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SUPPLEMENT D

TO

COMPILATION
OF
AIR POLLUTANT
EMISSION FACTORS

VOLUME I:
STATIONARY POINT
AND AREA SOURCES

AP-42
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Supplement D

INSTRUCTIONS FOR INSERTING VOLUME I SUPPLEMENT D INTO AP-42

Pp. iii and iv replace same. New Publications In Series.
Pp. v through viii replace same. New Contents.
Pp. ix through xvi (blank) replace same. New Key Word Index.
Pp. 1.4-1 and 2 replace same. Minor Revision.
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KEY WORD INDEX

1.4 NATURAL GAS COMBUSTION

1.4.1 General[1-2]

Natural gas is one of the major fuels used throughout the country. It is used mainly for power generation, for industrial process steam and heat production, and for domestic and commercial space heating. The primary component of natural gas is methane, although varying amounts of ethane and smaller amounts of nitrogen, helium and carbon dioxide are also present. Gas processing plants are required for recovery of liquefiable constitutents and removal of hydrogen sulfide (H_2S) before the gas is used (see Natural Gas Processing, Section 9.2). The average gross heating value of natural gas is approximately 9350 kilocalories per standard cubic meter (1050 British thermal units/standard cubic foot), usually varying from 8900 to 9800 kcal/scm (1000 to 1100 Btu/scf).

1.4.2 Emission And Controls[3-26]

Even though natural gas is considered to be a relatively clean fuel, some emissions can occur from the combustion reaction. For example, improper operating conditions, including poor mixing, insufficient air, etc., may cause large amounts of smoke, carbon monoxide and hydrocarbons. Moreover, because a sulfur containing mercaptan is added to natural gas to permit detection, small amounts of sulfur oxides will also be produced in the combustion process.

Nitrogen oxides are the major pollutants of concern when burning natural gas. Nitrogen oxide emissions are functions of combustion chamber temperature and combustion product cooling rate. Emission levels vary considerably with the type and size of unit and with operating conditions.

In some large boilers, several operating modifications may be used for NO_x control. Staged combustion, for example, including off-stoichiometric firing and/or two stage combustion, can reduce emissions by 5 to 50 percent.[26] In off-stoichiometric firing, also called "biased firing", some burners are operated fuel rich, some fuel lean, and others may supply air only. In two stage combustion, the burners are operated fuel rich (by introducing only 70 to 90 percent stoichiometric air), with combustion being completed by air injected above the flame zone through second stage "NO ports". In staged combustion, NO_x emissions are reduced because the bulk of combustion occurs under fuel rich conditions.

Other NO_x reducing modifications include low excess air firing and flue gas recirculation. In low excess air firing, excess air levels are kept as low as possible without producing unacceptable levels of unburned combustibles (carbon monoxide, volatile organic compounds and smoke) and/or other operating problems. This technique can reduce NO_x emissions 5 to 35 percent, primarily because of lack of oxygen during combustion. Flue gas recirculation into the primary combustion zone, because the flue gas is relatively cool and oxygen deficient, can also lower NO_x emissions 4 to 85 percent, depending on the amount of gas recirculated. Flue gas recirculation is best suited for new boilers. Retrofit application would require extensive burner modifications.

TABLE 1.4-1. UNCONTROLLED EMISSION FACTORS FOR NATURAL GAS COMBUSTION[a]

Furnace size & type (10^6 Btu/hr heat input)	Particulate[b]		Sulfur dioxide[c]		Nitrogen oxides[d,e]		Carbon monoxide[f,g]		Volatile organics			
									Nonmethane		Methane	
	$kg/10^6 m^3$	$lb/10^6 ft^3$	$kg/10^6 m^3$	$lb/10^6 ft^3$	$kg/10^6 m^3$	$lb/10^6 ft^3$	$kg/10^6 m^3$	$lb/10^6 ft^3$	$kg/10^6 m^3$	$lb/10^6 ft^3$	$kg/10^6 m^3$	$lb/10^6 ft^3$
Utility boilers (> 100)	16 - 80	1 - 5	9.6	0.6	8800[h]	550[h]	640	40	23	1.4	4.8	0.3
Industrial boilers (10 - 100)	16 - 80	1 - 5	9.6	0.6	2240	140	560	35	44	2.8	48	3
Domestic and commercial boilers (< 10)	16 - 80	1 - 5	9.6	0.6	1600	100	320	20	84	5.3	43	2.7

[a] Expressed as weight/volume fuel fired.

[b] References 15-18.

[c] Reference 4. Based on avg. sulfur content of natural gas, 4600 $g/10^6$ Nm^3 (2000 $gr/10^6$ scf).

[d] References 4-5, 7-8, 11, 14, 18-19, 21.

[e] Expressed as NO_2. Tests indicate about 95 weight % NO_x is NO_2.

[f] References 4, 7-8, 16, 18, 22-25.

[g] References 16, 18. May increase 10 - 100 times with improper operation or maintenance.

[h] For tangentially fired units, use 4400 $kg/10^6$ m^3 (275 $lb/10^6$ ft^3). At reduced loads, multiply factor by load reduction coefficient in Figure 1.4-1. For potential NO_x reductions by combustion modification, see text. Note that NO_x reduction from these modifications will also occur at reduced load conditions.

1.9 RESIDENTIAL FIREPLACES

1.9.1 General[1-2]

Fireplaces are used primarily for supplemental heating and for aesthetic effects in houses and other dwellings. Wood is the most common fuel for fireplaces, but coal, compacted wood waste "logs", paper and rubbish may also be burned. The user intermittently adds fuel to the fire by hand.

Fireplaces can be divided into two broad categories, 1) masonry (generally brick and/or stone, assembled on site, and integral to a structure) and 2) prefabricated (usually metal, installed on site as a package with appropriate duct work).

Masonry fireplaces typically have large fixed openings to the fire bed and have dampers above the combustion area in the chimney to limit room air and heat losses when the fireplace is not being used. Some masonry fireplaces are designed or retrofitted with doors and louvers to reduce the intake of combustion air during use.

Prefabricated fireplaces are commonly equipped with louvers and glass doors to reduce the intake of combustion air, and some are surrounded by ducts through which floor level air is drawn by natural convection, heated and returned to the room. Many varieties of prefabricated fireplaces are now available on the market. One general class is the freestanding fireplace, the most common of which consists of an inverted sheet metal funnel and stovepipe directly above the fire bed. Another class is the "zero clearance" fireplace, an iron or heavy gauge steel firebox lined inside with firebrick and surrounded by multiple steel walls with spaces for air circulation.

Some zero clearance fireplaces can be inserted into existing masonry fireplace openings, and thus are sometimes called "inserts". Some of these units are equipped with close fitting doors and have operating and combustion characteristics similar to wood stoves. (See Section 1.10, Residential Wood Stoves.)

Masonry fireplaces usually heat a room by radiation, with a significant fraction of the combustion heat lost in the exhaust gases or through the fireplace walls. Moreover, some of the radiant heat entering the room must go toward warming the air that is pulled into the residence to make up for that drawn up the chimney. The net effect is that masonry fireplaces are usually inefficient heating devices. Indeed, in cases where combustion is poor, where the outside air is cold, or where the fire is allowed to smolder (thus drawing air into a residence without producing appreciable radiant heat energy), a net heat loss may occur in a residence using a fireplace. Fireplace heating efficiency may be improved by a number of measures that either reduce the excess air rate or transfer back into the residence some of the heat that would normally be lost in the exhaust gases or through fireplace walls. As noted above, such measures are commonly incorporated into prefabricated units. As a result, the energy efficiencies of prefabricated fireplaces are slightly higher than those of masonry fireplaces.

1.9.2 Emissions[1-12]

The major pollutants of concern from fireplaces are unburnt combustibles, including carbon monoxide, gaseous organics and particulate matter (i. e., smoke). Significant quantities of unburnt combustibles are produced because fireplaces are inefficient combustion devices, with high uncontrolled excess air rates and without any sort of secondary combustion. The latter is especially important in wood burning because of its high volatile matter content, typically 80 percent by dry weight. In addition to unburnt combustibles, lesser amounts of nitrogen oxides and sulfur oxides are emitted.

Polycyclic organic material (POM), a minor but potentially important component of wood smoke, is a group of organic compounds which includes potential carcinogens such as benzo(a)pyrene (BaP). POM results from the combination of free radical species formed in the flame zone, primarily as a consequence of incomplete combustion. Under reducing conditions, radical chain propagation is enhanced, allowing the buildup of complex organic material such as POM. The POM is generally found in or on smoke particles, although some sublimation into the vapor phase is probable.

Another important constituent of wood smoke is creosote. This tar-like substance will burn if the fire is hot enough, but at insufficient temperatures, it may deposit on surfaces in the exhaust system. Creosote deposits are a fire hazard in the flue, but they can be reduced if the exhaust duct is insulated to prevent creosote condensation or if the exhaust system is cleaned regularly to remove any buildup.

Fireplace emissions are highly variable and are a function of many wood characteristics and operating practices. In general, conditions which promote a fast burn rate and a higher flame intensity will enhance secondary combustion and thereby lower emissions. Conversely, higher emissions will result from a slow burn rate and a lower flame intensity. Such generalizations apply particularly to the earlier stages of the burning cycle, when significant quantities of combustible volatile matter are being driven out of the wood. Later in the burning cycle, when all volatile matter has been driven out of the wood, the charcoal that remains burns with relatively few emissions.

Emission factors and their ratings for wood combustion in residential fireplaces are given in Table 1.9-1.

Table 1.9-1. EMISSION FACTORS FOR RESIDENTIAL FIREPLACES

Pollutant	Wood Fuel		Emission Factor Ratings
	g/kg	lb/ton	
Particulate[a]	10.8	21.6	C
Sulfur oxides[b]	0.2	0.4	A
Nitrogen oxides[c]	0.9	1.8	C
Carbon monoxide[d]	61.1	122.2	C
VOC[e]			
Methane	ND	ND	
Nonmethane	13.0	26.0	D
POM[f]	0.8×10^{-3}	1.6×10^{-3}	F
PAH[f]	0.5	1.0	D
Aldehydes[f]	1.2×10^{-3}	2.4×10^{-3}	D
Total Hydrocarbons[f]	95.1	191.2	D

[a] References 2-8. Includes condensible organics. POM is carried by suspended particulate matter and has been found to range from 0.017 - 0.044 g/kg (References 2,8) which may include BaP of up to 1.7 mg/kg (Reference 2).

[b] References 1,8.

[c] References 2-11. Expressed as NO_2.

[d] References 2-12.

[e] References 2-12.

[f] References 2-7. ND = no data.

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1. D. G. DeAngelis, et al., Source Assessment: Residential Combustion Of Wood, EPA-600/2-80-042b, U. S. Environmental Protection Agency, Cincinnati, OH, March 1980.

2. W. D. Snowden, et al., Source Sampling of Residential Fireplaces For Emission Factor Development, EPA-450/3-76-010, U. S. Environmental Protection Agency, Research Triangle Park, NC, November 1975.

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1.10 RESIDENTIAL WOOD STOVES

1.10.1 General[1-3]

Wood stoves are used commonly in residences as space heaters to supplement conventional heating systems. They are increasingly found as the primary source of residential heat.

Because of differences in both the magnitude and the composition of wood stove emissions, four different categories of stove should be considered when estimating emissions:

- the conventional wood stove,
- the noncatalytic wood stove,
- the pellet stove, and
- the catalytic wood stove.

Among these categories, there are many variations in wood stove design and operation characteristics.

The conventional stove category comprises all stoves without catalytic combustors not included in the other noncatalytic categories (i. e., noncatalytic and pellet). Conventional stoves do not have any emission reduction technology or design features and, in most cases, were manufactured before July 1, 1986. Stoves of many different airflow designs may be in this category, such as updraft, downdraft, crossdraft and S-flow.

Noncatalytic wood stoves are those units that do not employ catalysts but that do have emission reducing technology or features, such as baffles and secondary combustion chambers.

Pellet stoves are those fueled with pellets of sawdust, wood products, and other biomass materials pressed into manageable shapes and sizes. These stoves have a specially designed or modified grate to accommodate this type of fuel.

Catalytic stoves are equipped with a ceramic or metal honeycomb device, called a combustor or converter, that is coated with a noble metal such as platinum or palladium. The catalyst material reduces the ignition temperature of the unburned volatile organic compounds (VOC) and carbon monoxide in the exhaust gases, thus augmenting their ignition and combustion at normal stove operating temperatures. As these components of the gases burn, the temperature inside the catalyst increases to a point at which the ignition of the gases is essentially self sustaining.

1.10.2 Emissions

The combustion and pyrolysis of wood in wood stoves produce atmospheric emissions of particulate matter, carbon monoxide, nitrogen oxides, organic compounds, mineral residues, and to a lesser extent, sulfur oxides. The quantities and types of emissions are highly variable, depending on a number of factors, including the stages of the combustion cycle. During initial burning stages, after a new wood charge is introduced, emissions increase dramatically and are primarily VOCs. After the initial period of high burn rate, there is a charcoal stage of the burn cycle, characterized by a slower burn rate and decreased emissions. Emission rates during this stage are cyclical, characterized by relatively long periods of low emissions and shorter episodes of emission spikes.

Particulate emissions are defined in this discussion as the total catch measured by the EPA Method 5H (Oregon Method 7) sampling train.[1] A small portion of wood stove particulate emissions includes "solid" particles of elemental carbon and wood. The vast majority of particulate emissions is condensed organic products of incomplete combustion equal to or less than 10 micrometers in aerodynamic diameter (PM-10). The particulate emission values shown in Table 1.10-1 for the Phase II stoves are estimates of emissions produced by wood heaters expected to be available over the next few years as cleaner, more reliable wood stoves are manufactured to meet the New Source Performance Standards.[1] The emission values in Table 1.10-1 are derived entirely from field test data on the best available wood stoves in actual operating conditions. Still, there is a potential for higher emissions from some wood stove models.

The emission factors in Table 1.10-1 are presented by stove type. Particulate and carbon monoxide emission factors are further classified by stove certification category. Phase II stoves are those certified to meet the July 1, 1990 EPA standards; Phase I stoves meet the July 1, 1988 EPA standards; and Pre-Phase I stoves do not meet any of the EPA standards but in most cases do meet the Oregon 1986 certification standards.[1]

Wood stove control devices may lose efficiency over a period of operation. Control degradation for any stoves, including noncatalytic wood stoves, may also occur as a result of deteriorated seals and gaskets, misaligned baffles and bypass mechanisms, broken refractories, or other damaged functional components. The increase in emissions from such control degradation has not been quantified.

Although reported particle size data are scarce, one reference states that 95 percent of the particles emitted from a wood stove were less than 0.4 micrometers in size.[4]

Sulfur oxides are formed by oxidation of sulfur in the wood. Nitrogen oxides are formed by oxidation of fuel and atmospheric nitrogen. Mineral constituents, such as potassium and sodium compounds, are released from the wood matrix during combustion. The high levels of organic compound and carbon monoxide emissions are results of incomplete combustion of the wood.

Organic constituents of wood smoke vary considerably in both type and volatility. These constituents include simple hydrocarbons of carbon numbers 1 through 7 (C1 - C7) (which exist as gases or which volatilize at ambient conditions) and complex low volatility substances that condense at ambient conditions. These low volatility condensible materials generally are considered to have boiling points below 300°C (572°F).

Polycyclic organic matter (POM) is an important component of the condensible fraction of wood smoke. POM contains a wide range of compounds, including organic compounds formed through incomplete combustion by the combination of free radical species in the flame zone. This group contains some potentially carcinogenic compounds, such as benzo(a)pyrene.

Table 1.10-1 EMISSION FACTORS FOR COMBUSTION IN RESIDENTIAL WOOD STOVES

Stove Type	Particulate ≤10µm[a,b,c]				Carbon Monoxide[a,b]						Volatile Organics[d]		
	All Stoves	Pre-Phase I	Phase I	Phase II	All Stoves	Pre-Phase I	Phase I	Phase II	Nitrogen oxides[b]	Sulfur oxides[b]	Nonmethane	Methane	Efficiency[e] %
Conventional	14.9 (29.8)	14.9 (29.8)	-	-	115.4 (230.8)	115.4 230.8	-	-	1.4 (2.8)[f]	0.2 (0.4)	14.0 (28.0)	32.0 (64.0)	52
Noncatalytic	9.3 (18.6)	12.3 (24.6)	9.5 (19.0)	7.0 (14.0)	70.4 (140.8)	-	-	70.4 (140.8)	-	0.2 (0.4)	-	-	63
Pellet	1.9 (3.8)	-	-	1.9 (3.8)	19.7 (39.4)	-	-	19.7 (39.4)	6.9 (13.8)[g]	0.2 (0.4)	-	-	78
Catalytic	9.7 (19.4)	11.6 (23.2)	9.4 (18.8)	7.7 (15.4)	52.4 (104.8)	-	52.2 (104.4)	53.5 (107.0)	1.0 (2.0)	0.2 (0.4)	8.6 (17.2)	13.0 (26.0)	72

[a] Units are g/kg (lb/ton) of dry wood burned. Pre-phase I stoves are those not certified to 1990 EPA emission standards. Phase I stoves are those certified to 1988 EPA standards, Phase II stoves certified to 1990 EPA emission standards. Dash = no data.

[b] References 5 - 12. Emission Factor Rating for particulate, CO, and SO_x: B; for NO_x: E.

[c] Reference 1. Defined as equivalent to total catch by EPA Method 5H train.

[d] References 13 - 14. Emission Factor Rating: E. Calculated by adding the estimated mass of simple hydrocarbon material C1-C7 data to total chromatographic organics.

[e] Reference 1. The product of combustion and heat transfer efficiencies. Values are averages of laboratory test results.

[f] References 15 - 16. Emission Factor Rating: C.

[g] Reference 13. Based on a single data point.

Emission factors and their ratings for wood combustion in residential wood stoves are presented in Table 1.10-1.

As mentioned, particulate emissions are defined as the total emissions equivalent to that collected by EPA Method 5H. This method employs a heated filter followed by three impingers, an unheated filter, and a final impinger. Particulate and carbon monoxide emissions data used to develop the factors in Table 1.10-1 are all from data collected during field testing programs, and they are presented as values equivalent to that collected with Method 5H.[8] Conversions are employed, as appropriate, for data collected with other methods. See Reference 2 for detailed discussions of EPA Methods 5H and 28. Emission factors in Table 1.10-1 for other pollutants have been developed from data collected during laboratory testing programs.

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TABLE 2.1-2. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR MUNICIPAL WASTE COMBUSTORS[a]

Particle Size (ug)	Cumulative mass % < stated size						Cumulative emission factor, kg/Mg (lb/ton)					
	Uncontrolled			Controlled			Uncontrolled			Controlled		
	MB	SA	RDF	MB	SA	RDF	MB	SA	RDF	MB	SA	RDF
15.0	47	79	60	53	87	71	9.0 (18)	0.75 (1.5)	24 (48)	0.10 (0.20)	0.013 (0.026)	0.39 (0.7)
10.0	37	74	55	47	80	67	7.0 (14)	0.70 (1.4)	22 (44)	0.090 (0.18)	0.012 (0.024)	0.37 (0.7)
5.0	32	68	53	42	73	65	6.0 (12)	0.65 (1.3)	21 (42)	0.080 (0.16)	0.011 (0.022)	0.36 (0.7)
2.5	24	63	40	39	67	53	4.6 (9.2)	0.60 (1.2)	16 (32)	0.075 (0.15)	0.010 (0.020)	0.29 (0.5)
1.0	18	53	25	34	63	35	3.5 (7.0)	0.50 (1.0)	10 (20)	0.065 (0.13)	0.0095 (0.019)	0.19 (0.3)
0.625	14	42	11	29	53	16	2.7 (5.4)	0.40 (0.80)	4.4 (8.8)	0.055 (0.11)	0.0080 (0.016)	0.09 (0.1)
Total	100	100	100	100	100	100	19 (38)	0.95 (1.9)	40 (80)	0.19 (0.38)	0.015 (0.030)	0.55 (1.1)

[a] Reference 3. MB = mass burn. SA = starved air. RDF = refuse-derived fuel.

TABLE 2.1-3. UNCONTROLLED EMISSION FACTORS FOR INDUSTRIAL/COMMERCIAL REFUSE COMBUSTORS[a]

EMISSION FACTOR RATING: A

Incinerator type	Particulate		Sulfur oxides[b]		Carbon monoxide		Volatile organics[c]		Nitrogen oxides[d]	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Multiple chambers[e]	3.5	7	1.25	2.5[f]	5	10	1.5	3	1.5	3
Single chamber[g]	7.5	15	1.25	2.5[f]	10	20	7.5	15	1	2
Trench[h]										
Wood	6.5	13	0.05	0.1[j]	NA	NA	NA	NA	2	4
Rubber tires	69	138	NA	NA	NA	NA	NA	NA	NA	NA
Municipal refuse	18.5	37	1.25	2.5[f]	NA	NA	NA	NA	NA	NA
Flue fed										
Single chamber[k]	15	30	0.25	0.5	10	20	7.5	15	1.5	3
Modified[m]	3	6	0.25	0.5	5	10	1.5	3	5	10
Domestic single chamber										
Without primary burner[n]	17.5	35	0.25	0.5	150	300	50	100	0.5	1
With primary burner[p]	3.5	7	0.25	0.5	Neg	Neg	1	2	1	2
Pathological[q]	4	8	Neg	Neg	Neg	Neg	Neg	Neg	1.5	3

[a] Factors are averages based on EPA procedures for incinerator stack testing. NA = not available. Neg = negligible.

[b] Expressed as SO_2.

[c] Expressed as methane.

[d] Expressed as NO_2.

[e] References 6,10-13.

[f] Based on municipal incinerator data.

[g] References 6,10-11,13.

[h] Reference 8.

[j] Based on data for wood combustion in conical burners.

[k] References 6,11-15.

[m] With afterburners and draft controls. References 6,13-14.

[n] References 10-11.

[p] Reference 10.

[q] Reference 6,16.

4.2.1 NONINDUSTRIAL SURFACE COATING[1,3,5]

Nonindustrial surface coating operations are nonmanufacturing applications of surface coating. Two major categories are architectural surface coating and automobile refinishing. Architectural surface coating is considered to involve both industrial and nonindustrial structures. Automobile refinishing pertains to the painting of damaged or worn highway vehicle finishes and not to the painting of vehicles during manufacture.

Emissions from coating a single architectural structure or an automobile are calculated by using total volume and content and specific application. To estimate emissions for a large geographical area which includes many major and minor applications of nonindustrial surface coatings requires that area source estimates be developed. Architectural surface coating and auto refinishing emissions data are often difficult to compile for a large geographical area. In cases where a large emissions inventory is being developed and/or where resources are unavailable for detailed accounting of actual coatings volume for these applications, emissions may be assumed proportional to population or to number of employees in the activity. Table 4.2.1-1 presents factors from national emission data and gives emissions per population or employee for architectural surface coating and automobile refinishing.

Table 4.2.1-1. NATIONAL EMISSIONS AND EMISSION FACTORS FOR VOC FROM ARCHITECTURAL SURFACE COATING AND AUTOMOBILE REFINISHING[a]

EMISSION FACTOR RATING: C

Emissions	Architectural Surface Coating	Automobile Refinishing
National		
Mg/yr	446,000	181,000
ton/yr	491,000	199,000
Per capita		
kg/yr (lb/yr)	2.09 (4.6)	0.84 (1.9)
g/day (lb/day)	5.8 (0.013)[b]	2.7 (0.006)[c]
Per employee		
Mg/yr (ton/yr)	-	2.3 (2.6)
kg/day (lb/day)	-	7.4 (16.3)[c]

[a] References 3, 5-8. All nonmethane organics. Dash = no data.
[b] Reference 8. Calculated by dividing kg/yr (lb/yr) by 365 days and converting to appropriate units.
[c] Assumes a 6 day operating week (312 days/yr).

Using waterborne architectural coatings reduces volatile organic compound emissions. Current consumption trends indicate increasing substitution of waterborne architectural coatings for those using solvent. Automobile refinishing often is done in areas only slightly enclosed, which makes emissions control difficult. Where automobile refinishing takes place in an enclosed area, control of the gaseous emissions can be accomplished by the use of adsorbers (activated carbon) or afterburners. The collection efficiency of activated carbon has been reported at 90 percent or greater. Water curtains or filler pads have little or no effect on escaping solvent vapors, but they are widely used to stop paint particulate emissions.

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4.13 WASTE WATER COLLECTION, TREATMENT AND STORAGE

4.13.1 General

Many different industries generate waste water streams that contain organic compounds. Nearly all of these streams undergo collection, contaminant treatment, and/or storage operations before they are finally discharged into either a receiving body of water or a municipal treatment plant for further treatment. During some of these operations, the waste water is open to the atmosphere, and volatile organic compounds (VOC) may be emitted from the waste water into the air.

