / Secretary: Team Members: Description: Drawing Number:

Item	Equipment/Activity	Questions	Causes	Consequence/Hazards	Safeguards	Safeguards Adequate?	Recommendations
4.1	Generic Pressure Vessel	What if the set pressure of the equipment SRV is more than the design pressure of the equipment?	Incorrectly set valve purchased or returned after maintenance at contractor's shop	Potential for rupture and release of vessel contents	Manufacturer or repair shop's QA	Y	None
4.2	Generic Pressure Vessel	What is the SRV is incorrectly sized?	Design basis for SRV incorrectly chosen or SRV sized for vapor flow when two-phase or liquid flow is possible	SRV cannot relieve pressure, potential rupture	Valves purchased for specific service	Y	None
4.3	Generic Pressure Vessel	What if the SRV opens below its set pressure?	Vibration, incorrect design, weakened SRV spring, failure due to inadequate PM program	Release of vapor at relatively low pressure	PM program	Ν	Develop PM program for SRVs
4.4	Generic Pressure Vessel	What if there is a fire near or under the vessel?	Spillage of flammable liquid from nearby vessel	High pressure in vessel, potential rupture	SRVs Deluge system Separation Distances Keep flammables away from vessel	Y	None

# Exhibit F-37 HAZOP Analysis Guide Words, Meanings, and Process Parameters

In this approach, each guide word is combined with relevant process parameters and applied at each point (study node, process section, or operating step) in the process that is being examined.

Guide Words	Meaning
No	Negation of the Design Intent
Less	Quantitative Decrease
More	Quantitative Increase
Part Of	Other Material Present by Intent
As Well As	Other Materials Present Unintentionally
Reverse	Logical Opposite of the Intent
Other Than	Complete Substitution

#### **Common HAZOP Analysis Process Parameters**

Flow	Time	Frequency	Mixing
Pressure	Composition	Viscosity	Addition
Temperature	pН	Voltage	Separation
Level	Speed	Information	Reaction

The following is an example of creating deviations using guide words and process parameters:

Guide Words		Parameter		<b>Deviation</b>
NO	+	FLOW	=	NO FLOW
MORE	+	PRESSURE	=	HIGH PRESSURE
AS WELL AS	5 +	ONE PHASE	=	TWO PHASE
OTHER THA	N +	OPERATION	=	MAINTENANCE
MORE	+	LEVEL	=	HIGH LEVEL

Guide words are applied to both the more general parameters (e.g., react, mix) and the more specific parameters (e.g., pressure, temperature). With the general parameters, it is not unusual to have more than one deviation from the application of one guide word. For example, "more reaction" could mean either that a reaction takes place at a faster rate, or that a greater quantity of product results. On the other hand, some combinations of guide words and parameters will yield no sensible deviation (e.g., "as well as" with "pressure").

#### How to Perform a Hazard and Operability (HAZOP) Review

1. Select the team.

2. Assemble information (P&IDs, PFDs, operating procedures, equipment drawings, etc.).

3. Assemble your team in a room where each team member can view P&IDs.

4. Divide the system you are reviewing into nodes (you can preset the nodes, or the team can choose them as you go along).

5. Apply appropriate deviations to each node. For each deviation, address the following questions:

- What can cause the deviation from design intent?
- What adverse consequences might follow?
- What are the existing design and procedural safeguards?
- Are these safeguards adequate?
- If these safeguards are not adequate, what does the team recommend?

6. As the discussion proceeds, record the answers to these questions in tabular format as shown below.

Node No: From: To: Drawing No: Line ID: Date: Node Description:		1 Tanker Truck Ammonia Storage Vessel Liquid loading line from tanker truck to ammonia storage vessel					
Keyword	Deviation	Causes	Consequences	Safeguards	Adequate?	Recommendations	
Flow	High	None Identified	None	N/A		Ν	
Flow	Low	Malfunction of truck equipment, blockage in line, excess pressure in tank or check valve failure	Operational Problems	N/A		Ν	
Flow	No	Malfunction of truck equipment, or vapor line excess flow valve snaps shut	Operational Problems	N/A Emergency shutdown	N	N Y <sup>1</sup>	
		Hose Rupture	Ammonia Leak	features		_	
Flow	Reverse	Check valve and excess flow valve failure with hose rupture	Vapor release from vessel	Check valve, excess flow valve, and hose	Y	Ν	
		Block valves not closed when hose disconnected	Vapor release from vessel	Operator Training	Y	Ν	
Flow	Wrong Type	Delivery of wrong material	Unknown	Operational safeguards	Y	Ν	
Flow	In Addition	Water, oxygen, oil	Contamination, corrosion	Manufacturer's quality control	Y	Ν	
Pressure	High	Valve closed, blockage, overfill vessel	Ammonia overflow or rupture	Relief valves, level gauges	Y	Ν	

<sup>&</sup>lt;sup>1</sup>Arbitrary example of recommendation: Currently, the truck must park so far away from the tank that it is necessary to connect two lengths of hose. Investigate the ways in which truck unloading can be accomplished using only one length of hose.