Industrial waste water operations can range from pretreatment to full-scale treatment processes. In a typical pretreatment facility, process and/or sanitary waste water and/or storm water runoff is collected, equalized, and/or neutralized and then discharged to a municipal waste water plant, also known as a publicly owned treatment works (POTWs), where it is then typically treated further by biodegradation.

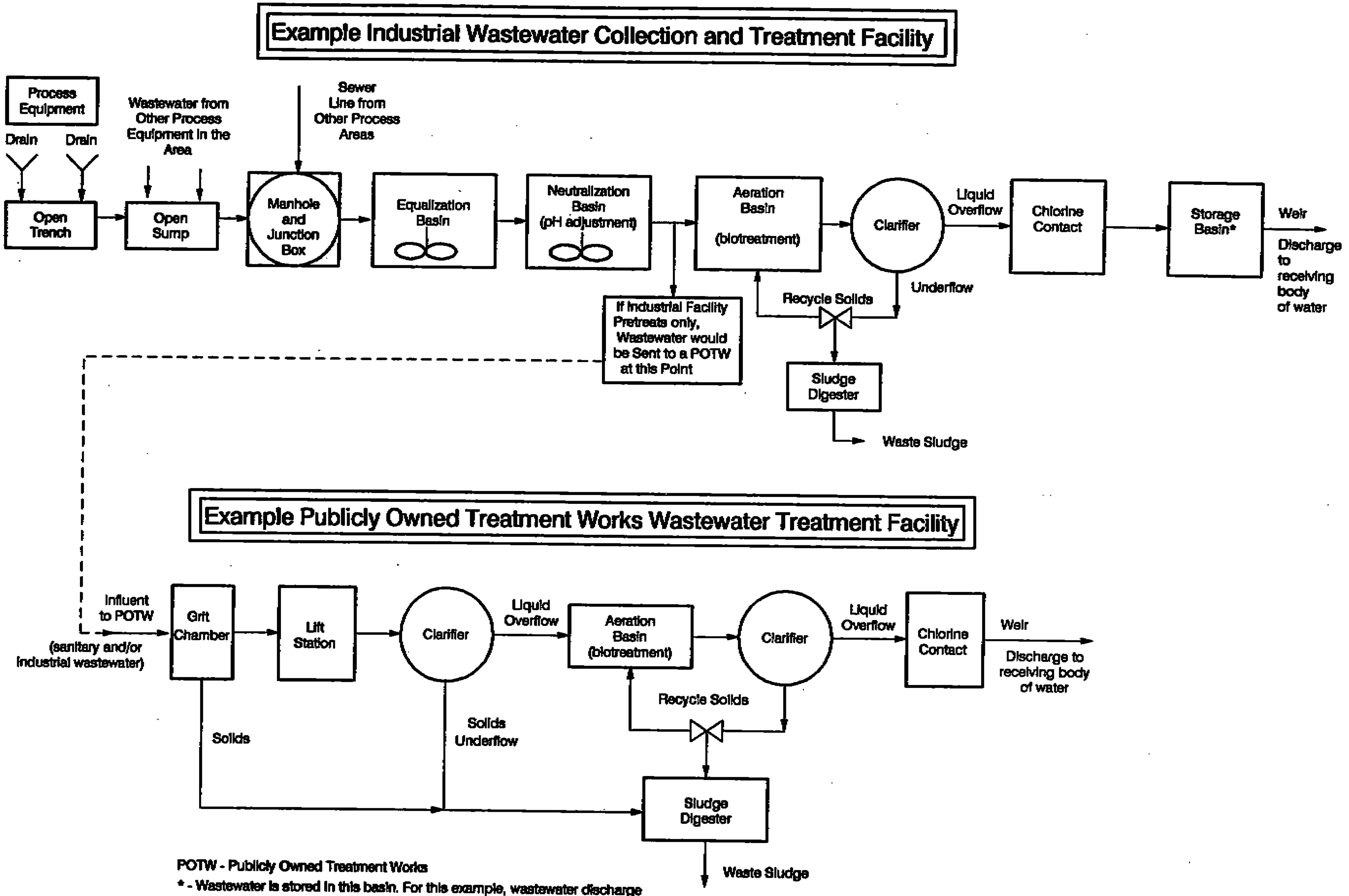
In a full-scale treatment operation, the waste water must meet Federal and/or state quality standards before it is finally discharged into a receiving body of water. Figure 4.13-1 shows a generic example of collection, equalization, neutralization and biotreatment of process waste water in a full-scale industrial treatment facility. If required, chlorine is added as a disinfectant. A storage basin contains the treated water until the winter months (usually January to May), when the facility is allowed to discharge to the receiving body of water. In the illustration, the receiving body of water is a slow-flowing stream. The facility is allowed to discharge in the rainy season when the facility waste water is diluted.

Figure 4.13-1 also presents a typical treatment system at a POTW waste water facility. Industrial waste water sent to POTWs may be treated or untreated. POTWs may also treat waste water from residential, institutional, and commercial facilities; from infiltration (water that enters the sewer system from the ground); and/or storm water runoff. These types of waste water generally do not contain VOCs. A POTW usually consists of a collection system, primary settling, biotreatment, secondary settling, and disinfection.

Collection, treatment and storage systems are facility-specific. All facilities have some type of collection system, but the complexity will depend on the number and volume of waste water streams generated. As mentioned above, treatment and/or storage operations also vary in size and degree of treatment. The size and degree of treatment of waste water streams will depend on the volume and degree of contamination of the waste water and on the extent of contaminant removal desired.

Collection Systems - There are many types of waste water collection systems. In general, a collection system is located at or near the point of waste water generation and is designed to receive one or more waste water streams and then to direct these streams to treatment and/or storage systems.

A typical industrial collection system may include drains, manholes, trenches, junction boxes, sumps, lift stations, and/or weirs. Waste water streams from different points throughout the industrial facility normally enter the collection system through individual drains or



POTW - Publicly Owned Treatment Works

* - Wastewater is stored in this basin. For this example, wastewater discharge is allowed January through May only.

Figure 4.13-1. Typical industrial and municipal waste water collection and treatment systems.

trenches connected to a main sewer line. The drains and trenches are usually open to the atmosphere. Junction boxes, sumps, trenches, lift stations, and weirs will be located at points requiring waste water transport from one area or treatment process to another.

A typical POTW facility collection system will contain a lift station, trenches, junction boxes and manholes. Waste water is received into the POTW collection system through open sewer lines from all sources of influent waste water. As mentioned previously, these sources may convey sanitary, pretreated or untreated industrial, and/or storm water runoff waste water.

The following paragraphs briefly describe some of the most common types of waste water collection system components found in industrial and POTW facilities. Because the arrangement of collection system components is facility-specific, the order in which the collection system descriptions are presented is somewhat arbitrary.

Waste water streams normally are introduced into the collection system through individual or area drains, which can be open to the atmosphere or sealed to prevent waste water contact with the atmosphere. In industry, individual drains may be dedicated to a single source or piece of equipment. Area drains will serve several sources and are located centrally among the sources or pieces of equipment that they serve.

Manholes into sewer lines permit service, inspection and cleaning of a line. They may be located where sewer lines intersect or where there is a significant change in direction, grade or sewer line diameter.

Trenches can be used to transport industrial waste water from point of generation to collection units such as junction boxes and lift stations; from one process area of an industrial facility to another, or from one treatment unit to another. POTWs also use trenches, to transport waste water from one treatment unit to another. Trenches are likely to be either open or covered with a safety grating.

Junction boxes typically serve several process sewer lines, which meet at the junction box to combine multiple waste water streams into one. Junction boxes normally are sized to suit the total flow rate of the entering streams.

Sumps are used typically for collection and equalization of waste water flow from trenches or sewer lines before treatment or storage. They are usually quiescent and open to the atmosphere.

Lift stations are usually the last collection unit before the treatment system, accepting waste water from one or several sewer lines. Their main function is to lift the collectedwaste water to a treatment and/or storage system, usually by pumping or by use of a hydraulic lift, such as a screw.

Weirs can act as open channel dams, or they can be used to discharge cleaner effluent from a settling basin, such as a clarifier. When used as a dam, the weir's face is normally aligned perpendicular to the bed and walls of the channel. Water from the channel usually flows over the weir and falls to the receiving body of water. In some cases, the water may pass through a notch or opening in the weir face. With this type of weir, flow rate through the channel can be measured. Weir height, generally the distance the water falls, is usually no more than 2 meters. A typical clarifier weir is designed to allow settled waste water to overflow to the next treatment process. The weir is generally placed around the perimeter of the settling basin, but it can also be towards the middle. Clarifier weir height is usually only about 0.1 meters.

Treatment And/or Storage Systems - These systems are designed to hold liquid wastes or waste water for treatment, storage or disposal. They are usually composed of various types of earthen and/or concrete-lined basins, known as surface impoundments. Storage systems are used typically for accumulating waste water before its ultimate disposal or for temporarily holding batch (intermittent) streams before treatment.

Treatment systems are divided into three categories, primary, secondary or tertiary, depending on their design, operation and application. In primary treatment systems, physical operations remove floatable and settleable solids. In secondary treatment systems, biological and chemical processes remove most of the organic matter in the waste water. In tertiary treatment systems, additional processes remove constituents not taken out by secondary treatment.

Examples of primary treatment include oil/water separators, primary clarification, equalization basins, and primary treatment tanks. The first process in an industrial waste water treatment plant is often the removal of heavier solids and lighter oils by means of oil/water separators. Oils are usually removed continuously with a skimming device, while solids can be removed with a sludge removal system.

In primary treatment, clarifiers are located usually near the beginning of the treatment process and are used to settle and remove settleable or suspended solids contained in the influent waste water. Figure 4.13-2 presents an example design of a clarifier. Clarifiers are generally cylindrical and are sized according to both the settling rate of the suspended solids and the thickening characteristics of the sludge. Floating scum is generally skimmed continuously from the top of the clarifier, while sludge is typically removed continuously from the bottom of the clarifier.

Equalization basins are used to reduce fluctuations in the waste water flow rate and organic content before the waste is sent to downstream treatment processes. Flow rate equalization results in a more uniform effluent quality in downstream settling units such as clarifiers. Biological treatment performance can also benefit from the damping of concentration and flow fluctuations, protecting biological processes from upset or failure from shock loadings of toxic or treatment-inhibiting compounds.

In primary treatment, tanks are generally used to alter the chemical or physical properties of the waste water by, for example, neutralization and the addition and dispersion of chemical nutrients. Neutralization can control the pH of the waste water by adding an acid or a base. It usually precedes biotreatment, so that the system is not upset by high or low pH values. Similarly, chemical nutrient addition/dispersion precedes biotreatment, to assure that the biological organisms have sufficient nutrients.

An example of a secondary treatment process is biodegradation. Biological waste treatment usually is accomplished by aeration in basins with mechanical surface aerators or with a diffused air system. Mechanical surface aerators float on the water surface and rapidly mix the water. Aeration of the water is accomplished through splashing. Diffused air systems, on the other hand, aerate the water by bubbling oxygen through the water from the bottom of the tank or device. Figure 4.13-3 presents an example design of a mechanically aerated biological treatment basin. This type of basin is usually an earthen or concrete-lined pond and is used to treat large flow rates of waste water. Waste waters with high pollutant concentrations, and in

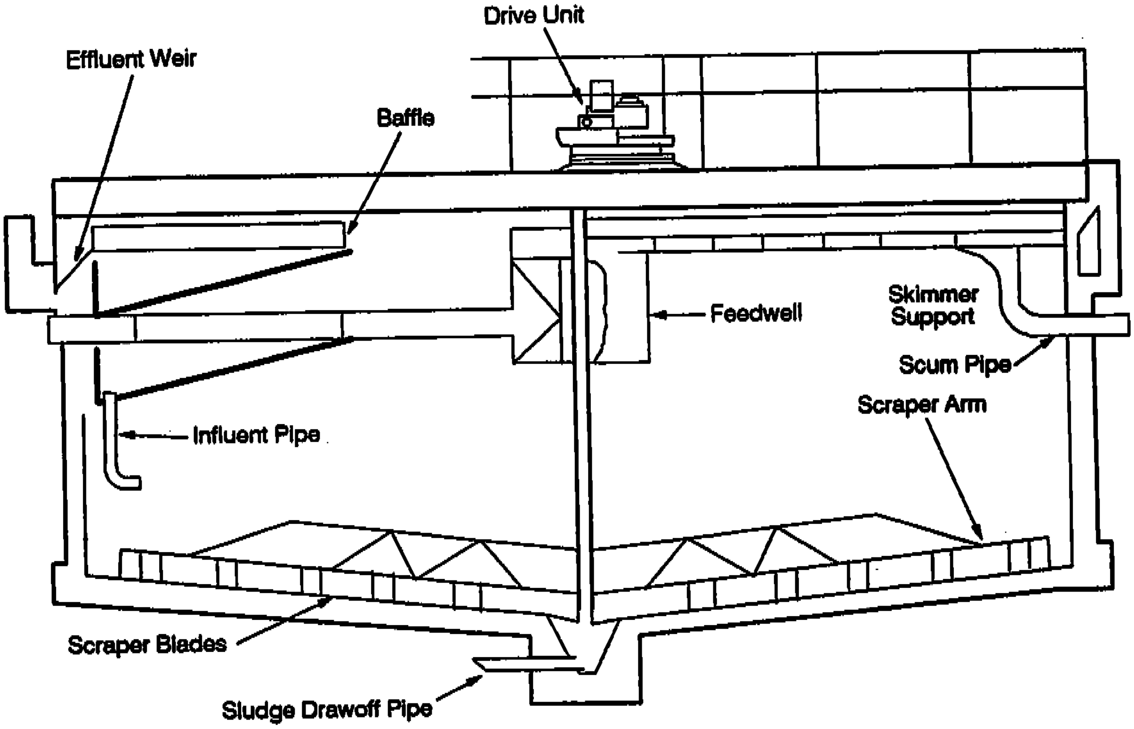


Figure 4.13-2. Example clarifier configuration.

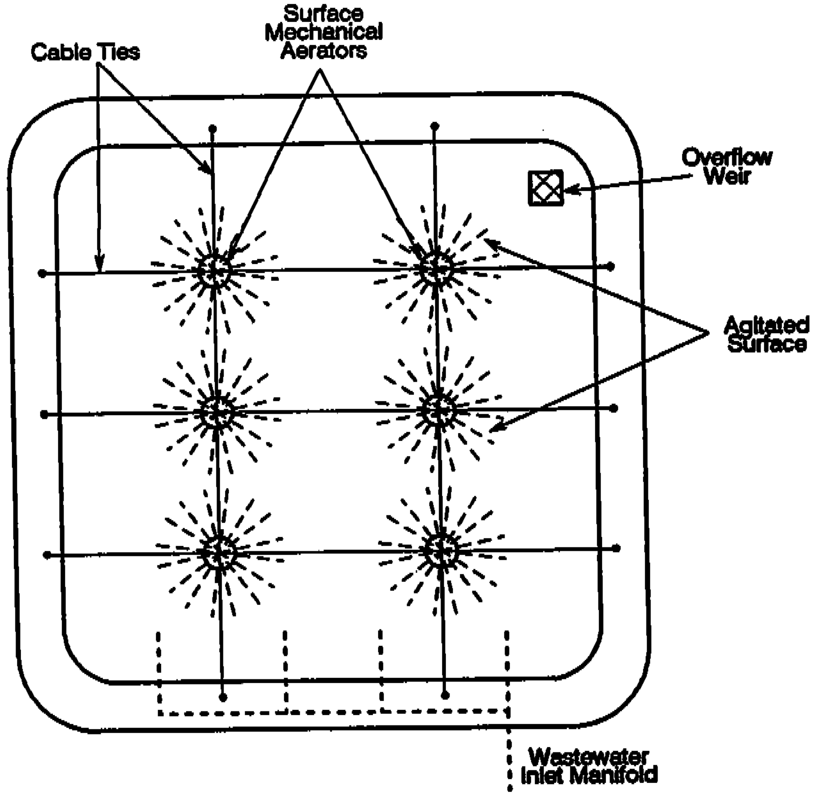


Figure 4.13-3. Example aerated biological treatment basin.

particular high flow sanitary waste waters, are typically treated using an activated sludge system where biotreatment is followed by secondary clarification. In this system, settled solids containing biomass are recycled from clarifier sludge to the biotreatment system. This creates a high biomass concentration and therefore allows biodegradation to occur over a shorter residence time. An example of a tertiary treatment process is nutrient removal. Nitrogen and phosphorus are removed after biodegradation as a final treatment step before waste water is discharged to a receiving body of water.

Applications - As previously mentioned, waste water collection, treatment, and storage are common in many industrial categories and in POTW. Most industrial facilities and POTW collect, contain, and treat waste water. However, some industries do not treat their waste water, but use storage systems for temporary waste water storage or for accumulation of waste water for ultimate disposal. For example, the Agricultural Industry does little waste water treatment but needs waste water storage systems, while the Oil and Gas Industry also has a need for waste water disposal systems.

The following are waste water treatment and storage applications identified by type of industry:

1. Mining And Milling Operations - Storage of various waste waters such as acid mine water, solvent wastes from solution mining, and leachate from disposed mining wastes. Treatment operations include settling, separation, washing, sorting of mineral products from tailings, and recovery of valuable minerals by precipitation.

2. Oil And Gas Industry - One of the largest sources of waste water. Operations treat brine produced during oil extraction and deep-well pressurizing operations, oil-water mixtures, gaseous fluids to be separated or stored during emergency conditions, and drill cuttings and drilling muds.

3. Textile And Leather Industry - Treatment and sludge disposal. Organic species treated or disposed of include dye carriers such as halogenated hydrocarbons and phenols. Heavy metals treated or disposed of include chromium, zinc and copper. Tanning and finishing wastes may contain sulfides and nitrogenous compounds.

4. Chemical And Allied Products Industry - Process waste water treatment and storage, and sludge disposal. Waste constituents are process-specific and include organics and organic phosphates, fluoride, nitrogen compounds, and assorted trace metals.

5. Other Industries - Treatment and storage operations are found at petroleum refining, primary metals production, wood treating, and metal finishing facilities. Various industries store and/or treat air pollution scrubber sludge and dredging spoils sludge (i. e., settled solids removed from the floor of a surface impoundment).

4.13.2 Emissions

VOCs are emitted from waste water collection, treatment, and storage systems through volatilization of organic compounds at the liquid surface. Emissions can occur by diffusive or convective mechanisms, or both. Diffusion occurs when organic concentrations at the water surface are much higher than ambient concentrations. The organics volatilize, or diffuse into the air, in an attempt to reach equilibrium between aqueous and vapor phases. Convection occurs when air flows over the water surface, sweeping organic vapors from the water surface into the air. The rate of volatilization relates directly to the speed of the air flow over the water surface.

Other factors that can affect the rate of volatilization include waste water surface area, temperature, and turbulence; waste water retention time in the system(s); the depth of the waste water in the system(s); the concentration of organic compounds in the waste water and their physical properties, such as volatility and diffusivity in water; the presence of a mechanism that inhibits volatilization, such as an oil film; or a competing mechanism, such as biodegradation.

The rate of volatilization can be determined by using mass transfer theory. Individual gas phase and liquid phase mass transfer coefficients (k_g and k_ℓ, respectively) are used to estimate overall mass transfer coefficients (K, K_{oil}, and K_D) for each VOC.[1-2] Figure 4.13-4 presents a flow diagram to assist in determining the appropriate emissions model for estimating VOC emissions from various types of waste water treatment, storage and collection systems. Tables 4.13-1 and 4.13-2, respectively present the emission model equations and definitions.

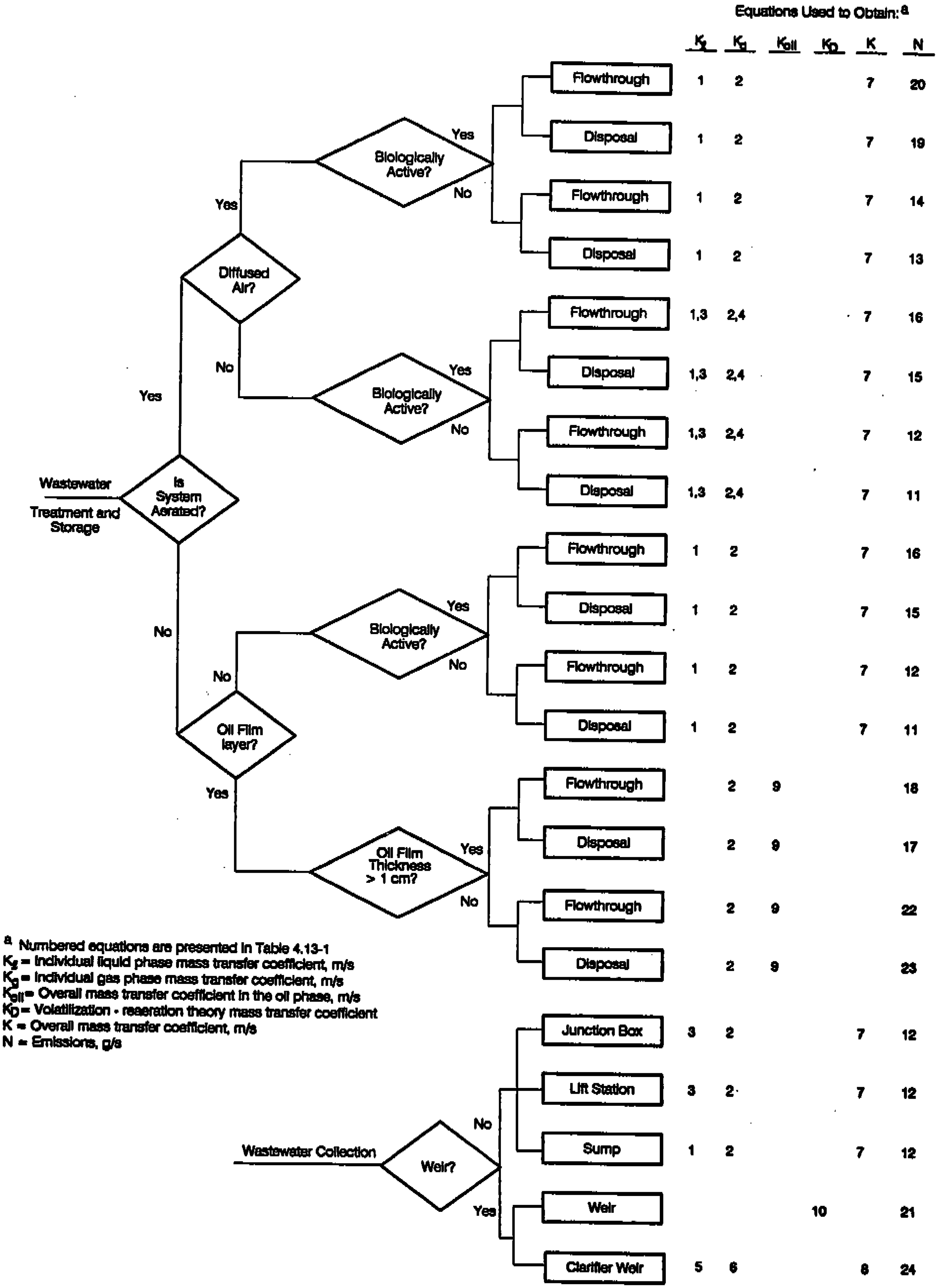
VOCs vary in their degree of volatility. The emission models presented in this section can be used for high, medium and low volatility organic compounds. The Henry's Law Constant (HLC) is often used as a measure of a compound's volatility, or the diffusion of organics into the air relative to diffusion through liquids. High volatility VOCs are HLC > 10^{-3} atm-m^3/gmol; medium volatility VOCs are 10^{-3} < HLC < 10^{-5} atm m^3/gmol; and low volatility VOCs are HLC < 10^{-5} atm-m^3/gmol.[1]

The design and arrangement of collection, treatment and storage systems are facility - specific, therefore the most accurate waste water emissions estimate will come from actual tests of a facility (i. e., tracer studies or direct measurement of emissions from openings). If actual data are unavailable, the emission models provided in this section can be used.

Emission models should be given site-specific information whenever it is available. The most extensive characterization of an actual system will produce the most accurate estimates from an emissions model. In addition, when addressing systems involving biodegradation, the accuracy of the predicted rate of biodegradation is improved when site-specific compound biorates are input. Reference 3 contains information on a test method for measuring site-specific biorates, and Table 4.13-4 presents estimated biorates for approximately 150 compounds.

To estimate an emissions rate (N), the first step is to calculate individual gas phase and liquid phase mass transfer coefficients k_g and k_ℓ. These individual coefficients are then used to calculate the overall mass transfer coefficient, K. Exceptions to this procedure are the calculation of overall mass transfer coefficients in the oil phase, K_{oil}, and the overall mass transfer coefficient for a weir, K_D. K_{oil} requires only k_g, and K_D does not require any individual mass transfer coefficients. The overall mass transfer coefficient is then used to calculate the emissions rates. The following discussion describes how to use Figure 4.13-4 to determine an emission rate. An example calculation is presented in 4.13.2.1 below.

Figure 4.13-4 is divided into two sections: Waste water treatment and storage systems, and 2) waste water collection systems. Waste water treatment and storage systems are further segmented into aerated/nonaerated systems, biologically active systems, oil film layer systems, and surface impoundment flowthrough or disposal. In flowthrough systems, waste water is treated and discharged to a POTW or a receiving body of water, such as a river or stream. All waste water collection systems are by definition flowthrough. Disposal systems, on the other hand, do not discharge any waste water.



Equations Used to Obtain:[a]

	K_ℓ	K_g	K_{oil}	K_D	K	N
Flowthrough	1	2			7	20
Disposal	1	2			7	19
Flowthrough	1	2			7	14
Disposal	1	2			7	13
Flowthrough	1,3	2,4			7	16
Disposal	1,3	2,4			7	15
Flowthrough	1,3	2,4			7	12
Disposal	1,3	2,4			7	11
Flowthrough	1	2			7	16
Disposal	1	2			7	15
Flowthrough	1	2			7	12
Disposal	1	2			7	11
Flowthrough		2	9			18
Disposal		2	9			17
Flowthrough		2	9			22
Disposal		2	9			23
Junction Box	3	2			7	12
Lift Station	3	2			7	12
Sump	1	2			7	12
Weir				10		21
Clarifier Weir	5	6			8	24

[a] Numbered equations are presented in Table 4.13-1

K_ℓ = Individual liquid phase mass transfer coefficient, m/s

K_g = Individual gas phase mass transfer coefficient, m/s

K_{oil} = Overall mass transfer coefficient in the oil phase, m/s

K_D = Volatilization - reaeration theory mass transfer coefficient

K = Overall mass transfer coefficient, m/s

N = Emissions, g/s

Figure 4.13-4. Flow diagram for estimating VOC emissions from waste water collection, treatment and storage systems.

Table 4.13-1. MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS[a].

Equation No.	Equations
	<u>Individual liquid (k_ℓ) and gas (k_g) phase mass transfer coefficients</u>
1	$k_\ell \text{ (m/s)} = (2.78 \times 10^{-6})(D_w/D_{ether})^{2/3}$ For: $0 < U_{10} < 3.25$ m/s and all F/D ratios $k_\ell \text{ (m/s)} = [(2.605 \times 10^{-9})(F/D) + (1.277 \times 10^{-7})](U_{10})^2(D_w/D_{ether})^{2/3}$ For: $U_{10} > 3.25$ m/s and $14 < F/D < 51.2$ $k_\ell \text{ (m/s)} = (2.61 \times 10^{-7})(U_{10})^2(D_w/D_{ether})^{2/3}$ For: $U_{10} > 3.25$ m/s and $F/D > 51.2$ $k_\ell \text{ (m/s)} = 1.0 \times 10^{-6} + 144 \times 10^{-4} (U^*)^{2.2} (Sc_L)^{-0.5}; U^* < 0.3$ $k_\ell \text{ (m/s)} = 1.0 \times 10^{-6} + 34.1 \times 10^{-4} U^* (Sc_L)^{-0.5}; U^* > 0.3$ For $U_{10} > 3.25$ m/s and $F/D < 14$ where: $U^* \text{ (m/s)} = (0.01)(U_{10})(6.1 + 0.63(U_{10}))^{0.5}$ $Sc_L = \mu_L/(\rho_L D_w)$ $F/D = 2 (A/\pi)^{0.5}$
2	$k_g \text{ (m/s)} = (4.82 \times 10^{-3})(U_{10})^{0.78} (Sc_G)^{-0.67} (d_e)^{-0.11}$ where: $Sc_G = \mu_a/(\rho_a D_a)$ $d_e\text{(m)} = 2(A/\pi)^{0.5}$
3	$k_\ell \text{ (m/s)} = [(8.22 \times 10^{-9})(J)(POWR)(1.024)^{(T-20)}(O_t)(10^6) *$ $(MW_L)/(Va_v \rho_L)](D_w/D_{O2,w})^{0.5}$ where: POWR (hp) = (total power to aerators)(V) Va_v (ft^2) = (fraction of area agitated)(A)
4	$k_g \text{ (m/s)} = (1.35 \times 10^{-7})(Re)^{1.42} (P)^{0.4} (Sc_G)^{0.5} (Fr)^{-0.21}(D_a\, MW_a/d)$ where: $Re = d^2\, w\, \rho_a/\mu_a$ $P = [(0.85)(POWR)(550 \text{ ft-lb}_f\text{/s-hp})/N_I]\, g_c/(\rho_L (d^*)^5 w^3)$ $Sc_G = \mu_a/(\rho_a D_a)$ $Fr = (d^*)w^2/g_c$
5	$k_\ell \text{ (m/s)} = (f_{air,\ell})(Q)/[3600 \text{ s/min } (h_c)(\pi d_c)]$ where: $f_{air,\ell} = 1 - 1/r$ $r = \exp [0.77(h_c)^{0.623}(Q/\pi d_c)^{0.66}(D_w/D_{O2,w})^{0.66}]$

Table 4.13-1. MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS[a].

Equation No.	Equations
6	k_g (m/s) = $0.001 + (0.0462(U^{**})(Sc_G)^{-0.67})$ where: U^{**} (m/s) = $[6.1 + (0.63)(U_{10})]^{0.5}(U_{10}/100)$ $Sc_G = \mu_a/(\rho_a D_a)$
<u>Overall mass transfer coefficients for water (K) and oil K_{oil} phases and for Weirs (K_D)</u>	
7	$K = (k_\ell \, Keq \, k_g)/(Keq \, k_g + k_\ell)$ where: $Keq = H/(RT)$
8	K (m/s) = $[[MW_L/(k_\ell \rho_L{*}(100 \text{ cm/m})] + [MW_a/(k_g \rho_a H{*} 55{,}555(100 \text{ cm/m}))]]^{-1} \, MW_L/[(100 \text{ cm/m})\rho_L]$
9	$K_{oil} = k_g Keq_{oil}$ where: $Keq_{oil} = P^* \rho_a MW_{oil}/(\rho_{oil} \, MW_a \, P_o)$
10	$K_D = 0.16h \, (D_w/D_{O2,w})^{0.75}$
<u>Air emissions (N)</u>	
11	$N(g/s) = (1 - Ct/Co) \, V \, Co/t$ where: $Ct/Co = \exp[-K \, A \, t/V]$
12	$N(g/s) = K \, C_L \, A$ where: $C_L(g/m^3) = Q \, Co/(KA + Q)$
13	$N(g/s) = (1 - Ct/Co) \, V \, Co/t$ where: $Ct/Co = \exp[-(KA + KeqQ_a)t/V]$
14	$N(g/s) = (KA + Q_a Keq)C_L$ where: $C_L(g/m^3) = QCo/(KA + Q + Q_a Keq)$
15	$N(g/s) = (1 - Ct/Co) \, KA/(KA + Kmax \, b_i \, V/K_s) \, V \, Co/t$ where: $Ct/Co = \exp[-Kmax \, b_i \, t/K_s - K \, A \, t/V]$

Table 4.13-1. MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS[a].

Equation No.	Equations
16	$N(g/s) = K\,C_L\,A$ where: $C_L(g/m^3) = [-b + (b^2 - 4ac)^{0.5}]/(2a)$ and $a = KA/Q + 1$ $b = K_s(KA/Q + 1) + Kmax\ b_i\ V/Q - Co$ $c = -K_sCo$
17	$N(g/s) = (1 - Ct_{oil}/Co_{oil})V_{oil}Co_{oil}/t$ where: $Ct_{oil}/Co_{oil} = \exp[-K_{oil}\ t/D_{oil}]$ and: $Co_{oil} = Kow\ Co/[1 - FO + FO(Kow)]$ $V_{oil} = (FO)(V)$ $D_{oil} = (FO)(V)/A$
18	$N(g/s) = K_{oil}C_{L,oil}A$ where: $C_{L,oil}(g/m^3) = Q_{oil}Co_{oil}/(K_{oil}A + Q_{oil})$ and: $Co_{oil} = Kow\ Co/[1 - FO + FO(Kow)]$ $Q_{oil} = (FO)(Q)$
19	$N(g/s) = (1 - Ct/Co)(KA + Q_aKeq)/(KA + Q_aKeq + Kmax\ b_i\ V/K_s)\ V\ Co/t$ where: $Ct/Co = \exp[-(KA + KeqQ_a)t/V - Kmax\ b_i\ t/K_s]$
20	$N(g/s) = (KA + Q_aKeq)C_L$ where: $C_L(g/m^3) = [-b + (b^2 - 4ac)^{0.5}]/(2a)$ and: $a = (KA + Q_aKeq)/Q + 1$ $b = K_s[(KA + Q_aKeq)/Q + 1] + Kmax\ b_i\ V/Q - Co$ $c = -K_sCo$
21	$N\ (g/s) = (1 - \exp[-K_D])Q\ Co$
22	$N(g/s) = K_{oil}C_{L,oil}A$ where: $C_{L,oil}(g/m^3) = Q_{oil}(Co_{oil}^*)/(K_{oil}A + Q_{oil})$ and: $Co_{oil}^* = Co/FO$ $Q_{oil} = (FO)(Q)$

Table 4.13-1. MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS[a].

Equation No.	Equations
23	$N(g/s) = (1 - Ct_{oil}/Co_{oil}^*)(V_{oil})(Co_{oil}^*)/t$ where: $Ct_{oil}/Co_{oil}^* = \exp[-K_{oil}\, t/D_{oil}]$ and: $Co_{oil}^* = Co/FO$ $V_{oil} = (FO)(V)$ $D_{oil} = (FO)(V)/A$
24	$N\ (g/s) = (1 - \exp[-K\, \pi\, d_c\, h_c/Q])Q\ Co$

---

[a] All parameters in numbered equations are defined in Table 4.13-2.

Table 4.13-2. PARAMETER DEFINITIONS FOR MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS.

Parameter	Definition	Units	Code[a]
A	Waste water surface area	m^2 or ft^2	A
b_i	Biomass concentration (total biological solids)	g/m^3	B
C_L	Concentration of constituent in the liquid phase	g/m^3	D
$C_{L,oil}$	Concentration of constituent in the oil phase	g/m^3	D
Co	Initial concentration of constituent in the liquid phase	g/m^3	A
Co_{oil}	Initial concentration of constituent in the oil phase considering mass transfer resistance between water and oil phases	g/m^3	D
Co_{oil}^*	Initial concentration of constituent in the oil phase considering no mass transfer resistance between water and oil phases	g/m^3	D
Ct	Concentration of constituent in the liquid phase at time = t	g/m^3	D
Ct_{oil}	Concentration of constituent in the oil phase at time = t	g/m^3	D
d	Impeller diameter	cm	B
D	Waste water depth	m or ft	A,B
d^*	Impeller diameter	ft	B
D_a	Diffusivity of constituent in air	cm^2/s	C
d_c	Clarifier diameter	m	B
d_e	Effective diameter	m	D
D_{ether}	Diffusivity of ether in water	cm^2/s	$(8.5x10^{-6})^b$
$D_{O2,w}$	Diffusivity of oxygen in water	cm^2/s	$(2.4x10^{-5})^b$

Table 4.13-2. PARAMETER DEFINITIONS FOR MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS.

Parameter	Definition	Units	Code[a]
D_{oil}	Oil film thickness	m	B
D_w	Diffusivity of constituent in water	cm^2/s	C
$f_{air,\ell}$	Fraction of constituent emitted to the air, considering zero gas resistance	dimensionless	D
F/D	Fetch to depth ratio, d_e/D	dimensionless	D
FO	Fraction of volume which is oil	dimensionless	B
Fr	Froude number	dimensionless	D
g_c	Gravitation constant (a conversion factor)	$lb_m\text{-}ft/s^2\text{-}lb_f$	32.17
h	Weir height (distance from the waste water overflow to the receiving body of water)	ft	B
h_c	Clarifier weir height	m	B
H	Henry's Law Constant of constituent	$atm\text{-}m^3/gmol$	C
J	Oxygen transfer rating of surface aerator	lb 02/(hr-hp)	B
K	Overall mass transfer coefficient for transfer of constituent from liquid phase to gas phase	m/s	D
K_D	Volatilization-reaeration theory mass transfer coefficient	dimensionless	D
Keq	Equilibrium constant or partition coefficient (concentration in gas phase/concentration in liquid phase)	dimensionless	D
Keq_{oil}	Equilibrium constant or partition coefficient (concentration in gas phase/concentration in oil phase)	dimensionless	D
k_g	Gas phase mass transfer coefficient	m/s	D

Table 4.13-2. PARAMETER DEFINITIONS FOR MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS.

Parameter	Definition	Units	Code[a]
k_ℓ	Liquid phase mass transfer coefficient	m/s	D
Kmax	Maximum biorate constant	g/s-g biomass	A,C
K_{oil}	Overall mass transfer coefficient for transfer of constituent from oil phase to gas phase	m/s	D
Kow	Octanol-water partition coefficient	dimensionless	C
K_s	Half saturation biorate constant	g/m^3	A,C
MW_a	Molecular weight of air	g/gmol	29
MW_{oil}	Molecular weight of oil	g/gmol	B
MW_L	Molecular weight of water	g/gmol	18
N	Emissions	g/s	D
N_I	Number of aerators	dimensionless	A,B
O_t	Oxygen transfer correction factor	dimensionless	B
P	Power number	dimensionless	D
P^*	Vapor pressure of the constituent	atm	C
P_o	Total pressure	atm	A
POWR	Total power to aerators	hp	B
Q	Volumetric flow rate	m^3/s	A
Q_a	Diffused air flow rate	m^3/s	B
Q_{oil}	Volumetric flow rate of oil	m^3/s	B
r	Deficit ratio (ratio of the difference between the constituent concentration at solubility and actual constituent concentration in the upstream and the downstream)	dimensionless	D

Table 4.13-2. PARAMETER DEFINITIONS FOR MASS TRANSFER CORRELATIONS AND EMISSIONS EQUATIONS.

Parameter	Definition	Units	Code[a]
R	Universal gas constant	atm-m3/gmol-K	8.21×10^{-5}
Re	Reynolds number	dimensionless	D
Sc_G	Schmidt number on gas side	dimensionless	D
Sc_L	Schmidt number on liquid side	dimensionless	D
T	Temperature of water	°C or Kelvin (K)	A
t	Residence time of disposal	s	A
U^*	Friction velocity	m/s	D
U^{**}	Friction velocity	m/s	D
U_{10}	Wind speed at 10 m above the liquid surface	m/s	B
V	Waste water Volume	m^3 or ft^3	A
Va_v	Turbulent surface area	ft^2	B
V_{oil}	Volume of oil	m^3	B
w	Rotational speed of impeller	rad/s	B
ρ_a	Density of air	g/cm^3	$(1.2 \times 10^{-3})^b$
ρ_L	Density of water	g/cm^3 or lb/ft^3	1^b or 62.4^b
ρ_{oil}	density of oil	g/m^3	B
μ_a	Viscosity of air	g/cm-s	$(1.81 \times 10^{-4})^b$
μ_L	Viscosity of water	g/cm-s	$(8.93 \times 10^{-3})^b$

---

[a] Code
A = Site-specific parameter.
B = Site-specific parameter. For default values, see Table 4.13-3.
C = Parameter can be obtained from literature. See Attachment 1 for a list of ~150 compound chemical properties at T = 25°C (298°K).
D = Calculated value.

[b] Reported values at 25°C (298°K).

Figure 4.13-4 includes information needed to estimate air emissions from junction boxes, lift stations, sumps, weirs, and clarifier weirs. Sumps are considered quiescent, but junction boxes, lift stations, and weirs are turbulent in nature. Junction boxes and lift stations are turbulent because incoming flow is normally above the water level in the component, which creates some splashing. Waste water falls or overflows from weirs and creates splashing in the receiving body of water (both weir and clarifier weir models). Waste water from weirs can be aerated by directing it to fall over steps, usually only the weir model.

Assessing VOC emissions from drains, manholes and trenches is also important in determining the total waste water facility emissions. As these sources can be open to the atmosphere and closest to the point of waste water generation (i. e., where water temperatures and pollutant concentrations are greatest), emissions can be significant. Currently, there are no well established emission models for these collection system types. However, work is being performed to address this need.

Preliminary models of VOC emissions from waste collection system units have been developed[4]. The emission equations presented in Reference 4 are used with standard collection system parameters to estimate the fraction of the constituents released as the waste water flows through each unit. The fractions released from several units are estimated for high, medium and low volatility compounds. The units used in the estimated fractions included open drains, manhole covers, open trench drains, and covered sumps.

The numbers in Figure 4.13-4 under the columns for k_ℓ, k_g, K_{oil}, K_D, K, and N refer to the appropriate equations in Table 4.13-1.[*] Definitions for all parameters in these equations are given in Table 4.13-2. Table 4.13-2 also supplies the units that must be used for each parameter, with codes to help locate input values. If the parameter is coded with the letter A, a site-specific value is required. Code B also requires a site-specific parameter, but defaults are available. These defaults are typical or average values and are presented by specific system in Table 4.13-3.

Code C means the parameter can be obtained from literature data. Table 4.13-4 contains a list of approximately 150 chemicals and their physical properties needed to calculate emissions from waste water, using the correlations presented in Table 4.13-1. All properties are at 25°C. (A more extensive chemical properties data base is contained in Appendix C of Reference 1.) Parameters coded D are calculated values.

Calculating air emissions from waste water collection, treatment and storage systems is a complex procedure, especially if several systems are present. Performing the calculations by hand may result in errors and will be time consuming. A personal computer program called the Surface Impoundment Modeling System (SIMS) is now available for estimating air emissions. The program is menu driven and can estimate air emissions from all surface impoundment models presented in Figure 4.13-4, individually or in series. The program requires for each collection, treatment or storage system component, at a minimum, the waste water flow rate and component surface area. All other inputs are provided as default values. Any available site-specific information should be entered in place of these defaults, as the most fully characterized system will provide the most accurate emissions estimate.

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[*] All emission model systems presented in Figure 4.13-4 imply a completely mixed or uniform waste water concentration system. Emission models for a plug flow system, or system in which there is no axial, or horizontal mixing, are too extensive to be covered in this document. (An example of plug flow might be a high waste water flow in a narrow channel.) For information on emission models of this type, see Reference 1.

The SIMS program with user's manual and background technical document, can be obtained through state air pollution control agencies and through the U.S. Environmental Protection Agency's Control Technology Center in Research Triangle Park, NC, telephone (919) 541-0800 (FTS 629-0800). The user's manual and background technical document should be followed to produce meaningful results.

The SIMS program and user's manual also can be downloaded from EPA's Clearinghouse For Inventories and Emission Factors (CHIEF) electronic bulletin board (BB). The CHIEF BB is open to all persons involved in air emission inventories. To access this BB, one needs a computer, modem, and communication package capable of communicating at 1200, 2400, or 9600 baud, 8 data bits, 1 stop bit, and no parity (8-N-1).

This BB is part of EPA's Technical Support Division bulletin local system and its telephone numbers are:

1) (919) 541-5742 (1200 or 2400 baud), and
2) (919) 541-5384 (9600 baud).

First-time users must register before access is allowed.

Emissions estimates from SIMS are based on mass transfer models developed by Emissions Standards Division (ESD) during evaluations of TSDFs and VOC emissions from industrial waste water. As a part of the TSDF project, a Lotus® spreadsheet program called CHEMDAT7 was developed for estimating VOC emissions from waste water land treatment systems, open landfills, closed landfills, and waste storage piles, as well as from various types of surface impoundments. For more information about CHEMDAT7, contact the ESD's Chemicals And Petroleum Branch (MD 13), US EPA, Research Triangle Park, NC 27711.

Table 4.13-3. SITE-SPECIFIC DEFAULT PARAMETERS[a]

Default Parameter[b]	Definition	Default Value
General		
T	Temperature of water	298°K
U_{10}	Windspeed	4.47 m/s
Biotreatment Systems		
b_i	Biomass concentration (for biologically active systems)	
	Quiescent treatment systems	50 g/m^3
	Aerated treatment systems	300 g/m^3
	Activated sludge units	4000 g/m^3
POWR	Total power to aerators (for aerated treatement systems) (for activated sludge)	 0.75 $hp/1000\ ft^3$ (V) 2 $hp/1000\ ft^3$ (V)
W	Rotational speed of impeller (for aerated treatment systems)	126 rad/s(1200 rpm)
$d(d^*)$	Impeller diameter (for aerated treatment systems)	61 cm(2 ft)
Va_v	Turbulent surface area (for aerated treatment systems) (for activated sludge)	 0.24 (A) 0.52 (A)
J	Oxygen transfer rating to surface aerator (for aerated treatment systems)	3 lb O_2/hp•hr
O_t	Oxygen transfer correction factor (for aerated treatment systems)	0.83
N_I	Number of aerators	POWR/75
Diffused Air Systems		
Q_a	Diffused air volumetric flow rate	0.0004(V) m^3/s

Table 4.13-3. SITE-SPECIFIC DEFAULT PARAMETERS[a]

Default Parameter	Definition	Default Value
Oil Film Layers		
MW_{oil}	Molecular weight of oil	282 g/gmol
D_{oil}	Depth of oil layer	0.001 (V/A) m
V_{oil}	Volume of oil	0.001 (V) m^3
Q_{oil}	Volumetric flow rate of oil	0.001 (Q) m^3/s
ρ_{oil}	Density of oil	0.92 g/cm^3
FO	Fraction of volume which is oil[c]	0.001
Junction Boxes		
D	Depth of Junction Box	0.9 m
N_I	Number of aerators	1
Lift Station		
D	Depth of Lift Station	1.5 m
N_I	Number of aerators	1
Sump		
D	Depth of sump	5.9 m
Weirs		
d_c	Clarifier weir diameter[d]	28.5 m
h	Weir height	1.8 m
h_c	Clarifier weir height[e]	0.1 m

[a] Reference 1.
[b] As defined in Table 4.13-2.
[c] Reference 4.
[d] Reference 2.
[e] Reference 5.

4.13.2.1 Example Calculation

An example industrial facility operates a flowthrough, mechanically aerated biological treatment impoundment that receives waste water contaminated with benzene at a concentration of 10.29 g/m^3.

The following format is used for calculating benzene emissions from the treatment process:

I. Determine which emission model to use
II. User-supplied information
III. Defaults
IV. Pollutant physical property data and water, air, and other properties
V. Calculate individual mass transfer coefficient
VI. Calculate the overall mass transfer coefficients
VII. Calculate VOC emissions

I. Determine Which Emission Model To Use - Following the flow diagram in Figure 4.13-4, the emission model for a treatment system that is aerated, but not by diffused air, is biologically active, and is a flowthrough system, contains the following equations:

Parameter	Definition	Equation Nos. from Table 4.13-1
k_ℓ	Individual liquid phase mass transfer coefficient, m/s	1,3
k_g	Individual gas phase mass transfer coefficient, m/s	2,4
K	Overall mass transfer coefficient, m/s	7
N	VOC emissions, g/s	16

II. User-supplied Information - Once the correct emission model is determined, some site-specific parameters are required. As a minimum for this model, site-specific flow rate, waste water surface area, and depth, and pollutant concentration should be provided. For this example, these parameters have the following values:

Q = Volumetric flow rate = 0.0623 m^3/s
D = Waste water depth = 1.97 m
A = Waste water surface area = 17,652 m^2
Co = Initial benzene concentration in the liquid phase = 10.29 g/m^3

III. Defaults - Defaults for some emission model parameters are presented in Table 4.13-3. Generally, site-specific values should be used when available. For this facility, all available general and biotreatment system defaults from Table 4.13-3 were used:

U_{10} = Wind speed at 10 m above the liquid surface = e = 4.47 m/s
T = Temperature of water = 25°C (298°K)
b_i = Biomass concentration for aerated treatment systems = 300 g/m^3
J = Oxygen transfer rating to surface aerator = 3 lb O_2/hp-hr

POWR = Total power to aerators = 0.75 hp/1,000 ft3 (V)
O_t = Oxygen transfer correction factor = 0.83
Va_v = Turbulent surface area = 0.24 (A)
d = Impeller diameter = 61 cm
d^* = Impeller diameter = 2 ft
w = Rotational speed of impeller = 126 rad/s
N_I = Number of aerators = POWR/75 hp

IV. Pollutant Physical Property Data, And Water, Air and Other Properties - For each pollutant, the specific physical properties needed by this model are listed in Table 4.13-4. Water, air and other property values are given in Table 4.13-2.

A. Benzene (from Table 4.13-4)

$D_{w,benzene}$ = Diffusivity of benzene in water = 9.8×10^{-6} cm^2/s
$D_{a,benzene}$ = Diffusivity of benzene in air = 0.088 cm^2/s
$H_{benzene}$ = Henry's Law Constant for benzene = 0.0055 atm-m^3/gmol
$Kmax_{benzene}$ = Maximum biorate constant for benzene = 5.28×10^{-6} g/g-s
$K_{s,benzene}$ = Half saturation biorate constant for benzene = 13.6 g/m^3

B. Water, Air and Other Properties (from Table 4.13-3)

ρ_a = Density of air = 1.2×10^3 g/cm^3
ρ_L = Density of water = 1 g/cm^3 (62.4 lb_m/ft^3)
μ_a = Viscosity of air = 1.81×10^{-4} g/cm-s
$D_{O2,w}$ = Diffusivity of oxygen in water = 2.4×10^{-5} cm^2/s
D_{ether} = Diffusivity of ether in water = 8.5×10^{-6} cm^2/s
MW_L = Molecular weight of water = 18 g/gmol
MW_a = Molecular weight of air = 29 g/gmol
g_c = Gravitation constant = 32.17 lb_m-ft/lb_f-s^2
R = Universal gas constant = 8.21×10^{-5} atm-m^3/gmol

V. Calculate Individual Mass Transfer Coefficients - Because part of the impoundment is turbulent and part is quiescent, individual mass transfer coefficients are determined for both turbulent and quiescent areas of the surface impoundment.

Turbulent area of impoundment - Equations 3 and 4 from Table 4.13-1.

A. Calculate the individual liquid mass transfer coefficient, k_ℓ:

$$k_\ell(m/s) = [(8.22 \times 10^{-9})(J)(POWR)(1.024)^{(T-20)} * (O_t)(10^6)MW_L/(Va_v\rho_L)](D_w/D_{O2,w})^{0.5}$$

The total power to the aerators, POWR, and the turbulent surface area, Va_v, are calculated separately [Note: some conversions are necessary.]:

1) Calculate total power to aerators, POWR (Default presented in III):

POWR (hp) = 0.75 hp/1,000 ft^3 (V)

$V =$ waste water volume, m3

$V\ (m^3) = (A)(D) = (17{,}652\ m^2)(1.97\ m)$

$V = 34{,}774\ m^3$

$POWR = (0.75\ hp/1{,}000\ ft^3)(ft^3/0.028317\ m^3)(34{,}774\ m^3)$

$POWR = 921\ hp$

2) Calculate turbulent surface area, Va_v, (Default presented in III):

$Va_v\ (ft^2) = 0.24\ (A)$

$Va_v = 0.24(17{,}652\ m^2)(10.758\ ft^2/m^2)$

$Va_v = 45{,}576\ ft^2$

Now, calculate k_ℓ, using the above calculations and information from II, III, and IV:

$$k_\ell\ (m/s) = [(8.22 \times 10^{-9})(3\ lbO_2/hp\text{-}hr)(921\ hp) * (1.024)^{(25-20)}(0.83)(10^6)(18\ g/gmol)/((45{,}576\ ft^2)(1\ g/cm^3))] * [(9.8 \times 10^{-6}\ cm^2/s)/(2.4 \times 10^{-5}\ cm^2/s)]^{0.5}$$

$k_\ell\ (m/s) = (0.00838)(0.639)$

$k_\ell = 5.35 \times 10^{-3}\ m/s$

B. Calculate the individual gas phase mass transfer coefficient, k_g:

$$k_g\ (m/s) = (1.35 \times 10^{-7})(Re)^{1.42}(P)^{0.4}(Sc_G)^{0.5}(Fr)^{-0.21}(D_a\ MW_a/d)$$

The Reynolds number, Re, power number, P, Schmidt number on the gas side, Sc_G, and Froude's number Fr, are calculated separately:

1) Calculate Reynolds Number, Re:

$Re = d^2\ w\ \rho_a/\mu_a$

$Re = (61\ cm)^2(126\ rad/s)(1.2 \times 10^{-3}\ g/cm^3)/(1.81 \times 10^{-4}\ g/cm\text{-}s)$

$Re = 3.1 \times 10^6$

2) Calculate power number, P:

$P = [(0.85)(POWR)(550\ ft\text{-}lb_f/s\text{-}hp)/N_I]\ g_c/(\rho_L(d^*)^5\ w^3)$

$N_I = POWR/75\ hp$ (default presented in III)

$$P = (0.85)(75\ hp)(POWR/POWR)(550\ ft\text{-}lb_f/s\text{-}hp) * (32.17\ lb_m\text{-}ft/lb_f\text{-}s^2)/[(62.4\ lb_m/ft^3)(2\ ft)^5(126\ rad/s)^3]$$

$P = 2.8 \times 10^{-4}$

3) Calculate Schmidt Number on the gas side, Sc_G:

$Sc_G = \mu_a/(\rho_a D_a)$

$Sc_G = (1.81 \times 10^{-4}\ g/cm\text{-}s)/[(1.2 \times 10^{-3}\ g/cm^3)(0.088\ cm^2/s)]$

$Sc_G = 1.71$

4) Calculate Froude Number, Fr:

$Fr = (d^*)w^2/g_c$

$Fr = (2\ ft)(126\ rad/s)^2/(32.17\ lb_m\text{-}ft/lb_f\text{-}s^2)$

$Fr = 990$

Now calculate k_g using the above calculations and information from II, III, and IV:

$$k_g\ (m/s) = (1.35 \times 10^{-7})(3.1 \times 10^6)^{1.42}(2.8 \times 10^{-4})^{0.4}(1.71)^{0.5} *$$

$$(990)^{-0.21}(0.088\ \text{cm}^2/\text{s})(29\ \text{g/gmol})/(61\ \text{cm})$$
$$k_g = 0.109\ \text{m/s}$$

<u>Quiescent surface area of impoundment</u> - Equations 1 and 2 from Table 4.13-1

A. Calculate the individual liquid phase mass transfer coefficient, k_ℓ:

$$F/D = 2(A/\pi)^{0.5}/D$$
$$= 2(17{,}652\ \text{m}^2/\pi)^{0.5}/(1.97\ \text{m})$$
$$= 76.1$$
$$U_{10} = 4.47\ \text{m/s}$$

For $U_{10} > 3.25$ m/s and $F/D > 51.2$ use the following:

$$k_\ell\ (\text{m/s}) = (2.61 \times 10^{-7})(U_{10})^2(D_w/D_{ether})^{2/3}$$
$$k_\ell\ (\text{m/s}) = (2.61 \times 10^{-7})(4.47\ \text{m/s})^2[(9.8 \times 10^{-6}\ \text{cm}^2/\text{s})/(8.5 \times 10^{-6}\ \text{cm}^2/\text{s})]^{2/3}$$
$$k_\ell = 5.74 \times 10^{-6}\ \text{m/s}$$

B. Calculate the individual gas phase mass transfer coefficient, k_g:

$$k_g = (4.82 \times 10^{-3})(U_{10})^{0.78}(Sc_G)^{-0.67}(d_e)^{-0.11}$$

The Schmidt number on the gas side, Sc_G, and the effective diameter, d_e, are calculated separately:

1) Calculate the Schmidt Number on the gas side, Sc_G:

$Sc_G = \mu_a/(\rho_a D_a) = 1.71$ (same as for turbulent impoundments)

2) Calculate the effective diameter, d_e:

$$d_e\ (\text{m}) = 2(A/\pi)^{0.5}$$
$$d_e\ (\text{m}) = 2(17{,}652\ \text{m}^2/\pi)^{0.5}$$
$$d_e = 149.9\ \text{m}$$
$$k_g\ (\text{m/s}) = (4.82 \times 10^{-3})(4.47\ \text{m/s})^{0.78}\,(1.71)^{-0.67}\,(149.9\ \text{m})^{-0.11}$$
$$k_g = 6.24 \times 10^{-3}\ \text{m/s}$$

VI. Calculate The Overall Mass Transfer Coefficient. Because part of the impoundment is turbulent and part is quiescent, the overall mass transfer coefficient is determined as an area-weighted average of the turbulent and quiescent overall mass transfer coefficients. (Equation number 7 from Table 4.13-1)

<u>Overall mass transfer coefficient for the turbulent surface area of impoundment, K_T</u>

$$K_T\ (\text{m/s}) = (k_\ell Keq k_g)/(Keq k_g + k_\ell)$$
$$Keq = H/RT$$
$$Keq = (0.0055\ \text{atm-m}^3/\text{gmol})/[(8.21 \times 10^{-5}\ \text{atm-m}^3/\ \text{gmol-°K})(298\text{°K})]$$
$$Keq = 0.225$$
$$K_T\ (\text{m/s}) = (5.35 \times 10^{-3}\ \text{m/s})(0.225)(0.109)/[(0.109\ \text{m/s})(0.225) + (5.35 \times 10^{-6}\ \text{m/s})]$$
$$K_T = 4.39 \times 10^{-3}\ \text{m/s}$$

Overall mass transfer coefficient for the quiescent surface area of impoundment, K_Q

$$K_Q\ (m/s) = (k_\ell Keq k_g)/(Keq k_g + k_\ell)$$
$$K_Q\ (m/s) = (5.74 \times 10^{-6}\ m/s)(0.225)(6.24 \times 10^{-3}\ m/s)/ [(6.24 \times 10^{-3}\ m/s)(0.225) + (5.74 \times 10^{-6}\ m/s)]$$
$$K_Q = 5.72 \times 10^{-6}\ m/s$$

Overall mass transfer coefficient, K, weighted by turbulent and quiescent surface areas, A_T and A_Q

$$K\ (m/s) = (K_T A_T + K_Q A_Q)/A$$
$$A_T = 0.24(A)\ \text{(Default value presented in III: } A_T = Va_v\text{)}$$
$$A_Q = (1 - 0.24)A$$
$$K\ (m/s) = [(4.39 \times 10^{-3}\ m/s)(0.24\ A) + (5.72 \times 10^{-6}\ m/s)(1 - 0.24)A]/A$$
$$K = 1.06 \times 10^{-3}\ m/s$$

VII. Calculate VOC Emissions for an Aerated Biological Flowthrough Impoundment - Equation number 16 from Table 4.13-1

$$N\ (g/s) = K\ C_L\ A$$

where:

$$C_L\ (g/m^3) = [-b + (b^2 - 4ac)^{0.5}]/(2a)$$

and:

$$a = KA/Q + 1$$
$$b = K_s(KA/Q + 1) + Kmax\ b_i\ V/Q - Co$$
$$c = -K_s Co$$

Calculate a, b, c, and the concentration of benzene in the liquid phase, C_L, separately:

1) Calculate a:

$$a = (KA/Q + 1) = [(1.06 \times 10^{-3}\ m/s)(17{,}652\ m^2)/(0.0623\ m^3/s)] + 1$$
$$a = 301.3$$

2) Calculate b ($V = 34{,}774\ m^3$ from IV):

$$b = K_s\ (KA/Q + 1) + Kmax\ b_i\ V/Q - Co$$
$$b = (13.6\ g/m^3)[(1.06 \times 10^{-3}\ m/s)(17{,}652\ m^2)/(0.0623\ m^3/s)] + [(5.28 \times 10^{-6}\ g/g\text{-}s)(300\ g/m^3)(34{,}774\ m^3)/(0.0623\ m^3/s)] - 10.29\ g/m^3$$
$$b = 4{,}084.6 + 884.1 - 10.29$$
$$b = 4{,}958.46\ g/m^3$$

3) Calculate c:

$$c = -K_s Co$$
$$c = -(13.6\ g/m^3)(10.29\ g/m^3)$$
$$c = -139.94$$

4) Calculate the concentration of benzene in the liquid phase, C_L, from a, b, and c above:

$$C_L\ (g/m^3) = [-b + (b^2 - 4ac)^{0.5}]/(2a)$$
$$C_L\ (g/m^3) = [(4{,}958.46\ g/m^3) + [(4{,}958.46\ g/m^3)^2 - [4(301.3)(-139.94)]]^{0.5}]/(2(301.3))$$

$$C_L = 0.0282 \text{ g/m3}$$

Now calculate N with the above calculations and information from II and V:

$$N \text{ (g/s)} = K\,A\,C_L$$
$$N \text{ (g/s)} = (1.06 \times 10^{-3} \text{ m/s})(17{,}652 \text{ m}^2)(0.0282 \text{ g/m}^3)$$
$$N = 0.52 \text{ g/s}$$

4.13.3 Controls

The types of control technology generally used in reducing VOC emissions from waste water include: steam stripping or air stripping, carbon adsorption (liquid phase), chemical oxidation, membrane separation, liquid-liquid extraction, and biotreatment (aerobic or anaerobic). For efficient control, all control elements should be placed as close as possible to the point of waste water generation, with all collection, treatment and storage systems ahead of the control technology being covered to suppress emissions. Tightly covered, well maintained collection systems can suppress emissions by 95 to 99 percent. However, if there is explosion potential, the components should be vented to a control device such as an incinerator or carbon adsorber.

The following are brief descriptions of the control technology listed above and of any secondary controls that may need to be considered for fugitive air emissions.

Steam stripping is the fractional distillation of waste water to remove volatile organic constituents, with the basic operating principle being the direct contact of steam with waste water. The steam provides the heat of vaporization for the more volatile organic constituents. Removal efficiencies vary with volatility and solubility of the organic impurities. For highly volatile compounds (HLC greater than 10^{-3} atm-m^3/gmol), average VOC removal ranges from 95 to 99 percent. For medium volatility compounds (HLC between 10^{-5} and 10^{-3} atm-m^3/gmol), average removal ranges from 90 to 95 percent. For low volatility compounds (HLC $<10^{-5}$ atm-m^3/gmol), average removal ranges from less than 50 to 90 percent.

Air stripping involves the contact of waste water and air to strip out volatile organic constituents. By forcing large volumes of air through contaminated water, the surface area of water in contact with air is greatly increased, resulting in an increase in the transfer rate of the organic compounds into the vapor phase. Removal efficiencies vary with volatility and solubility of organic impurities. For highly volatile compounds, average removal ranges from 90 to 99 percent, for medium to low volatility compounds, removal ranges from less than 50 to 90 percent.

Steam stripping and air stripping controls most often are vented to a secondary control, such as a combustion device or gas phase carbon adsorber. Combustion devices may include incinerators, boilers and flares. Vent gases of high fuel value can be used as an alternate fuel. Typically, vent gas is combined with other fuels such as natural gas and fuel oil. If the fuel value is very low, vent gases can be heated and combined with combustion air. It is important to note that organics such as chlorinated hydrocarbons can emit toxic pollutants when combusted.

Secondary control by gas phase carbon adsorption processes takes advantage of compound affinities for activated carbon. The types of gas phase carbon adsorption systems most commonly used to control VOC are fixed bed carbon adsorbers and carbon canisters. Fixed bed carbon adsorbers are used to control continuous organic gas streams with flow rates ranging from 30 to over 3000 m^3/min. Canisters are much simpler and smaller than fixed bed systems and are usually installed to control gas flows of less than 3 m^3/min.[4] Removal efficiencies depend highly on the type of compound being removed. Pollutant-specific activated carbon is usually required. Average removal efficiency ranges from 90 to 99 percent.

Like gas phase carbon adsorption, liquid phase carbon adsorption takes advantage of compound affinities for activated carbon. Activated carbon is an excellent adsorbent, because of its large surface area and because it is usually in granular or powdered form for easy handling. Two types of liquid phase carbon adsorption are the fixed bed and moving bed systems. The fixed bed system is used primarily for low flow waste water streams with contact times around 15 minutes, and it is a batch operation (i. e., once the carbon is spent, the system is taken off line). Moving bed carbon adsorption systems operate continuously with waste water typically being introduced from the bottom of the column and regenerated carbon from the top (countercurrent flow). Spent carbon is continuously removed from the bottom of the bed. Liquid phase carbon adsorption is usually used for low concentrations of nonvolatile components and for high concentrations of nondegradable compounds.[5] Removal efficiencies depend on whether the compound is adsorbed on activated carbon. Average removal efficiency ranges from 90 to 99 percent.

Chemical oxidation involves a chemical reaction between the organic compound and an oxidant such as ozone, hydrogen peroxide, permanganate, or chlorine dioxide. Ozone is usually added to the waste water through an ultraviolet - ozone reactor. Permanganate and chlorine dioxide are added directly into the waste water. It is important to note that adding chlorine dioxide can form chlorinated hydrocarbons in a side reaction. The applicability of this technique depends on the reactivity of the individual organic compound.

Two types of membrane separation processes are ultrafiltration and reverse osmosis. Ultrafiltration is primarily a physical sieving process driven by a pressure gradient across the membrane. This process separates organic compounds with molecular weights greater than 2000, depending on the size of the membrane pore. Reverse osmosis is the process by which a solvent is forced across a semipermeable membrane because of an osmotic pressure gradient. Selectivity is, therefore, based on osmotic diffusion properties of the compound and on the molecular diameter of the compound and membrane pores.[4]

Liquid-liquid extraction as a separation technique involves differences in solubility of compounds in various solvents. Contacting a solution containing the desired compound with a solvent in which the compound has a greater solubility may remove the compound from the solution. This technology is often used for product and process solvent recovery. Through distillation, the target compound is usually recovered, and the solvent reused.

Biotreatment is the aerobic or anaerobic chemical breakdown of organic chemicals by microorganisms. Removal of organics by biodegradation is highly dependent on the compound's biodegradability, its volatility, and its ability to be adsorbed onto solids. Removal efficiencies range from almost zero to 100 percent. In general, highly volatile compounds such as chlorinated hydrocarbons and aromatics will biodegrade very little because of their high volatility, while alcohols and other compounds soluble in water, as well as low volatility compounds, can be almost totally biodegraded in an acclimated system. In the acclimated biotreatment system, the microorganisms easily convert available organics into biological cells, or biomass. This often requires a mixed culture of organisms, where each organism utilizes the food source most suitable to its metabolism. The organisms will starve and the organics will not be biodegraded if a system is not acclimated, i. e., the organisms cannot metabolize the available food source.

4.13.4 Glossary Of Terms

Basin - an earthen or concrete-lined depression used to hold liquid.

Completely mixed - having the same characteristics and quality throughout or at all times.

Disposal - the act of permanent storage. Flow of liquid into, but not out of a device.

Drain - a device used for the collection of liquid. It may be open to the atmosphere or be equipped with a seal to prevent emissions of vapors.

Flowthrough - having a continuous flow into and out of a device.

Plug flow - having characteristics and quality not uniform throughout. These will change in the direction the fluid flows, but not perpendicular to the direction of flow (i. e., no axial movement)

Storage - any device to accept and retain a fluid for the purpose of future discharge. Discontinuity of flow of liquid into and out of a device.

Treatment - the act of improving fluid properties by physical means. The removal of undesirable impurities from a fluid.

VOC - Volatile Organic Compounds, refering to all organic compounds except the following, which have been shown not to be photochemically reactive: methane, ethane, trichlorotrifluoroethane, methylene chloride, 1,1,1,-trichloroethane, trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, trifluoromethane, dichlorotetrafluoroethane, and chloropentafluoroethane.

Table 4.13-4.

SIMS CHEMICAL PROPERTY DATA FILE

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ACETALDEHYDE	75-07-0	44.00	760	.000095	.0000141	.124	8.005	1600.017	291.809	.0000228944	419.0542	2.69153
ACETIC ACID	64-19-7	60.05	15.4	.0627	.000012	.113	7.387	1533.313	222.309	.0000038889	14.2857	.48978
ACETIC ANHYDRIDE	108-24-7	102.09	5.29	.00000591	.00000933	.235	7.149	1444.718	199.817	.0000026944	1.9323	1
ACETONE	67-64-1	58.00	266	.000025	.0000114	.124	7.117	1210.595	229.664	.0000003611	1.1304	.57544
ACETONITRILE	75-05-8	41.03	90	.0000058	.0000166	.128	7.119	1314.4	230	.00000425	152.6014	.45709
ACROLEIN	107-02-8	56.10	244.2	.0000566	.0000122	.105	2.39	0	0	.0000021667	22.9412	.81283
ACRYLAMIDE	79-06-1	71.09	.012	.00000000052	.0000106	.097	11.2932	3939.877	273.16	.00000425	56.2388	6.32182
ACRYLIC ACID	79-10-7	72.10	5.2	.0000001	.0000106	.098	5.652	648.629	154.683	.0000026944	54.7819	2.04174
ACRYLONITRILE	107-13-1	53.10	114	.000088	.0000134	.122	7.038	1232.53	222.47	.000005	24	.12023
ADIPIC ACID	124-04-9	146.14	.0000225	.00000000005	.00000684	.0659	0	0	0	.0000026944	66.9943	1.20226
ALLYL ALCOHOL	107-18-6	58.10	23.3	.000018	.0000114	.114	0	0	0	.0000048872	3.9241	1.47911
AMINOPHENOL(-O)	95-55-6	109.12	.511	.00000367	.00000864	.0774	0	0	0	.00000425	68.1356	3.81533
AMINOPHENOL(-P)	123-30-8	109.12	.893	.0000197	.00000239	.0774	-3.357	699.157	-331.343	.00000425	68.1356	3.81533
AMMONIA	7664-41-7	17.03	7470	.000328	.0000693	.259	7.5547	1002.711	247.885	.00000425	15.3	1
AMYL ACETATE(-N)	628-37-8	130.18	5.42	.000464	.0000012	.064	0	0	0	.0000026944	16.1142	51.10801
ANILINE	62-53-3	93.10	1	.0000026	.0000083	.07	7.32	1731.515	206.049	.0000019722	.3381	7.94328
BENZENE	71-43-2	78.10	95.2	.0055	.0000098	.088	6.905	1211.033	220.79	.0000052778	13.5714	141.25375
BENZO(A)ANTHRACENE	56-55-3	228.30	.00000015	.00000000138	.000009	.051	6.9824	2426.6	156.6	.0000086389	1.7006	407380.2778
BENZO(A)PYRENE	50-32-8	252.30	.00568	.00000000138	.000009	.043	9.2455	3724.363	273.16	.0000086389	1.2303	954992.58602
BENZYL CHLORIDE	100-44-7	126.60	1.21	.000433	.0000078	.075	0	0	0	.0000049306	17.5674	199.52623
BIS(2-CHLOROETHYL)ETHER	111-44-4	143.00	1.4	.000013	.0000075	.0692	0	0	0	.0000029889	20.0021	38.01894
BIS(2-CHLOROISOPROPYL)ETHER	39638-32-9	171.10	.85	.00011	.00000641	.0602	0	0	0	.0000029889	8.3382	380.1894
BIS(2-ETHYLHEXYL)PHTHALATE	117-81-7	390.68	.0000002	.0000003	.0000037	.0351	0	0	0	.0000002139	2.2	199526.2315
BROMOFORM	75-25-2	252.77	5.6	.000584	.0000101	.082	0	0	0	.0000029889	10.653	199.52623
BROMOMETHANE	74-83-9	94.95	1250	.221	.0000146	.116	0	0	0	.0000029889	30.4422	12.58925
BUTADIENE-(1,3)	106-99-0	54.09	2100	.142	.0000108	.249	6.849	930.546	238.854	.0000042534	15.3	74.32347
BUTANOL (ISO)	78-83-1	74.12	10	.0000022	.0000093	.086	7.4743	1314.19	186.55	.0000021667	70.9091	5.62341
BUTANOL-(1)	71-36-3	74.12	6.5	.0000089	.0000093	.08	7.4768	1362.39	178.77	.0000021667	70.9091	5.62341
BUTYL BENZYL PHTHALATE	85-68-7	312.39	.0000086	.0108	.0000048	.0458	0	0	0	.0000086389	14.1364	60255.95861
CARBON DISULFIDE	75-15-0	76.10	366	.0168	.00001	.104	6.942	1169.11	241.59	.0000042534	5.8175	1
CARBON TETRACHLORIDE	56-23-5	153.80	113	.03	.0000088	.078	6.934	1242.43	230	.0000004167	1	524.80746

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CHLORO(-P)CRESOL(-M)	59-50-7	142.60	.0035	.000000164	.0000076	.0709	0	0	0	.0000029889	5.2902	1258.92541
CHLOROACETALDEHYDE	107-20-0	78.50	60	.000026	.0000115	.099	0	0	0	.0000029889	49.838	3.4405
CHLOROBENZENE	108-90-7	112.60	11.8	.00393	.0000087	.073	6.978	1431.05	217.55	.0000001083	.039	316.22777
CHLOROFORM	67-66-3	119.40	208	.00339	.00001	.104	6.493	929.44	196.03	.0000008167	3.7215	91.20108
CHLORONAPHTHALENE-(2)	91-58-7	162.51	.017	.018	.0000074	.0653	0	0	0	.0000029889	2.167	13182.56739
CHLOROPRENE	126-99-8	88.50	273	.331	.00001	.104	6.161	783.45	179.7	.0000029968	6.3412	1
CRESOL(-M)	108-39-4	108.10	.08	.000000443	.00001	.074	7.508	1856.36	199.07	.0000064472	1.3653	93.32543
CRESOL(-O)	95-48-7	108.10	.24	.0000026	.0000083	.074	6.911	1435.5	165.16	.0000063278	1.34	95.49926
CRESOL(-P)	106-44-5	108.10	.11	.000000443	.00001	.074	7.035	1511.08	161.85	.0000064472	1.3653	87.09636
CRESYLIC ACID	1319-77-3	108.00	.3	.0000017	.0000083	.074	0	0	0	.0000041667	15	1
CROTONALDEHYDE	4170-30-0	70.09	30	.0000154	.0000102	.0903	0	0	0	.0000026944	27.6285	12.36833
CUMENE (ISOPROPYLBENZENE)	98-82-8	120.20	4.6	.0146	.0000071	.065	6.963	1460.793	207.78	.0000086458	16.5426	1
CYCLOHEXANE	110-82-7	84.20	100	.0137	.0000091	.0839	6.841	1201.53	222.65	.0000042534	15.3	338.0687
CYCLOHEXANOL	108-93-0	100.20	1.22	.00000447	.00000831	.214	6.255	912.87	109.13	.0000026944	18.0816	37.74314
CYCLOHEXANONE	108-94-1	98.20	4.8	.00000413	.00000862	.0784	7.8492	2137.192	273.16	.0000031917	41.8921	6.45654
DI-N-OCTYL PHTHALATE	117-84-0	390.62	0	.137	.0000041	.0409	0	0	0	.000000083	.02	141253.7
DIBUTYLPHTHALATE	84-74-2	278.30	.00001	.00000028	.0000079	.0438	6.639	1744.2	113.59	.0000001111	.4	158489.31925
DICHLORO(-2)BUTENE(1,4)	764-41-0	125.00	2.87	.000259	.00000812	.0725	0	0	0	.0000029889	9.8973	242.1542
DICHLOROBENZENE(1,2) (-O)	95-50-1	147.00	1.5	.00194	.0000079	.069	.176	0	0	.0000006944	4.3103	2398.83292
DICHLOROBENZENE(1,3) (-M)	541-73-1	147.00	2.28	.00361	.0000079	.069	0	0	0	.0000017778	2.7826	2398.83292
DICHLOROBENZENE(1,4) (-P)	106-46-7	147.00	1.2	.0016	.0000079	.069	.079	0	0	.0000017778	2.7826	2454.70892
DICHLORODIFLUOROMETHANE	75-71-8	120.92	5000	.401	.00001	.0001	0	0	0	.0000029889	12.0413	144.54398
DICHLOROETHANE(1,1)	75-34-3	99.00	234	.00554	.0000105	.0914	0	0	0	.0000029889	4.6783	61.6595
DICHLOROETHANE(1,2)	107-06-2	99.00	80	.0012	.0000099	.104	7.025	1272.3	222.9	.0000005833	2.1429	61.6595
DICHLOROETHYLENE(1,2)	156-54-2	96.94	200	.0319	.000011	.0935	6.965	1141.9	231.9	.0000029889	6.3294	1
DICHLOROPHENOL(2,4)	120-83-2	163.01	.1	.0000048	.0000076	.0709	0	0	0	.0000069444	7.5758	562.34133
DICHLOROPHENOXYACETIC ACID(2,4)	94-75-7	221.00	290	.0621	.00000649	.0588	0	0	0	.0000029889	14.8934	82.61445
DICHLOROPROPANE(1,2)	78-87-5	112.99	40	.0023	.0000087	.0782	6.98	1380.1	22.8	.0000047222	12.1429	1
DIETHYL (N,N) ANILIN	91-66-7	149.25	.00283	.0000000574	.00000587	.0513	7.466	1993.57	218.5	.00000425	27.0047	43.57596
DIETHYL PHTHALATE	84-66-2	222.00	.003589	.0111	.0000058	.0542	0	0	0	.000000753	1.28	1412.537
DIMETHYL FORMAMIDE	68-12-2	73.09	4	.0000192	.0000103	.0939	6.928	1400.87	196.43	.00000425	15.3	1

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DIMETHYL HYDRAZINE(1,1)	57-14-7	60.10	157	.000124	.0000109	.106	7.408	1305.91	225.53	.00000425	15.3	1
DIMETHYL PHTHALATE	131-11-3	194.20	.000167	.00000215	.0000063	.0568	4.522	700.31	51.42	.0000006111	.7097	74.13102
DIMETHYLBENZ(A)ANTHRACENE	57-97-6	256.33	0	.0000000027	.00000498	.0461	0	0	0	.0000086389	.3377	28680056.33087
DIMETHYLPHENOL(2,4)	105-67-9	122.16	.0573	.000921	.0000084	.0712	0	0	0	.0000029722	2.2766	263.0268
DINITROBENZENE (-M)	99-65-0	168.10	.05	.000022	.00000764	.279	4.337	229.2	-137	.00000425	29.9146	33.28818
DINITROTOLUENE(2,4)	121-14-2	182.10	.0051	.00000407	.00000706	.203	5.798	1118	61.8	.00000425	19.5233	102.3293
DIOXANE(1,4)	123-91-1	88.20	37	.0000231	.0000102	.229	7.431	1554.68	240.34	.0000026944	24.7001	16.60956
DIOXIN	NOCAS2	322.00	0	.0000812	.0000056	.104	12.88	6465.5	273	.0000029968	6.3412	1
DIPHENYLAMINE	122-39-4	169.20	.00375	.00000278	.00000631	.058	0	0	0	.0000052778	8.4103	1659.58691
EPICHLOROHYDRIN	106-89-8	92.50	17	.0000323	.0000098	.086	8.2294	2086.816	273.16	.0000029968	6.3412	1.07152
ETHANOL	64-17-5	46.10	50	.0000303	.000013	.123	8.321	1718.21	237.52	.0000024444	9.7778	.47863
ETHANOLAMINE(MONO-)	141-43-5	61.09	.4	.000000322	.0000114	.107	7.456	1577.67	173.37	.00000425	223.0321	.16865
ETHYL ACRYLATE	140-88-5	100.00	40	.00035	.0000086	.077	7.9645	1897.011	273.16	.0000026944	39.4119	4.85667
ETHYL CHLORIDE	75-00-3	64.52	1200	.014	.0000115	.271	6.986	1030.01	238.61	.0000029889	22.8074	26.91535
ETHYL-(2)PROPYL-(3) ACROLEIN	645-62-5	92.50	17	.0000323	.0000098	.086	0	0	0	.00000425	15.3	1
ETHYLACETATE	141-78-6	88.10	100	.000128	.00000966	.0732	7.101	1244.95	217.88	.0000048833	17.58	1
ETHYLBENZENE	100-41-4	106.20	10	.00644	.0000078	.075	6.975	1424.255	213.21	.0000018889	3.2381	1412.53754
ETHYLENEOXIDE	75-21-8	44.00	1250	.000142	.0000145	.104	7.128	1054.54	237.76	.0000011667	4.6154	.50003
ETHYLETHER	60-29-7	74.10	520	.00068	.0000093	.074	6.92	1064.07	228.8	.0000026944	17.1206	43.57596
FORMALDEHYDE	50-00-0	30.00	3500	.0000576	.0000198	.178	7.195	970.6	244.1	.0000013889	20	87.09636
FORMIC ACID	64-18-6	46.00	42	.0000007	.00000137	.079	7.581	1699.2	260.7	.0000026944	161.3977	.1191
FREONS	NOCAS3	120.92	5000	.401	.00001	.104	0	0	0	.0000029968	6.3412	1
FURAN	110-00-9	68.08	596	.00534	.0000122	.104	6.975	1060.87	227.74	.0000026944	14.1936	71.37186
FURFURAL	96-01-1	96.09	2	.0000811	.0000104	.0872	6.575	1198.7	162.8	.0000026944	18.0602	37.86047
HEPTANE (ISO)	142-82-5	100.21	66	1.836	.00000711	.187	6.8994	1331.53	212.41	.0000042534	15.3	1453.372
HEXACHLOROBENZENE	118-74-1	284.80	1	.00068	.00000591	.0542	0	0	0	.0000029889	.6651	295120.92267
HEXACHLOROBUTADIENE	87-68-3	260.80	.15	.0256	.0000062	.0561	-.824	0	0	.000003	6.3412	5495.408
HEXACHLOROCYCLOPENTADIENE	77-47-4	272.80	.081	.016	.00000616	.0561	0	0	0	.0000029968	.3412	9772.372
HEXACHLOROETHANE	67-72-1	237.00	.65	.00000249	.0000068	.00249	0	0	0	.0000029889	3.3876	4068.32838
HEXANE(-N)	100-54-3	86.20	150	.122	.00000777	.2	6.876	1171.17	224.41	.0000042534	15.3	534.0845
HEXANOL(-1)	111-27-3	102.18	.812	.0000182	.00000753	.059	7.86	1761.26	196.66	.0000026944	15.2068	59.52851

SIMS PHASE IV
CHEMICAL PROPERTY DATA FILE

CHEMICAL NAME	CAS NUMBER	MOLE WT	VAPOR PRESSURE AT 25 C (mm Hg)	HENRY'S LAW CONSTANT AT 25 (atm-m3/mol)	DIFFUSIVITY OF CHEM IN WATER AT 25 (cm2/s)	DIFFUSIVITY OF CHEM IN AIR AT 25 (cm2/s)	ANTOINE EQ VP COEFF A	ANTOINE EQ VP COEFF B	ANTOINE EQ VP COEFF C	MAX BIODEGRADE RATE CONSTANT (g/g biomass-s)	HALF SATURATE CONSTANT (g/m3)	OCTANOL-WATER PART COEFF AT 25 C
HYDROCYANIC ACID	74-90-8	27.00	726	.000000465	.0000182	.197	7.528	1329.5	260.4	.0000026944	1.9323	1
HYDROFLUORIC ACID	7664-39-3	20.00	900	.000237	.000033	.388	7.217	1268.37	273.87	.0000026944	1.9323	1
HYDROGEN SULFIDE	7783-06-4	34.10	15200	.023	.0000161	.176	7.614	885.319	250.25	.0000029889	6.3294	1
ISOPHORONE.	78-59-1	138.21	.439	.00000576	.00000676	.0623	0	0	0	.00000425	25.6067	50.11872
METHANOL	67-56-1	32.00	114	.0000027	.0000164	.15	7.897	1474.08	229.13	.000005	90	.19953
METHYL ACETATE	79-20-9	74.10	235	.000102	.00001	.104	7.065	1157.63	219.73	.0000055194	159.2466	.81283
METHYL CHLORIDE	74-87-3	50.50	3830	.00814	.0000065	.126	7.093	948.58	249.34	.0000029889	14.855	83.17638
METHYL ETHYL KETONE	78-93-3	72.10	100	.0000435	.0000098	.0808	6.9742	1209.6	216	.0000005556	10	1.90546
METHYL ISOBUTYL KETONE	108-10-1	100.20	15.7	.0000495	.0000078	.075	6.672	1168.4	191.9	.0000002056	1.6383	23.98833
METHYL METHACRYLATE	80-62-6	100.10	39	.000066	.0000086	.077	8.409	2050.5	274.4	.0000026944	109.2342	.33221
METHYL STYRENE (ALPHA)	98-83-9	118.00	.076	.00591	.0000114	.264	6.923	1486.88	202.4	.000008639	11.12438	2907.589
METHYLENE CHLORIDE	75-09-2	85.00	438	.00319	.0000117	.101	7.409	1325.9	252.6	.0000061111	54.5762	17.78279
MORPHOLINE	110-91-8	87.12	10	.0000573	.0000096	.091	7.7181	1745.8	235	.00000425	291.9847	.08318
NAPHTHALENE	91-20-3	128.20	.23	.00118	.0000075	.059	7.01	1733.71	201.86	.0000117972	42.47	1
NITROANILINE(-O)	88-74-4	138.14	.003	.0000005	.000008	.073	8.868	336.5	273.16	.00000425	22.8535	67.6083
NITROBENZENE	98-95-3	123.10	.3	.0000131	.0000086	.076	7.115	1746.6	201.8	.0000030556	4.7826	69.1831
PENTACHLOROBENZENE	608-93-5	250.34	.0046	.0073	.0000063	.057	0	0	0	.0000029889	.4307	925887.02902
PENTACHLOROETHANE	76-01-7	202.30	4.4	.021	.0000073	.066	6.74	1378	197	.0000029889	.4307	925887.02902
PENTACHLOROPHENOL	87-86-5	266.40	.00099	.0000028	.0000061	.056	0	0	0	.0000361111	38.2353	102329.29923
PHENOL	108-95-2	94.10	.34	.000000454	.0000091	.082	7.133	1516.79	174.95	.0000269444	7.4615	28.84032
PHOSGENE	75-44-5	98.92	1390	.171	.00000112	.108	6.842	941.25	230	.00000425	70.8664	3.4405
PHTHALIC ACID	100-21-0	166.14	121	.0132	.0000068	.064	0	0	0	.0000026944	34.983	6.64623
PHTHALIC ANHYDRIDE	85-44-9	148.10	.0015	.0000009	.0000086	.071	8.022	2868.5	273.16	.0000048872	3.9241	.23988
PICOLINE(-2)	108-99-6	93.12	10.4	.000127	.0000096	.075	7.032	1415.73	211.63	.00000425	44.8286	11.48154
POLYCHLORINATED BIPHENYLS	1336-36-3	290.00	.00185	.0004	.00001	.104	0	0	0	.000005278	20	1
PROPANOL (ISO)	71-23-8	60.09	42.8	.00015	.0000104	.098	8.117	1580.92	219.61	.0000041667	200	.69183
PROPIONALDEHYDE	123-38-6	58.08	300	.00115	.0000114	.102	16.2315	2659.02	-44.15	.0000026944	39.2284	4.91668
PROPYLENE GLYCOL	57-55-6	76.11	.3	.0000015	.0000102	.093	8.2082	2085.9	203.5396	.0000026944	109.3574	.33141
PROPYLENE OXIDE	75-66-9	58.10	525	.00134	.00001	.104	8.2768	1656.884	273.16	.0000048872	3.9241	1
PYRIDINE	110-86-1	79.10	20	.0000236	.0000076	.091	7.041	1373.8	214.98	.0000097306	146.9139	4.46684
RESORCINOL	108-46-3	110.11	.00026	.0000000188	.0000087	.078	6.9243	1884.547	186.0596	.0000026944	35.6809	6.30957

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CHEMICAL PROPERTY DATA FILE

CHEMICAL NAME	CAS NUMBER	MOLE WT	VAPOR PRESSURE AT 25 C (mm Hg)	HENRY'S LAW CONSTANT AT 25 (atm-m3/mol)	DIFFUSIVITY OF CHEM IN WATER AT 25 (cm2/s)	DIFFUSIVITY OF CHEM IN AIR AT 25 (cm2/s)	ANTOINE EQ VP COEFF A	ANTOINE EQ VP COEFF B	ANTOINE EQ VP COEFF C	MAX BIODEGRADE RATE CONSTANT (g/g biomass-s)	HALF SATURATE CONSTANT (g/m3)	OCTANOL-WATER PART COEFF AT 25 C
STYRENE	100-42-5	104.20	7.3	.00261	.000008	.071	7.14	1574.51	224.09	.0000086389	282.7273	1445.43977
TETRACHLOROETHANE(1,1,1,2)	630-20-6	167.85	6.5	.002	.0000079	.071	6.898	1365.88	209.74	.0000029889	6.3294	1
TETRACHLOROETHANE(1,1,2,2)	79-34-5	167.85	6.5	.00038	.0000079	.071	6.631	1228.1	179.9	.0000017222	9.1176	363.07805
TETRACHLOROETHYLENE	127-18-4	165.83	19	.029	.0000082	.072	6.98	1386.92	217.53	.0000017222	9.1176	398.10717
TETRAHYDROFURAN	109-99-9	72.12	72.1	.000049	.0000105	.098	6.995	1202.29	226.25	.0000026944	20.3702	27.58221
TOLUENE	109-88-3	92.40	30	.00668	.0000086	.087	6.954	1344.8	219.48	.0000204111	30.6167	489.77882
TOLUENE DIISOCYANATE(2,4)	584-84-9	174.16	.08	.0000083	.0000062	.061	0	0	0	.00000425	15.3	1
TRICHLORO(1,1,2)TRIFLUOROETHANE	76-13-1	187.38	300	.435	.0000082	.078	6.88	1099.9	227.5	.0000029889	3.3876	4068.32838
TRICHLOROBENZENE(1,2,4)	120-82-1	181.50	.18	.00142	.0000077	.0676	0	0	0	.0000029889	2.4495	9549.92586
TRICHLOROBUTANE(1,2,3)	NOCAS5	161.46	4.39	4.66	.0000072	.066	0	0	0	.0000029968	6.3412	1450901.06626
TRICHLOROETHANE(1,1,1)	71-55-6	133.40	123	.00492	.0000088	.078	8.643	2136.6	302.8	.0000009722	4.7297	309.02954
TRICHLOROETHANE(1,1,2)	79-00-5	133.40	25	.000742	.0000088	.078	6.951	1314.41	209.2	.0000009722	4.7297	1
TRICHLOROETHYLENE	79-01-6	131.40	75	.0091	.0000091	.079	6.518	1018.6	192.7	.0000010833	4.4318	194.98446
TRICHLOROFLUOROMETHANE	75-69-4	137.40	796	.0583	.0000097	.087	6.884	1043.004	236.88	.000003	6.3412	338.8441
TRICHLOROPHENOL(2,4,6)	88-06-2	197.46	.0073	.0000177	.0000075	.0661	0	0	0	.00000425	58.8462	4897.78819
TRICHLOROPROPANE(1,1,1)	NOCAS6	147.43	3.1	.029	.0000079	.071	0	0	0	.0000029889	10.7719	193.7827
TRICHLOROPROPANE(1,2,3)	96-18-4	147.43	3	.028	.0000079	.071	6.903	788.2	243.23	.0000029889	10.7719	193.7827
UREA	57-13-6	60.06	6.69	.000264	.0000137	.122	0	0	0	.00000425	4.8169	4068.32838
VINYL ACETATE	108-05-4	86.09	115	.00062	.0000092	.085	7.21	1296.13	226.66	.0000026944	31.8363	8.51722
VINYL CHLORIDE	75-01-4	62.50	2660	.086	.0000123	.106	3.425	0	0	.000003	6.3412	1.14815
VINYLIDENE CHLORIDE	75-35-4	97.00	591	.015	.0000104	.09	6.972	1099.4	237.2	.0000029968	6.3412	1
XYLENE(-M)	1330-20-7	106.17	8	.0052	.0000078	.07	7.009	1426.266	215.11	.0000086389	14.0094	1584.89319
XYLENE(-O)	95-47-6	106.17	7	.00527	.00001	.087	6.998	1474.679	213.69	.0000113306	22.8569	891.25094

References for Section 4.13

1. Hazardous Waste Treatment, Storage, And Disposal Facilities (TSDF) - Air Emission Models, EPA-450/3-87-026, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1989.

2. Waste Water Treatment Compound Property Processor Air Emissions Estimator (WATER 7). Office of Air Quality Planning And Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC, available early 1992.

3. Evaluation of Test Method For Measuring Biodegradation Rates Of Volatile Organics, Draft, EPA Contract No. 68-D90055, Entropy Environmental, Research Triangle Park, NC, September 1989.

4. Industrial Waste Water Volatile Organic Compound Emissions - Background Information For BACT/LAER Determinations, EPA-450/3-90-004, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1990.

5. Evan K. Nyer, Ground Water Treatment Technology, Van Nostrand Reinhold Company, New York, 1985.

5.13 PLASTICS

5.13.1 POLYVINYL CHLORIDE AND POLYPROPYLENE

5.13.1.1 Process Description[1]

The manufacture of most resins or plastics begins with the polymerization or linking of the basic compound (monomer), usually a gas or liquid, into high molecular weight noncrystalline solids. The manufacture of the basic monomer is not considered part of the plastics industry and is usually accomplished at a chemical or petroleum plant.

The manufacture of most plastics involves an enclosed reaction or polymerization step, a drying step, and a final treating and forming step. These plastics are polymerized or otherwise combined in completely enclosed stainless steel or glass-lined vessels. Treatment of the resin after polymerization varies with the proposed use. Resins for moldings are dried and crushed or ground into molding powder. Resins such as the alkyd to be used for protective coatings are usually transferred to an agitated thinning tank, where they are thinned with some type of solvent and then stored in large steel tanks equipped with water-cooled condensers to prevent loss of solvent to the atmosphere. Still other resins are stored in latex form as they come from the kettle.

5.13.1.2 Emissions And Controls[1]

The major sources of air contamination in plastics manufacturing are the raw materials or monomers, solvents, or other volatile liquids emitted during the reaction; sublimed solids such as phthalic anhydride emitted in alkyd production, and solvents lost during storage and handling of thinned resins. Emission factors for the manufacture of polyvinyl chloride and polypropylene are shown in Table 5.13-1.

Table 5.13.1-1. UNCONTROLLED EMISSION FACTORS FOR PLASTICS MANUFACTURING[a]

EMISSION FACTOR RATING: E

Type of Plastic	Particulate		Gases	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Polyvinyl chloride	17.5[b]	35[b]	8.5[c]	17[c]
Polypropylene	1.5	3	0.35[d]	0.7[d]

[a] References 2-3.
[b] Usually controlled with fabric filter, efficiency of 98-99%.
[c] As vinyl chloride.
[d] As propylene.

Much of the control equipment used in this industry is a basic part of the system, serving to recover a reactant or product. These controls include floating roof tanks or vapor recovery systems on volatile material, storage units, vapor recovery systems (adsorption or condensers), purge lines venting to a flare system, and vacuum exhaust line recovery systems.

References for Section 5.13

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, VA. Prepared for National Air Pollution Control Administration, Durham, NC, under Contract Number CPA-22-69-119. April 1970.

2. Unpublished data. U. S. Department of Health and Human Services, National Air Pollution Control Administration, Durham, NC, 1969.

3. Communication between Resources Research, Inc., Reston, VA, and State Department of Health, Baltimore, MD, November 1969.

5.13.2 POLY(ETHYLENE TEREPHTHALATE)[1-2]

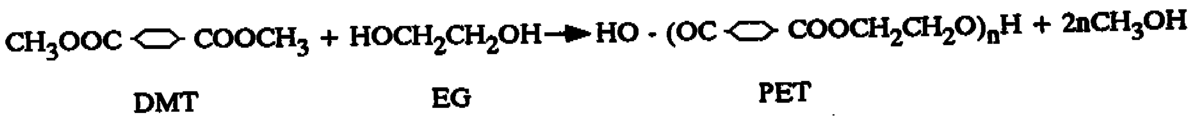
5.13.2.1 General

Poly(ethylene terephthalate), or PET, is a thermoplastic polyester resin. Such resins may be classified as low viscosity or high viscosity resins. Low viscosity PET typically has an intrinsic viscosity of less than 0.75, while high viscosity PET typically has an intrinsic viscosity of 0.9 or higher. Low viscosity resins, which are sometimes referred to as "staple" PET (when used in textile applications), are used in a wide variety of products, such as apparel fiber, bottles, and photographic film. High viscosity resins, sometimes referred to as "industrial" or "heavy denier" PET, are used in tire cord, seat belts, and the like.

PET is used extensively in the manufacture of synthetic fibers (i. e., polyester fibers), which compose the largest segment of the synthetic fiber industry. Since it is a pure and regulated material meeting FDA food contact requirements, PET is also widely used in food packaging, such as beverage bottles and frozen food trays that can be heated in a microwave or conventional oven. PET bottles are used for a variety of foods and beverages, including alcohol, salad dressing, mouthwash, syrups, peanut butter, and pickled food. Containers made of PET are being used for toiletries, cosmetics, and household and pharmaceutical products (e. g., toothpaste pumps). Other applications of PET include molding resins, X-ray and other photographic films, magnetic tape, electrical insulation, printing sheets, and food packaging film.

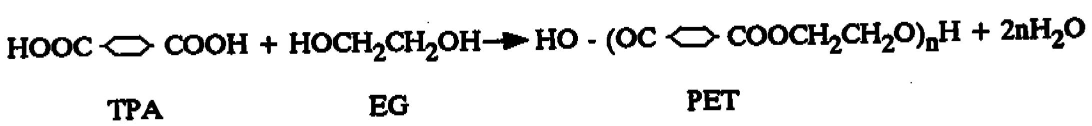
5.13.2.2 Process Description[3-15]

PET resins are produced commercially from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). DMT and TPA are solids. DMT has a melting point of 140°C (284°F), while TPA sublimes (goes directly from the solid phase to the gaseous phase). Both processes first produce the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer and either methanol (DMT process) or water (TPA process). The BHET monomer is then polymerized under reduced pressure with heat and catalyst to produce PET resins. The primary reaction for the DMT process is:



$$CH_3OOC \text{⬡} COOCH_3 + HOCH_2CH_2OH \rightarrow HO\text{-}(OC \text{⬡} COOCH_2CH_2O)_nH + 2nCH_3OH$$

The primary reaction for the TPA process is:



$$HOOC \text{⬡} COOH + HOCH_2CH_2OH \rightarrow HO\text{-}(OC \text{⬡} COOCH_2CH_2O)_nH + 2nH_2O$$

Both processes can produce low and high viscosity PET. Intrinsic viscosity is determined by the high polymerizer operating conditions of (1) vacuum level, (2) temperature, (3) residence time, and (4) agitation (mechanical design).

The DMT process is the older of the two processes. Polymerization grade TPA has been available only since 1963. The production of methanol in the DMT process creates the need for methanol recovery and purification operations. In addition, this methanol can produce major VOC emissions. To avoid the need to recover and purify the methanol and to eliminate the potential VOC emissions, newer plants tend to use the TPA process.

DMT Process - Both batch and continuous operations are used to produce PET using DMT. There are three basic differences between batch process and continuous process, (1) a column-type reactor replaces the kettle reactor for esterification (ester exchange between DMT and ethylene glycol), (2) "no-back-mix" (i. e., no stirred tank) reactor designs are required in the continuous operation, and (3) different additives and catalysts are required to ensure proper product characteristics (e. g., molecular weight, molecular weight distribution).

Figure 5.13.2-1 is a schematic representation of the PET/DMT continuous process, and the numbers and letters following refer to this figure. Ethylene glycol is drawn from raw material storage (1) and fed to a mix tank (2), where catalysts and additives are mixed in. From the mix tank, the mixture is fed, along with DMT, to the esterifiers, also known as ester exchange reactors (3). About 0.6 pounds (lbs) of ethylene glycol and 1.0 lbs of DMT are used for each pound of PET product. In the esterifiers, the first reaction step occurs at an elevated temperature (between 170 and 230°C [338 and 446°F]) and at or above atmospheric pressure. This reaction produces the intermediate BHET monomer and the byproduct methanol. The methanol vapor must be removed from the esterifiers to shift the conversion to produce more BHET.

The vent from the esterifiers is fed to the methanol recovery system (11), which separates the methanol by distillation in a methanol column. The recovered methanol is then sent to storage (12). Vapor from the top of the methanol column is sent to a cold water (or refrigerated) condenser, where the condensate returns to the methanol column, and noncondensables are purged with nitrogen before being emitted to the atmosphere. The bottom product of methanol column, mostly ethylene glycol from the column's reboiler, is reused.

The BHET monomer, with other esterifier products, is fed to a prepolymerization reactor (4) where the temperature is increased to 230 to 285°C (446 to 545°F), and the pressure is reduced to between 1 and 760 millimeters (mm) of mercury (Hg) (typically, 100 to 200 mm Hg). At these operating conditions, residual methanol and ethylene glycol are vaporized, and the reaction that produces PET resin starts.

Product from the prepolymerizer is fed to one or more polymerization reactors (5), in series. In the polymerization reactors, sometimes referred to as end finishers, the temperature is further increased to 260 to 300°C (500 to 572°F). The pressure is further reduced (e. g., to an absolute pressure of 4 to 5 mm Hg). The final temperature and pressure depend on whether low or high viscosity PET is being produced. For high viscosity PET, the pressure in the final (or second) end finisher is less than 2 mm Hg. With high viscosity PET, more process vessels are used than low viscosity PET, to achieve the higher temperatures and lower pressures needed.

The vapor (ethylene glycol, methanol, and other trace hydrocarbons from the prepolymerization and polymerization reactors) typically is evacuated through scrubbers (spray condensers) using spent ethylene glycol. The recovered ethylene glycol is recirculated in the

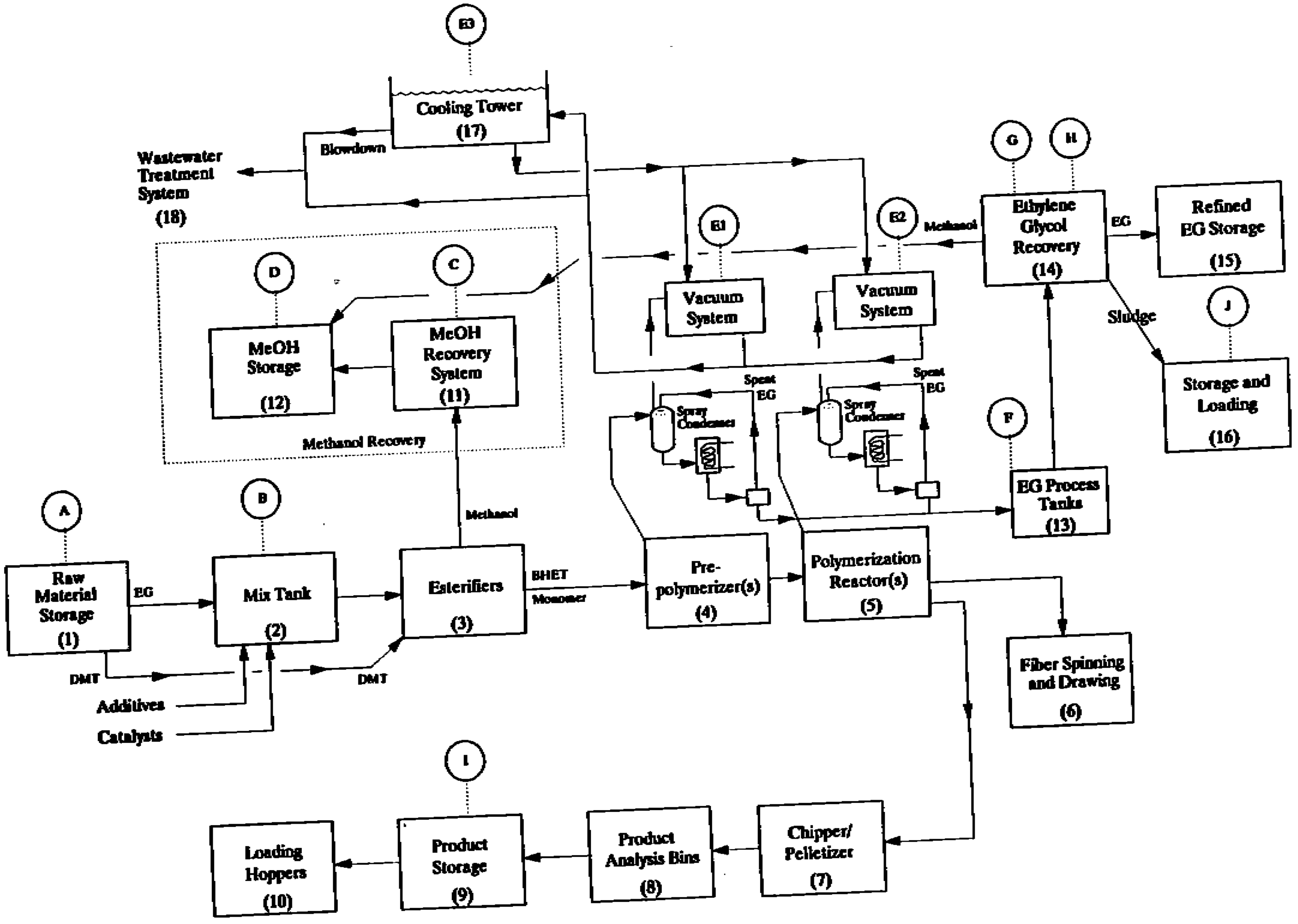


Figure 5.13.2-1. Simplified flow diagram of PET/DMT continuous process.

scrubber system, and part of the spent ethylene glycol from the scrubber system is sent to storage in process tanks (13), after which it is sent to the ethylene glycol recovery system (14).

The ethylene glycol recovery system (14) usually is a distillation system composed of a low boiler column, a refining column, and associated equipment. In such a system, the ethylene glycol condensate is fed to the low boiler column. The top product from this column is sent to a condenser, where methanol is condensed and sent to methanol storage. The noncondensable vent (from the low boiler condenser) is purged with nitrogen and sent to the atmosphere (Stream G in the flow diagram). The bottom product of the low boiler column goes to its reboiler, with the vapor recycled back to the low boiler column and the underflow sent to the refining column. The refining column is under vacuum and is evacuated to the atmosphere. Top product from the refining column goes through a condenser, and the condensate is collected in a reflux tank. Part of the ethylene glycol condensate returns to the refining column. The remaining liquid goes to refined ethylene glycol storage (15). The reflux tank is purged with nitrogen. (The purge gas vented to the atmosphere from the reflux tank consists of only nitrogen.) The bottom product of the refining column goes to a reboiler, vapor returns to the column, and what remains is a sludge byproduct (16).

The vacuum conditions in the prepolymerization and polymerization reactors are created by means of multi-stage steam jet ejector (venturi) systems. The vacuum system typically is composed of a series of steam jets, with condensers on the discharge side of the steam jet to cool the jets and to condense the steam. The condensed steam from the vacuum jets and the evacuated vapors are combined with the cooling water during the condensation process. This stream exiting the vacuum system goes either to a cooling tower (17), where the water is cooled and then recirculated through the vacuum system, or to a waste water treatment plant (once-through system) (18).

Product from the polymerization reactor (referred to as the polymer melt) may be sent directly to fiber spinning and drawing operations (6). Alternatively, the polymer melt may be chipped or pelletized (7), put into product analysis bins (8), and then sent to product storage (9) before being loaded into hoppers (10) for shipment to the customer.

TPA Process - Figure 5.13.2-2 is a schematic diagram of a continuous PET/TPA process, and the numbers and letters following refer to this figure. Raw materials are brought on site and stored (1). Terephthalic acid, in powder form, may be stored in silos. The ethylene glycol is stored in tanks. The terephthalic acid and ethylene glycol, containing catalysts, are mixed in a tank (2) to form a paste. In the mix tank, ethylene glycol flows into a manifold that sprays the glycol through many small slots around the periphery of the vent line. The terephthalic acid and ethylene glycol are mixed by kneading elements working in opposite directions. Combining these materials into a paste is a simple means of introducing them to the process, allowing more accurate control of the feed rates to the esterification vessels. A portion of the paste is recycled to the mix tank. This paste recycle and feed rates of TPA and ethylene glycol are used to maintain an optimum paste density or weight percent of terephthalic acid.

The paste from the mix tanks is fed, using gear pumps to meter the flow, to a series of esterification vessels (referred to esterifiers, or ester exchange reactors). Two or more esterifiers may be used. Residence time is controlled by valves in the transfer lines between each vessel. These esterifiers are closed, pressurized reactors. Pressure and temperature operating conditions in the primary esterifier (3) are between 30 and 50 pounds per square inch gauge (psig) and 230 to 260°C (446 to 500°F), respectively. Vapors, primarily water (steam) and glycol, are vented to a

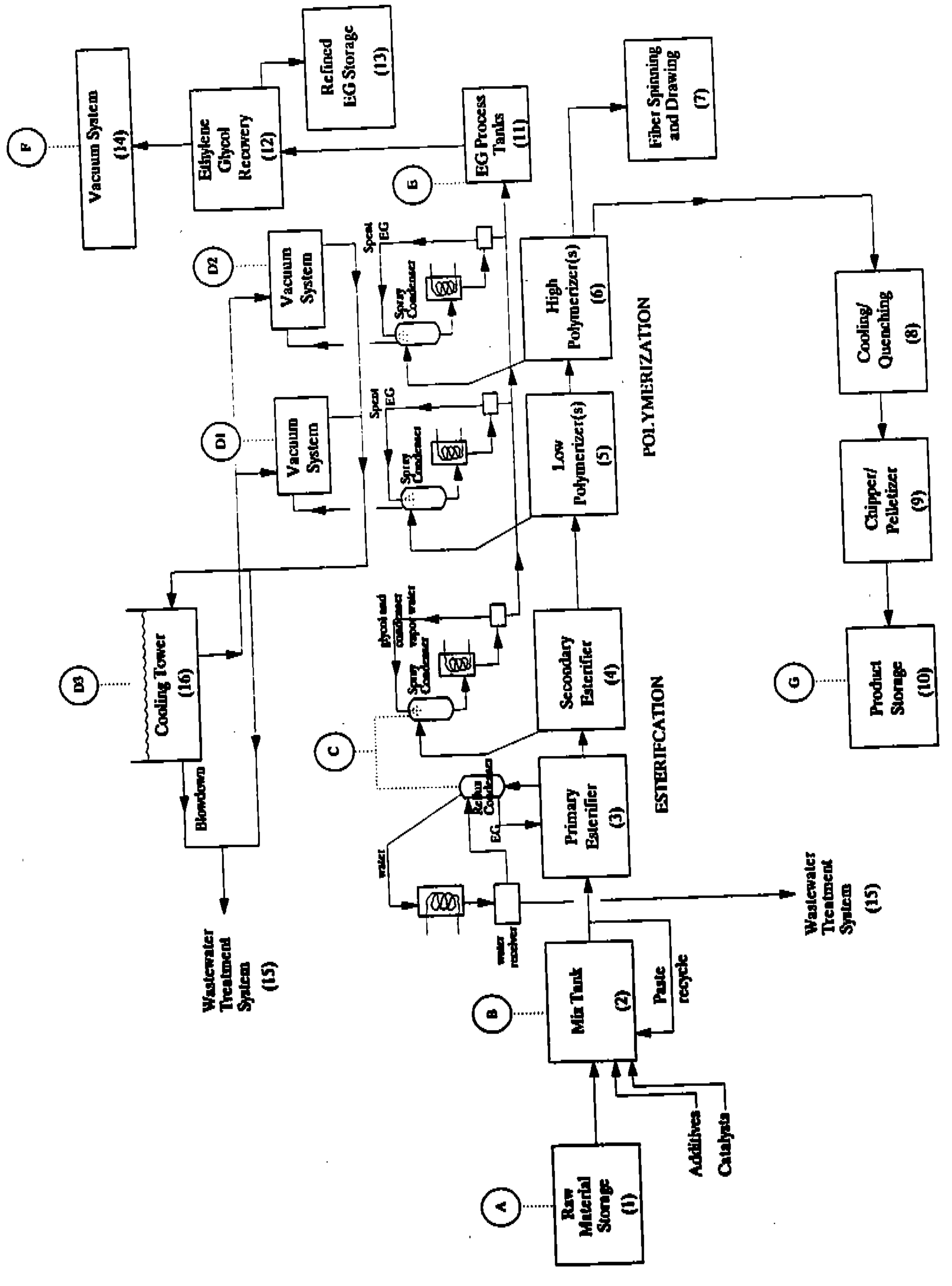


Figure 5.13.2-2. Simplified flow diagram of PET/TPA continuous process.

reflux column or distillation column. A heat exchanger cools the vapors. Recovered glycol is returned to the primary esterifier. The water vapor is condensed using 29°C (85°F) cooling water in a shell-and-tube condenser and then is discharged to the waste water treatment system. The monomer formed in the primary esterifier and the remaining reactants are pumped to the secondary esterifier.

The secondary esterifier (4) is operated at atmospheric pressure and at a temperature of 250 to 270°C (482 to 518°F). The vapors from the secondary esterifier, primarily water vapor, are vented to a spray condenser, and this condensate is sent to a central ethylene glycol recovery unit (12). The condensate water is cooled by cooling water in a shell-and-tube heat exchanger and then recycled.

At one plant, the secondary esterifiers for the staple PET lines have a manhole (or rotary valve on some lines) through which chips and reworked yarn pellets were recycled. These manholes are not present on the secondary esterifiers for the industrial PET lines. Water vapor and monomer are emitted from the manholes, and the monomer sublimates on piping near the manhole.

Monomer (BHET) from the secondary esterifier is then pumped to the polymerization reactors. The number of reactors and their operating conditions depend on the type of PET being produced. Typically, there will be at least two polymerization reaction vessels in series, an initial (low) polymerizer and a final (high) polymerizer. The former is sometimes referred to as a prepolymerizer or a prepolycondensation reactor. The latter is sometimes called an end finisher. In producing high viscosity PET, a second end finisher is sometimes used.

In the initial (low) polymerizer (5), esterification is completed and polymerization occurs (i. e., the joining of short molecular chains). Polymerization is "encouraged" by the removal of ethylene glycol. This reactor is operated under pressures of 20 to 40 mm Hg and at 270 to 290°C (518 to 554°F) for staple (low viscosity) PET, and 10 to 20 mm Hg and 280 to 300°C (536 to 572°F) for industrial filament PET. The latter conditions produce a longer molecule, with the greater intrinsic viscosity and tenacity required in industrial fiber. Glycol released in the polymerization process and any excess or unreacted glycol are drawn into a contact spray condenser (scrubber) countercurrent to a spent ethylene glycol spray. (At one facility, both the low and high polymerizer spray condensers have four spray nozzles, with rods to clear blockage by solidified polymer. Care is taken to ensure that the spray pattern and flow are maintained.) Recovered glycol is pumped to a central glycol recovery unit, a distillation column. Vacuum on the reactors is maintained by a series of steam jets with barometric intercondensers. At one plant, a two-stage steam ejector system with a barometric intercondenser is used to evacuate the low polymerizer. The condensate from the intercondensers and the last steam jets is discharged to an open recirculating water system, which includes an open trough (referred to as a "hot well") and cooling tower. The recirculation system supplies cooling water to the intercondensers.

In the production of high viscosity PET, the polymer from the low polymerizer is pumped to a high polymerizer vessel (6). In the high polymerizer, the short polymer chains formed in the low polymerizer are lengthened. Rotating wheels within these vessels are used to create large surface exposure for the polymer to facilitate removal of ethylene glycol produced by the interchange reaction between the glycol ester ends. The high polymerizer is operated at a low absolute pressure (high vacuum), 0.1 to 1.0 mm Hg, and at about 280 to 300°C. Vapors evolved in the high polymerizer, including glycol, are drawn through a glycol spray condenser. If very "hard" vacuums are drawn (e. g., 0.25 mm Hg), such spray condensers are very difficult, if not impossible, to use. At least one facility does not use any spray condensers off the polymerizers (low and high). Recovered glycol is collected in a receiver and is pumped to a central ethylene glycol recovery unit. At one plant, chilled water between -3.9 and 1.7°C (25 and 35°F) is used on the heat exchanger associated with the high polymerizer spray condenser.

At least one facility uses two high polymerizers (end finishers) to produce high viscosity PET. At this plant, the first end finisher is usually operated with an intermediate vacuum level of about 2 mm Hg. The polymer leaving this reactor then enters a second end finisher, which may have a vacuum level as low as 0.25 mm Hg.

Vapors from the spray condenser off the high polymerizers are also drawn through a steam jet ejector system. One facility uses a five-jet system. After the first three ejectors, there is a barometric intercondenser. Another barometric intercondenser is located between the fourth and fifth ejectors. The ejectors discharge to the cooling water hot well. The stream exiting the vacuum system is sent either to a cooling tower (16) where the water is recirculated through the vacuum system, or to a waste water treatment plant (once-through system) (15).

Vacuum pumps were installed at one plant as an alternative to the last two ejectors. These pumps were installed as part of an energy conservation program and are used at the operator's discretion. The vacuum pumps are operated about 50 percent of the time. The vacuum system was designed for a maximum vapor load of about 10 kilograms per hour (kg/hr). If vacuum is lost, or is insufficient in the low or high polymerizers, off-specification product results. Each process line has a dual vacuum system. One five-stage ejector/vacuum pump system is maintained as a standby for each industrial filament (high viscosity) process line. The staple (low viscosity) lines have a standby ejector system, but with only one vacuum pump per process line. Steam ejectors reportedly recover faster from a slug of liquid carryover than do vacuum pumps, but the spare system is used in the production of either high or low viscosity PET.

At many facilities, molten PET from the high polymerizer is pumped at high pressure directly through an extruder spinerette, forming polyester filaments (7). The filaments are air cooled and then either cut into staple or wound onto spools. Molten PET can also be pumped out to form blocks as it cools and solidifies (8), which are then cut into chips or are pelletized (9). The chips or pellets are stored (10) before being shipped to the customer, where they are remelted for end-product fabrication.

Ethylene glycol recovery (12) generally involves a system similar to that of the DMT process. The major difference is the lack of a methanol recovery step. At least one TPA facility has a very different process for ethylene glycol recovery. At this plant, ethylene glycol emissions from the low and high polymerizers are allowed to pass directly to the vacuum system and into the cooling tower. The ethylene glycol is then recovered from the water in the cooling tower. This arrangement allows for a higher ethylene glycol concentration in the cooling tower.

5.13.2.3 Emissions And Controls[3,5,11,13,16-21]

Table 5.13.2-1 shows the VOC and particulate emissions for the PET/DMT continuous process, with similar levels expected for batch processes. The extensive use of spray condensers and other ethylene glycol and methanol recovery systems is economically essential to PET production, and these are not generally considered "controls".

TABLE 5.13.2-1. EMISSION FACTORS FOR PET/DMT PROCESS[a]

Stream Identification	Emission Stream	Nonmethane VOC[b]	Particulate	Emission Factor Rating	References
A	Raw material storage	0.1	0.165[c]	C	17
B	Mix tanks	negligible[d]	-	C	13
C	Methanol recovery system	0.3[e]	-	C	3, 17
D	Recovered methanol storage	0.09[f]	-	C	3, 17
E	Polymerization reaction				
E1	Prepolymerizer vacuum system	0.009	-	C	17
E2	Polymerization reactor vacuum system	0.005	-	C	17
E3	Cooling tower[g]	0.2 3.4	-	C	18-19
F	Ethylene glycol process tanks	0.0009	-	C	17
G	Ethylene glycol recovery condenser	0.01	-	C	17
H	Ethylene glycol recovery vacuum system	0.0005	-	C	17
I	Product storage	-	0.0003[h]	C	17
J	Sludge storage and loading	0.02	-	C	17
Total Plant		0.73[i] 3.9[j]	0.17		

[a] Stream identification refers to Figure 5.13.2-1. Units are grams per kilogram of product. Dash = no data.

[b] Rates reflect extensive use of condensers and other recovery equipment as part of normal industry economical practice.

[c] From storage of DMT.

[d] Assumed same as for TPA process.

[e] Reference 3. For batch PET production process, estimated to be 0.15 grams VOC per kilogram of product.

[f] Reflects control by refrigerated condensers.

[g] Based on ethylene glycol concentrations at two PET/TPA plants. The lower estimate reflects emissions where spray condensers are used off the prepolymerizers and the polymerization reactors. The higher estimate reflects emissions where spray condensers are not used off the prepolymerizers and the polymerization reactors. A site-specific calculation is highly recommended for all cooling towers, because of the many variables. The following equation may be used to estimate windage emissions from cooling towers:

$$E = [EG_{wt\%} \times CT_{cr} \times 60 \times WR] \times [(4.2 \times EG_{wt\%}) + (3.78 \times H_2O_{wt\%})]$$

where E = Mass of VOC emitted (kilograms per hour)
$EG_{wt\%}$ = Concentration of ethylene glycol, weight percent (fraction)
CT_{cr} = Cooling tower circulation rate, gallons per minute
WR = Windage rate, fraction
4.2 = Density of ethylene glycol (kilograms per gallon)
3.78 = Density of water (kilograms per gallon)

$H_2O_{wt\%}$ = Concentration of water, weight percent (fraction)
60 = Minutes per hour

Example: The VOC emissions from a cooling tower with a ethylene glycol concentration of 8.95% by weight, a water concentration of 91.05% by weight, a cooling tower circulation rate of 1270 gallons per minute, and a windage rate of 0.03% are estimated to be:

$$E = [0.0895 \times 1270 \times 60 \times 0.0003] \times [(4.2 \times 0.0895) + (3.78 \times 0.9105)]$$

$$= 7.8 \text{ kilograms per hour}$$

[h] Emission rate is for "controlled" emissions. Without controls, the estimated emission rate is 0.4 grams per kilogram of product.

[i] With spray condensers off all prepolymerizers and the polymerization reactors.

[j] With no spray condensers off all prepolymerizers and the polymerization reactors.

Total VOC emissions will depend greatly on the type of system used to recover the ethylene glycol from the prepolymerizers and polymerization reactors, which give rise to emission streams E1, E2, E3, F, G, H, and J. The emission streams from the prepolymerizers and polymerization reactors are primarily ethylene glycol, with small amounts of methanol vapors and volatile impurities in the raw materials. Of these emission streams, the greatest emission potential is from the cooling tower (Stream E3). The amount of emissions from the cooling tower depends on a number of factors, including ethylene glycol concentration and windage rate. The ethylene glycol concentration depends on a number of factors, including use of spray condensers off of the polymerization vessels, circulation rate of the cooling water in the cooling tower, blowdown rate (the rate are which water is drawn out of the cooling tower), and sources of water to cooling tower (e. g., dedicated cooling tower versus plant-side cooling tower).

Most plants recover the ethylene glycol by using a spent ethylene glycol spray scrubber condenser directly off these process vessels and before the stream passes through the vacuum system. The condensed ethylene glycol may then be recovered through distillation. This type of recovery system results in relatively low concentrations of ethylene glycol in the cooling water at the tower, which in turn lowers emission rates for the cooling tower and the process as a whole. At one PET/TPA plant, a typical average concentration of about 0.32 weight percent ethylene glycol was reported, from which an emission rate of 0.2 grams VOC per kilogram (gVOC/kg) of product was calculated.

Alternatively, a plant may send the emission stream directly through the vacuum system (typically steam ejectors) without using spent ethylene glycol spray condensers. The steam ejectors used to produce a vacuum will produce in contaminated water, which is then cooled for reuse. In this system, ethylene glycol is recovered from the water in the cooling tower by drawing off water from the tower (blowdown) and sending the blowdown to distillation columns. This method of recovering ethylene glycol can result in much higher concentrations of ethylene glycol in the cooling tower than when the ethylene glycol is recovered with spray condensers directly off of the process vessels. (The actual concentration of ethylene glycol in the cooling water depends, in part, on the blowdown rate.) Higher concentrations in the cooling tower result in greater ethylene glycol emissions from the cooling tower and, in turn, from the process as a whole. At one PET/TPA plant recovering the ethylene glycol from the cooling tower, emissions from the cooling tower were approximately 3.4 gVOC/kg of product.

Next to the cooling tower, the next largest potential emission source in the PET/DMT process is the methanol recovery system. Methanol recovery system emissions (Stream C) from a plant using a continuous process are estimated to be approximately 0.3 gVOC/kg of product and about 0.09 gVOC/kg of product from the recovered methanol storage tanks. The emissions from the methanol recovery system (Stream C) for a batch process were reported to be 0.15 gVOC/kg of product, and typically are methanol and nitrogen.

The other emission streams related to the prepolymerizer and polymerization reactors are collectively relatively small, being about 0.04 gVOC/kg of product. VOC emissions from raw material storage (mostly ethylene glycol) are estimated to be about 0.1 gVOC/kg of product. Fixed roof storage tanks (ethylene glycol) and bins (DMT) are used throughout the industry. Emissions are vapors of ethylene glycol and DMT result from vapor displacement and tank breathing. Emissions from the mix tank are believed to be negligible.

Particulate emissions occur from storage of both raw material (DMT) and end product. Those from product storage may be controlled before release to the atmosphere. Uncontrolled particulate emissions from raw material storage are estimated to be approximately 0.17 g/kg of product. Particulate emissions from product storage are estimated to be approximately 0.0003 g/kg of product after control and approximately 0.4 g/kg of product before control.

In summary, total VOC emissions from a PET/DMT continuous process are approximately 0.74 gVOC/kg of product, if spray condensers are used off all of the prepolymerizers and polymerization reaction vessels. For a batch process, this total decreases to approximately 0.59 gVOC/kg of product. If spray condensers are not used, the ethylene glycol concentration in the cooling tower is expected to be higher, and total VOC emissions will be greater. Calculation of cooling tower emissions for site-specific plants is recommended. Total particulate emissions are approximately 0.17 g/kg of product, if product storage emissions are controlled.

Table 5.13.2-2 summarizes VOC and particulate emissions for the PET/TPA continuous process, and similar emission levels are expected for PET/TPA batch processes. VOC emissions are generally "uncontrolled", in that the extensive use of spray condensers and other ethylene glycol recovery systems are essential to the economy of PET production.

Emissions from raw material storage include losses from the raw materials storage and transfer (e. g., ethylene glycol). Fixed roof storage tanks and bins with conservation vents are used throughout the process. The emissions, vapors of ethylene glycol, TPA, and TPA dust, are from working and breathing losses. The VOC emission estimate for raw materials storage is assumed to be the same as that for the PET/DMT process. No emission estimate was available for the storage and transfer of TPA.

VOC emissions from the mix tank are believed to be negligible. They are emitted at ambient temperatures through a vent line from the mixer.

VOC emissions from the esterifiers occur from the condensers/distillation columns on the esterifiers. Emissions, which consist primarily of steam and ethylene glycol vapors, with small amounts of feed impurities and volatile side reaction products, are estimated to be 0.04 gVOC/kg of product. Exit temperature is reported to be approximately 104°C (220°F). At least one plant

Table 5.13.2-2. EMISSION FACTORS FOR PET/TPA PROCESS[a]

Stream Identification	Emission Stream	Nonmethane VOC[b]	Particulate	Emission Factor Rating	References
A	Raw material storage	0.1[c]	-	C	17
B	Mix tanks	negligible	-	C	13
C	Esterification	0.04[d]	-	A	20-21
D	Polymerization reaction				
D1	Prepolymerizer vacuum system	0.009[c]	-	C	17
D2	Polymerization reactor vacuum system	0.005[c]	-	C	17
D3	Cooling tower[e]	0.2 3.4	-	C	18-19
E	Ethylene glycol process tanks	0.0009[c]	-	C	17
F	Ethylene glycol recovery vacuum system	0.0005[c]	-	C	17
G	Product storage	-	0.0003[c,f]	C	17
Total Plant		0.36[g] 3.6[h]			

[a] Stream identification refers to Figure 5.13.2-2. Units are grams per kilogram of product. Dash = no data.

[b] Rates reflect extensive use of condensers and other recovery equipment as part of normal industry economical practice.

[c] Assumed same as for DMT process.

[d] At least one plant controls the primary esterifier condenser vent with a second condenser. Emissions were 0.0008 grams VOC per kilograms of product with the second condenser operating, and 0.037 grams VOC per kilogram of product without the second condenser operating.

[e] Based on ethylene glycol concentrations at two PET/TPA plants. The lower estimate reflects emissions where spray condensers are used off the prepolymerizers and the polymerization reactors. The higher estimate reflects emissions where spray condensers are not used off the prepolymerizers and the polymerization reactors. It is highly recommended that a site-specific calculation be done for all cooling towers as many variables affect actual emissions. The equation found in footnote g for Table 5.13.2-1 may be used to estimate windage emissions from cooling towers.

[f] Reflects control of product storage emissionss. Without controls, the estimated emission rate is 0.4 grams per kilogram of product.

[g] With spray condensers off all prepolymerizers and the polymerization reactors.

[h] With no use of spray condensers off all prepolymerizers and the polymerization reactors.

controls the primary esterifier condenser vent with a second condenser. At this plant, emissions were 0.0008 gVOC/kg of product with the second condenser operating, and 0.037 gVOC/kg of product without the second condenser operating. The temperature for the emission stream from the second condenser was reported to be 27 to 38°C (80 to 100°F). The emissions from the second condenser were composed di-iso-propyl amine (DIPA) and acetaldehyde, with small amounts of ethylene.

Emissions from the prepolymerizers and polymerization reaction vessels in both PET/TPA and PET/DMT processes should be very similar. The emissions were discussed earlier under the DMT process.

The estimates of VOC emissions from the ethylene glycol process tanks and the ethylene glycol recovery system, and of particulate emissions from product storage, are assumed to be the same as for the DMT process.

In summary, total VOC emissions from the PET/TPA process are approximately 0.36 gVOC/kg of product, if spray condensers are used with all of the prepolymerizers and polymerization reaction vessels. If spray condensers are not used with all of these process vessels, the concentration in the cooling tower can be expected to be higher, and total VOC emissions will be greater. For example, at one plant, emissions from the cooling tower were calculated to be approximately 3.4 gVOC/kg of product, resulting in a plant-wide estimate of 3.6 gVOC/kg of product. Calculation of cooling tower emissions for site-specific plants is recommended. Excluding TPA particulate emissions (no estimate available), total particulate emissions are expected to be small.

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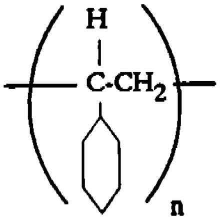
5.13.3 POLYSTYRENE[1-2]

5.13.3.1 General

Styrene readily polymerizes to polystyrene by a relatively conventional free radical chain mechanism. Either heat or initiators will begin the polymerization. Initiators thermally decompose, thereby forming active free radicals that are effective in starting the polymerization process. Typically initiators used in the suspension process include benzoyl peroxide and di-tert-butyl per-benzoate. Potassium persulfate is a typical initiator used in emulsion polymerizations. In the presence of inert materials, styrene monomer will react with itself to form a homopolymer. Styrene monomer will react with a variety of other monomers to form a number of copolymers.

Polystyrene is an odorless, tasteless, rigid thermoplastic. Pure polystyrene has the following structure.



The homopolymers of styrene are also referred to as general purpose, or crystal, polystyrene. Because of the brittleness of crystal polystyrene, styrene is frequently polymerized in the presence of dissolved polybutadiene rubber to improve the strength of the polymer. Such modified polystyrene is called high impact, or rubber-modified, polystyrene. The styrene content of high impact polystyrene varies from about 88 to 97 percent. Where a blowing (or expanding) agent is added to the polystyrene, the product is referred to as an expandable polystyrene. The blowing agent may be added during the polymerization process (as in the production of expandable beads), or afterwards as part of the fabrication process (as in foamed polystyrene applications).

Polystyrene is the fourth largest thermoplastic by production volume. It is used in applications in the following major markets (listed in order of consumption): packaging, consumer/institutional goods, electrical/electronic goods, building/construction, furniture, industrial/machinery, and transportation.

Packaging applications using crystal polystyrene biaxial film include meat and vegetable trays, blister packs, and other packaging where transparency is required. Extruded polystyrene foam sheet is formed into egg carton containers, meat and poultry trays, and fast food containers requiring hot or cold insulation. Solid polystyrene sheet is formed into drinking cups and lids, and disposable packaging of edibles. Injection molded grades of polystyrene are used extensively in the manufacture of cosmetic and personal care containers, jewelry and photo equipment boxes, and photo film packages. Other formed polystyrene items include refrigerator door liners, audio and video cassettes, toys, flower pots, picture frames, kitchen utensils, television and radio cabinets, home smoke detectors, computer housings, and profile moldings in the construction/home-building industry.

5.13.3.2 General Purpose And High Impact Polystyrene[1-2]

Homopolymers and copolymers can be produced by bulk (or mass), solution (a modified bulk), suspension, or emulsion polymerization techniques. In solution (or modified bulk) polymerization, the reaction takes place as the monomer is dissolved in a small amount of solvent, such as ethylbenzene. Suspension polymerization takes place with the monomer suspended in a water phase. The bulk and solution polymerization processes are homogenous (taking place in one phase), whereas the suspension and emulsion polymerization processes are heterogeneous (taking place in more than one phase). The bulk (mass) process is the most widely used process for polystyrene today. The suspension process is also common, especially in the production of expandable beads. Use of the emulsion process for producing styrene homopolymer has decreased significantly since the mid-1940s.

5.13.3.1.1 Process Descriptions[1-3]

Batch Process - Various grades of polystyrene can be produced by a variety of batch processes. Batch processes generally have a high conversion efficiency, leaving only small amounts of unreacted styrene to be emitted should the reactor be purged or opened between batches. A typical plant will have multiple process trains, each usually capable of producing a variety of grades of polystyrene.

Figure 5.13.3-1 is a schematic representation of the polystyrene batch bulk polymerization process, and the following numbered steps refer to that figure. Pure styrene monomer (and comonomer, if a copolymer product is desired) is pumped from storage (1) to the feed dissolver (2). For the production of impact grade polystyrene, chopped polybutadiene rubber is added to the feed dissolver, where it is dissolved in the hot styrene. The mixture is agitated for 4 to 8 hours to complete rubber dissolution. From the feed dissolver, the mixture usually is fed to an agitated tank (3), often a prepolymerization reactor, for mixing the reactants. Small amounts of mineral oil (as a lubricant and plasticizer), the dimer of alpha-methylstyrene (as a polymerization regulator), and an antioxidant are added. The blended or partially polymerized feed is then pumped into a batch reactor (4). During the reactor filling process, some styrene vaporizes and is vented through an overflow vent drum (5). When the reactor is charged, the vent and reactor are closed. The mixture in the reactor is heated to the reaction temperature to initiate (or continue) the polymerization. The reaction may also be begun by introducing a free radical initiator into the feed dissolver (2) along with other reactants. After polymerization is complete, the polymer melt (molten product), containing some unreacted styrene monomer, ethylbenzene (an impurity from the styrene feed) and low molecular weight polymers (dimers, trimers, and other oligomers), is pumped to a vacuum devolatilizer (6). Here, the residual styrene monomer, ethylbenzene, and the low molecular weight polymers are removed, condensed (7), passed through a devolatilizer condensate tank (9), and then sent to the byproduct recovery unit. Overhead vapors from the condenser are usually exhausted through a vacuum system (8). Molten polystyrene from the bottom of the devolatilizer, which may be heated to 250 to 280°C (482 to 536°F), is extruded (10) through a stranding die plate (a plate with numerous holes to form strands), and then immersed in a cold water bath. The cooled strands are pelletized (10) and sent to product storage (11).

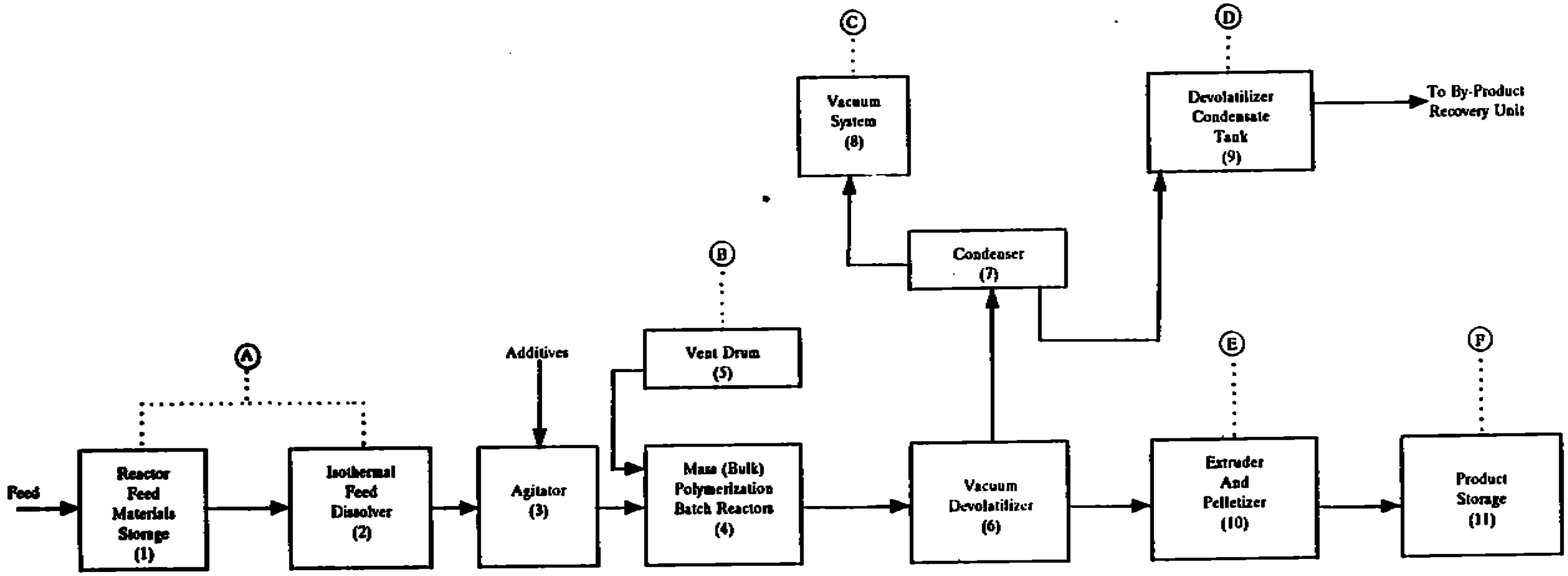


Figure 5.13.3-1. Simplified flow diagram of a batch polystyrene process.

Continuous Process - As with the batch process, various continuous steps are used to make a variety of grades of polystyrene or copolymers of styrene. In continuous processes, the chemical reaction does not approach completion as efficiently as in batch processes. As a result, a lower percentage of styrene is converted to polystyrene, and larger amounts of unreacted styrene may be emitted from continuous process sources. A typical plant may contain more than one process line, producing either the same or different grades of polymer or copolymer.

A typical bulk (mass) continuous process is represented in Figure 5.13.3-2. Styrene, polybutadiene (if an impact grade product is desired), mineral oil (lubricant and plasticizer), and small amounts of recycled polystyrene, antioxidants, and other additives, are charged from storage (1) into the feed dissolver mixer (2) in proportions that vary according to the grade of resin to be produced. Blended feed is pumped continuously to the reactor system (3) where it is thermally polymerized to polystyrene. A process line usually employs more than one reactor in series. Some polymerization occurs in the initial reactor, often referred to as the prepolymerizer. Polymerization to successively higher levels occurs in subsequent reactors in the series, either stirred autoclaves or tower reactors. The polymer melt, which contains unreacted styrene monomer, ethylbenzene (an impurity from the styrene feed) and low molecular weight polymers, is pumped to a vacuum devolatilizer (4). Here, most of the monomer, ethylbenzene, and low molecular weight polymers are removed, condensed (5), and sent to the styrene recovery unit (8 and 9). Noncondensables (overhead vapors) from the condenser typically are exhausted through a vacuum pump (10). Molten polystyrene from the bottom of the devolatilizer is pumped by an extruder (6) through a stranding die plate into a cold water bath. The solidified strands are then pelletized (6) and sent to storage (7).

In the styrene recovery unit, the crude styrene monomer recovered from the condenser (5) is purified in a distillation column (8). The styrene overhead from the tower is condensed (9) and returned to the feed dissolver mixer. Noncondensables are vented through a vacuum system (11). Column bottoms containing low molecular weight polymers are used sometimes as a fuel supplement.

5.13.3.2.2 Emissions And Controls[3-9]

As seen in Figure 5.13.3-1, six emission streams have been identified for batch processes, (1) the monomer storage and feed dissolver vent (Stream A); (2) the devolatilizer condensate tank (Stream B); (3) the reactant vent drum vent (Stream C); (4) the devolatilizer condenser vent (Stream D): (5) the extruder quench vent (Stream E); and (6) product storage emissions (Stream F). Table 5.13.3-1 summarizes the emission factors for these streams.

The major vent is the devolatilizer condenser vent (Stream D). This continuous offgas vent emits 0.25 to 0.75 grams of VOC per kilogram (gVOC/kg) of product, depending on the molecular weight of the polystyrene product being produced. The higher emission factor is more likely during the manufacture of lower molecular weight products. The emissions are unreacted styrene, which is flashed from the product polymer in the vacuum devolatilizer, and it is extremely diluted in air through leakage. The stream is exhausted through a vacuum system and then through an oil demister to the atmosphere. The oil demister is used primarily to separate out organic mist.

Table 5.13.3-1. EMISSION FACTORS FOR BATCH PROCESS POLYSTYRENE[a]

EMISSION FACTOR RATING: C

Stream Identification	Emission Stream	Nonmethane VOC	References
A	Monomer storage and feed dissolver tanks	0.09[b]	3
B	Devolatilizer condensate tank	0.002[b]	3
C	Reactor vent drum vent	0.12 - 1.35[c]	3 - 4
D	Devolatilizer condenser vent	0.25 - 0.75[c]	3 - 4
E	Extruder quench vent	0.15 - 0.3[c]	3 - 4
F	Product storage	negligible	3
Total Plant		0.6 - 2.5	

[a] Stream identification refers to Figure 5.13.3-1. Units are grams VOC per kilogram of product.
[b] Based on fixed roof design.
[c] Reference 4. The higher factors are more likely during the manufacture of lower molecular weight products. Factor for any given process train will change with product grade.

The second largest vent stream is likely to be the reactor vent drum vent, with an emission rate ranging from 0.12 to 1.35 gVOC/kg of product, this range also being associated with the molecular weight of the polystyrene product being produced. The higher emission factor is more likely during the manufacture of lower molecular weight products. These emissions, which are the only intermittent emissions from the process, occur only during reactor filling periods and they are vented to the atmosphere. The rate of 0.12 gVOC/kg of product is based on a facility having two batch reactors that are operated alternately on 24 hour cycles.

Stream E, the extruder quench vent, is the third largest emission stream, with an emission rate of 0.15 to 0.3 gVOC/kg of product. This stream, composed of styrene in water vapor, is formed when the hot, extruded polystyrene strands from the stranding die plate contact the cold water in the quenching bath. The resulting stream of steam with styrene is usually vented through a forced draft hood located over the water bath and then passed through a mist separator or electrostatic precipitator before venting to the atmosphere.

The other emission streams are relatively small continuous emissions. Streams A and B represent emissions from various types of tanks and dissolver tanks. Emissions from these streams are estimated, based on fixed roof tanks. Emissions from product storage, Stream F, have been reported to be negligible.

There are no VOC control devices typically used at polystyrene plants employing batch processes. The condenser (7) off the vacuum devolatilizer (6) typically is used for process reasons (recovery of unreacted styrene and other reactants). This condenser reduces VOC emissions, and its operating characteristics will affect the quantity of emissions associated with batch processes (Stream D in particular).

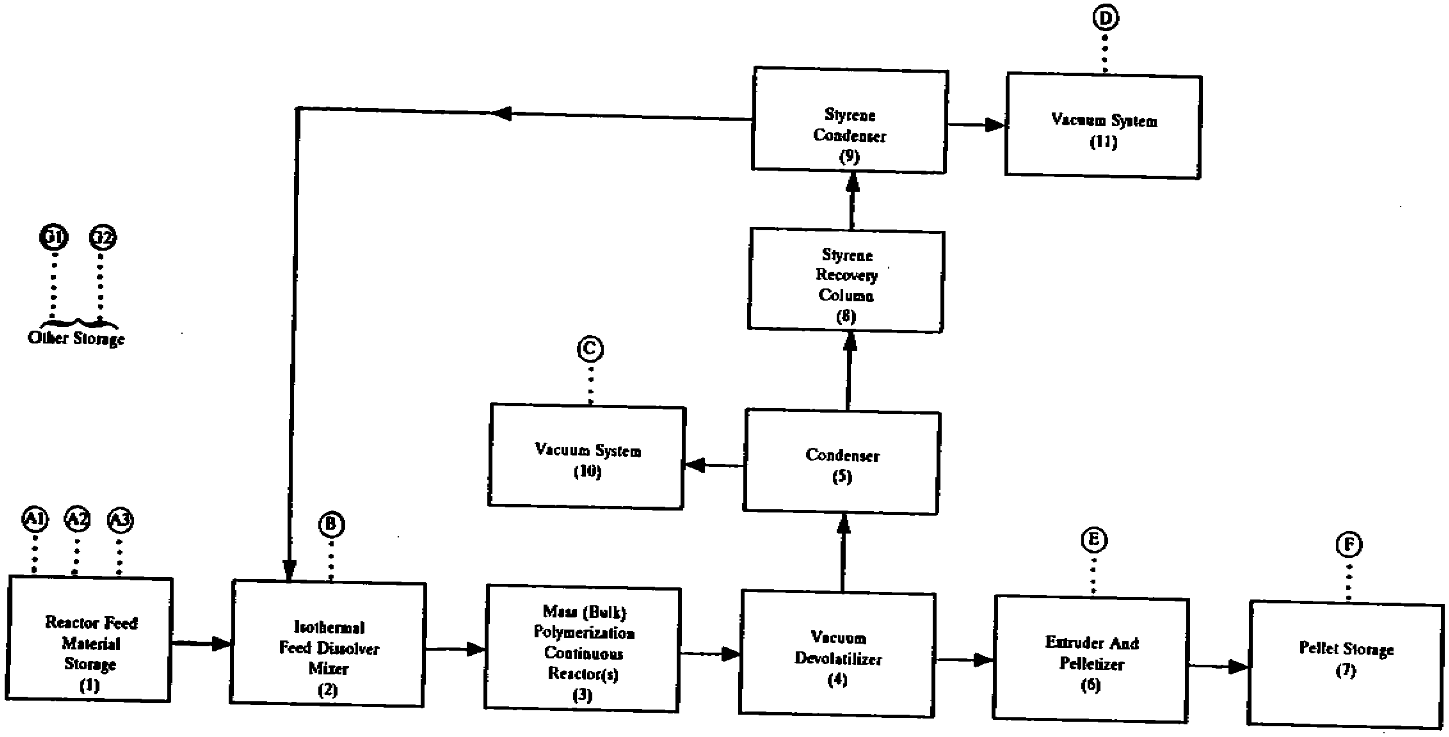


Figure 5.13.3-2. Simplified flow diagram of a continuous polystyrene process.

Total process uncontrolled emissions are estimated to range from 0.6 to 2.5 gVOC/kg of product. The higher emission rates are associated with the manufacture of lower molecular weight polystyrene. The emission factor for any given process line will change with changes in the grade of the polystyrene being produced.

Emission factors for the continuous polystyrene process are presented in Table 5.13.3-2, and the following numbered steps refer to that figure. Emissions from the continuous process are similar to those for the batch process, although the continuous process lacks a reactor vent drum. The emission streams, all of which are continuous, are (1) various types of storage (Streams A and G); (2) the feed dissolver vent (Stream B); (3) the devolatilizer condenser vent (Stream C); (4) the styrene recovery unit condenser vent (Stream D); (5) the extruder quench vent (Stream E); and (6) product storage emissions (Stream G).

Industry's experience with continuous polystyrene plants indicates a wide range of emission rates from plant to plant, depending in part on the type of vacuum system used. Two types are now used in the industry, one relying on steam ejectors and the other on vacuum pumps. Where steam ejectors are used, the overheads from the devolatilizer condenser vent and the styrene recovery unit condenser vent are composed mainly of steam. Some companies have recently replaced these steam ejectors with mechanical vacuum pumps. Emissions from vacuum pumps usually are lower than from steam ejectors.

It is estimated that the typical total VOC emission rate for plants using steam ejectors is about 3.34 gVOC/kg of product. The largest emission stream being the devolatilizer condenser vent (2.96 gVOC/kg of product). Emissions from the styrene recovery condenser vent and the extruder quench vent are estimated to be 0.13 and 0.15 gVOC/kg of product, respectively, although the latter may vary significantly depending on overall plant design. One plant designed to minimize emissions reported an emission factor of 0.0012 gVOC/kg product for the extruder quench vent.

For plants using vacuum pumps, it is estimated that the total VOC emission rate is about 0.21 gVOC/kg of product. In these plants, emissions from the devolatilizer condenser vent and the styrene recovery condenser vent are estimated to be 0.05 gVOC/kg of product. Styrene monomer and other storage emissions can be the largest emission sources at such plants, approximately 0.1 gVOC/kg of product. Some plants combine emissions from the dissolvers with those from the devolatilizer condenser vent. Other plants may combine the dissolver, devolatilizer condenser vent, and styrene recovery condenser vent emissions. One plant uses an organic scrubber to reduce these emissions to 0.004 gVOC/kg of product.

Condensers are a critical, integral part of all continuous polystyrene processes. The amount of unreacted styrene recovered for reuse in the process can vary greatly, as condenser operating parameters vary from one plant to another. Lowering the coolant operating temperature will lower VOC emissions, all other things being equal.

Other than the VOC reduction achieved by the process condensers, most plants do not use VOC control devices. A plant having controls, however, can have significantly reduce the level of VOC emissions. One company, for example, uses an organic scrubber to reduce VOC air emissions. Another uses a condenser downstream from the primary process condensers to control VOCs.

Table 5.13.3-2. EMISSION FACTORS FOR CONTINUOUS PROCESS POLYSTYRENE[a]

EMISSION FACTOR RATING: C

Stream Identification	Emission Stream	Nonmethane VOC Uncontrolled	 Controlled	References
A1	Styrene monomer storage	0.08		3,5
A2	Additives			
	General purpose	0.002		5
	High impact	0.001		5 - 6
A3	Ethylbenzene storage	0.001		5
B	Dissolvers	0.008		3,5
C	Devolatilizer condenser vent[b]	0.05[c]	0.04[d]	4 - 5,7
		2.96[e]		3
D	Styrene recovery unit condenser vent	0.05[c]		4,7
		0.13[e]		3
C+D		0.024 - 0.3[f]	0.004[g]	5 - 6,8
E	Extruder quench vent	0.01[c]		4
		0.15[e,g,h]		3
F	Pellet storage	negligible		3
	Other storage			
G1	General purpose	0.008		3,5
G2	High impact	0.007		3,5
Total Plant		0.21[c]		
		3.34[e]		

[a] Stream identification refers to Figure 5.13.3-2. Units are grams VOC per kilogram of product.
[b] Reference 9. Larger plants may route this stream to the styrene recovery section. Smaller plants may find this too expensive.
[c] For plants using vacuum pumps.
[d] Condenser is used downstream of primary process condensers; includes emissions from dissolvers. Plant uses vacuum pumps.
[e] For plants using steam jets.
[f] Lower value based on facility using refrigerated condensers as well as conventional cooling water exchangers; vacuum pumps in use. Higher value for facility using vacuum pumps.
[g] Plant uses an organic scrubber to reduce emissions. Nonsoluble organics are burned as fuel.
[h] This factor may vary significantly depending on overall process. Reference 6 indicates an emission factor of 0.0012 gVOC/kg product at a plant whose process design is "intended to minimize emissions".

5.13.3.3 Expandable Polystyrene[1-2,10-11]

The suspension process is a batch polymerization process that may be used to produce crystal, impact, or expandable polystyrene beads. An expandable polystyrene (EPS) bead typically consists of high molecular weight crystal grade polystyrene (to produce the proper structure when the beads are expanded) with 5 to 8 percent being a low boiling aliphatic hydrocarbon blowing agent dissolved in the polymer bead. The blowing agent typically is pentane or isopentane although others, such as esters, alcohols, and aldehydes, can be used. When used to produce an EPS bead, the suspension process can be adapted in one of two ways for the impregnation of the bead with the blowing agent. One method is to add the blowing agent to a reactor after polymerization, and the other is to add the blowing agent to the monomer before polymerization. The former method, called the "post-impregnation" suspension process, is more common than the latter, referred to as the "in-situ" suspension process. Both processes are described below.

EPS beads generally are processed in one of three ways, (1) gravity or air fed into closed molds, then heated to expand up to 50 times their original volume; (2) pre-expanded by heating and then molding in a separate processing operation; and (3) extended into sheets. EPS beads are used to produce a number of foamed polystyrene materials. Extruded foam sheet is formed into egg cartons, meat and poultry trays, and fast food containers. In the building/construction industry, EPS board is used extensively as a low temperature insulator.

5.13.3.3.1 Process Description[1,10-12]

Post-impregnation Suspension Process - This process is essentially a two part process using two process lines in series. In the first process line, raw styrene monomer is polymerized and a finished polystyrene bead is produced. The second process line takes the finished bead from the first line, impregnates the bead with a blowing agent, and produces a finished EPS bead. Figure 5.13.3-3 is a schematic representation of this process.

In the first line, styrene monomer, water, initiator, and suspending agents form the basic charge to the suspension reactor (1). The styrene-to-water ratio varies with the type of polystyrene required. A typical ratio is about one-quarter to one-half monomer to water volume. Initiators are commonly used because the reaction temperature is usually too low for adequate thermal initiation of polymerization. Suspending agents are usually protective colloids and insoluble inorganic salts. Protective colloids are added to increase the viscosity of the continuous water phase, and insoluble inorganic salts such as magnesium carbonate ($MgCO_3$) are added to prevent coalescence of the drops upon collision.

In the reactor, the styrene is suspended, through use of mechanical agitation and suspending agents, in the form of droplets throughout the water phase. Droplet size may range from about 0.1 to 1.0 mm. The reactor is heated to start the polymerization, which takes place within the droplets. An inert gas, such as nitrogen, is frequently used as a blanketing agent in order to maintain a positive pressure at all times during the cycle, to prevent air leaks. Once polymerization starts, temperature control is typically maintained through a water-cooled jacket around the reactor and is facilitated by the added heat capacity of the water in the reactor. The size of the product bead depends on both the strength of agitation and the nature of the monomer and suspending system. Between 20 and 70 percent conversion, agitation becomes extremely critical. If agitation weakens or stops between these limits, excessive agglomeration of the polymer particles may occur, followed by a runaway reaction. Polymerization typically occurs within several hours, the actual time varying largely with the temperature and with the amount

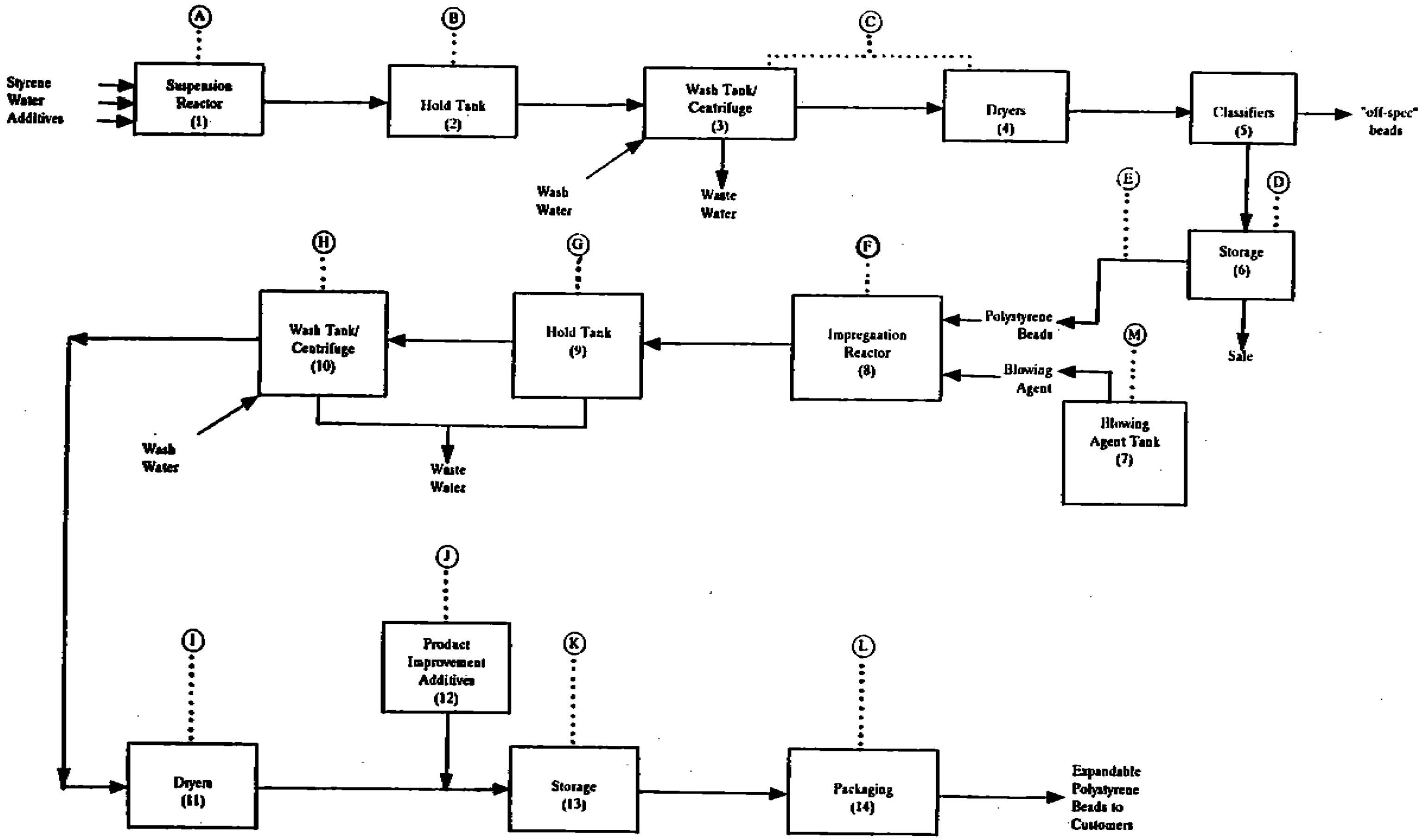


Figure 5.13.3-3. Simplified flow diagram of the expandable polystyrene post-impregnation suspension process.

and type of initiator(s) used. Residual styrene concentrations at the end of a run are frequently as low as 0.1 percent.

Once the reaction has been completed (essentially 100 percent conversion), the polystyrene-water slurry is normally pumped from the reactor to a hold tank (2), which has an agitator to maintain dispersion of the polymer particles. Hold tanks have at least three functions, (1) the polymer-water slurry is cooled to below the heat distortion temperature of the polymer (generally 50 to 60°C [122 to 140°F]); (2) chemicals are added to promote solubilization of the suspension agents; and (3) the tank serves as a storage tank until the slurry can be centrifuged. From the hold tanks, the polymer-water slurry is fed to a centrifuge (3) where the water and solids are separated. The solids are then washed with water, and the wash water is separated from the solids and is discarded. The polymer product beads, which may retain between 1 and 5 percent water, are sent to dryers (4). From the dryers, they may be sent to a classifier (5) to separate the beads according to size, and then to storage bins or tanks (6). Product beads do not always meet criteria for further processing into expandable beads, and "off-spec" beads may be processed and sold as crystal (or possibly impact) polystyrene.

In the second line, the product bead (from the storage bins of the first line), water, blowing agent (7), and any desired additives are added to an impregnation reactor (8). The beads are impregnated with the blowing agent through utilization of temperature and pressure. Upon completion of the impregnation process, the bead-water slurry is transferred to a hold tank (9) where acid may be added and part of the water is drained as wastewater. From the hold tanks, the slurry is washed and dewatered in centrifuges (10) and then dried in low temperature dryers (11). In some instances, additives (12) may be applied to the EPS bead to improve process characteristics. From the dryers, the EPS bead may undergo sizing, if not already done, before being transferred to storage silos (13) or directly to packaging (14) for shipment to the customer.

In-situ Suspension Process - The in-situ suspension process is shown schematically in Figure 5.13.3-4. The major difference between this process and the post-impregnation suspension process is that polymerization and impregnation takes place at the same time in a single reactor. The reaction mixture from the mix tank (1), composed of styrene monomer, water, polymerization catalysts, and additives, are charged to a reactor (2) to which a blowing agent is added. The styrene monomer is polymerized at elevated temperatures and pressure in the presence of the blowing agent, so that 5 to 7 percent of the blowing agent is entrapped in the polymerized bead. After polymerization and impregnation have taken place, the EPS bead-water slurry follows essentially the same steps as in the post-impregnation suspension process. These steps are repeated in Figure 5.13.3-4.

5.13.3.3.2 Emissions And Controls[10,12-16]

Emission rates have been determined from information on three plants using the post-impregnation suspension process. VOC emissions from this type of facility are generally uncontrolled. Two of these plants gave fairly extensive information, and of these, one reported an overall uncontrolled VOC emission rate of 9.8 g/kg of product. For the other, an overall uncontrolled VOC emission rate of 7.7 g/kg is indicated, by back-calculating two emission streams controlled by condensers.

The information on emission rates for individual streams varied greatly from plant to plant. For example, one plant reported a VOC emission rate for the suspension reactor of 0.027 g/kg of product, while another reported a rate of 1.9 g/kg of product. This inconsistency in

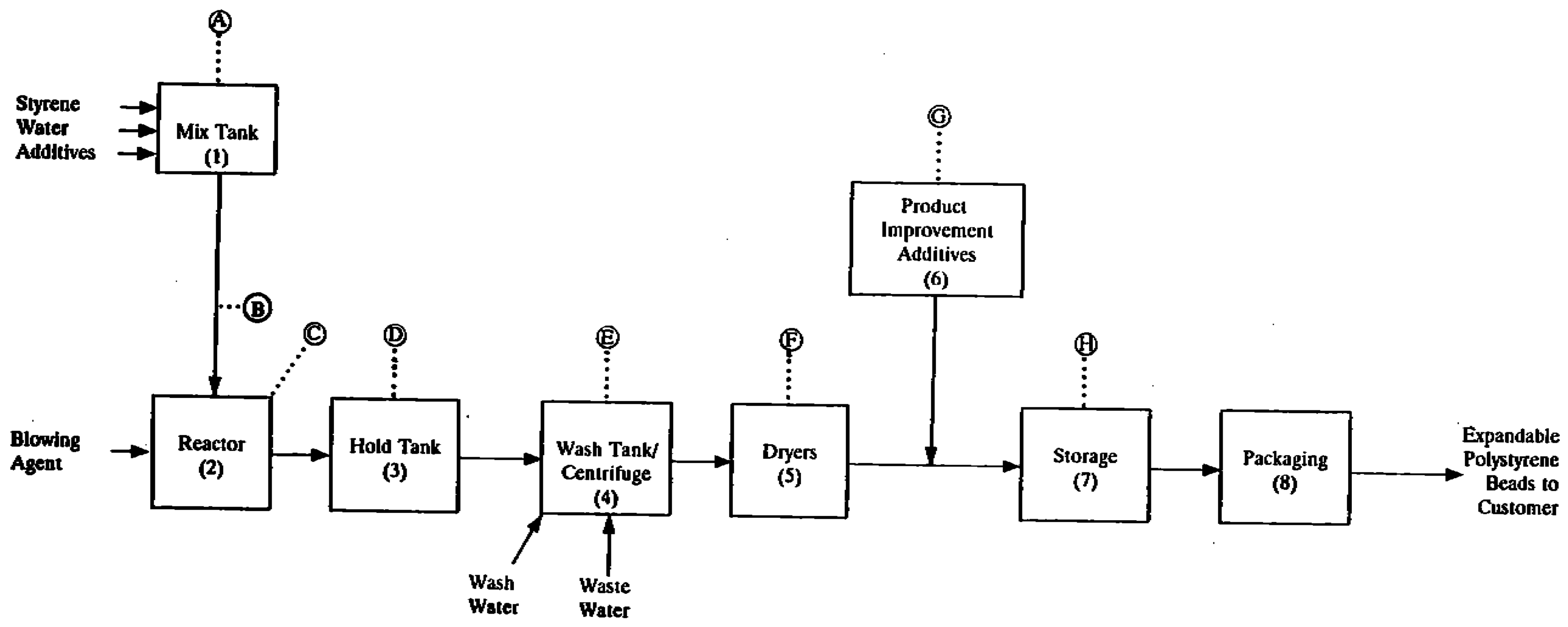


Figure 5.13.3-4. Simplified flow diagram of the expandable polystyrene in-situ suspension process.

emission rates may be because of differences in process reactors, operating temperatures, and/or reaction times, but sufficient data to determine this are not available. Therefore, individual stream emission rates for the post-impregnation process are not given here.

Particulate emissions (emissions of fines from dryers, storage and pneumatic transfer of the polymer) usually are controlled by either cyclones alone or cyclones followed by baghouses. Overall, controlled particulate emissions are relatively small, approximately 0.18 g particulate/kg of product or less. Control efficiencies of 99 percent were indicated and thus, uncontrolled particulate emissions might be around 18 g particulate/kg of product.

Table 5.13.3-3 summarizes uncontrolled VOC emissions factors for the in-situ process, based on a study of a single plant. An uncontrolled emission rate of about 5.4 gVOC/kg of product is estimated for this suspension EPS process. Most emission streams are uncontrolled at this plant. However, reactor emissions are vented to the boiler as primary fuel, and some of the dryer emissions are vented to the boiler as supplementary fuel, thereby resulting in some VOC control.

The blowing agent, which continually diffuses out of the bead both in manufacturing and during storage, constitutes almost all of VOCs emitted from both processes. A small amount of styrene is emitted from the suspension reactors in the post-impregnation process and from the mix tanks and reactors in the in-situ process.

Because of the diffusing of the blowing agent, the EPS bead is unstable for long periods of time. Figure 5.13.3-5 shows the loss of blowing agent over time when beads are stored under standard conditions. This diffusion means that the stock of beads must be rotated. An up-to-date analysis of the blowing agent content of the bead (measured as percent volatiles at 100°C [212°F]) also needs to be maintained, because the blowing agent content determines processing characteristics, ultimate density, and economics. Expandable beads should be stored below 32°C (90°F) and in full containers (to reduce gas volume space).

Since pentane, a typical blowing agent, forms explosive mixtures, precautions must be taken whenever it is used. For example, after storage containers are opened, a time lag of 10 minutes is suggested to allow fumes or pentane vapors to dissipate out of the containers. Care must be taken to prevent static electricity and sparks from igniting the blowing agent vapors.

Table 5.13.3-3. EMISSION FACTORS FOR IN-SITU PROCESS EXPANDABLE POLYSTYRENE[a]

EMISSION FACTOR RATING: C

Stream Identification	Emission Stream	Nonmethane VOC	References
A	Mix tank vents	0.13	16
B	Regranulator hoppers	negligible	16
C	Reactor vents	1.09[b]	17
D	Holding tank vents	0.053	16
E	Wash tank vents	0.023	16
F	Dryer vents	2.77[b]	16
G	Product improvement vents	0.008	16
H	Storage vents and conveying loses	1.3	16
Total Plant		5.37[c]	

[a] Stream identification refers to Figure 5.13.3-4. Units are grams VOC per kilogram of product.

[b] Reference 16. All reactor vents and some dryer vents are controlled in a boiler. Rates are before control.

[c] At plant where all reactor vents and some dryer vents are controlled in a boiler (and assuming 99% reduction), an overall emission rate of 3.75 is estimated.

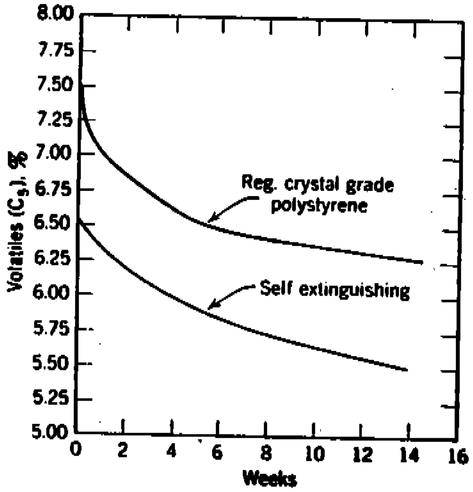


Figure 5.13.3-5. EPS beads stored in fiber drum at 21 - 24°C (70 - 75°F).

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2. Modern Plastics Encyclopedia, 1981-1982, McGraw Hill, New York, 1982.

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16. Written communication from A. D. Gillen, BASF Wyandotte Corporation, Parsippany, NJ, to J. R. Farmer, U. S. Environmental Protection Agency, Research Triangle Park, NC, February 18, 1983.

17. Telephone communication between K. Meardon, Pacific Environmental Services, Inc., Durham, NC, and A. Gillen, BASF Wyandotte Corporation, Parsippany, NJ, June 21, 1983.

emissions of gaseous ammonia, gaseous fluorides (HF and SiF_4) and particulate ammonium phosphates. These two exhaust streams generally are combined and passed through primary and secondary scrubbers.

Exhaust gases from the dryer and cooler also contain ammonia, fluorides and particulates, and these streams commonly are combined and passed through cyclones and primary and secondary scrubbers. Particulate emissions and low levels of ammonia and fluorides from product sizing and material transfer operations are controlled the same way.

Emission factors for ammonium phosphate production are summarized in Table 6.10.3-1. These emission factors are averages based on recent source test data from controlled phosphate fertilizer plants in Florida.

Exhaust streams from the reactor and ammoniator-granulator pass through a primary scrubber, in which phosphoric acid recovers ammonia and particulate. Exhaust gases from the dryer, cooler and screen go first to cyclones for particulate recovery, and from there to primary scrubbers. Materials collected in the cyclone and primary scrubbers are returned to the process. The exhaust is sent to secondary scrubbers, where recycled gypsum pond water is used as a scrubbing liquid to control fluoride emissions. The scrubber effluent is returned to the gypsum pond.

Primary scrubbing equipment commonly includes venturi and cyclonic spray towers, while cyclonic spray towers, impingement scrubbers, and spray-crossflow packed bed scrubbers are used as secondary controls. Primary scrubbers generally use phosphoric acid of 20 to 30 percent as scrubbing liquor, principally to recover ammonia. Secondary scrubbers generally use gypsum and pond water, for fluoride control.

Throughout the industry, however, there are many combinations and variations. Some plants use reactor-feed concentration phosphoric acid (40 percent P_2O_5) in both primary and secondary scrubbers, and some use phosphoric acid near the dilute end of the 20 to 30 percent P_2O_5 range in only a single scrubber. Existing plants are equipped with ammonia recovery scrubbers on the reactor, ammoniator-granulator and dryer, and particulate controls on the dryer and cooler. Additional scrubbers for fluoride removal are common but not typical. Only 15 to 20 percent of installations contacted in an EPA survey were equipped with spray-crossflow packed bed scrubbers or their equivalent for fluoride removal.

Emission control efficiencies for ammonium phosphate plant control equipment have been reported as 94 - 99 percent for ammonium, 75 - 99.8 percent for particulates, and 74 - 94 percent for fluorides.

TABLE 6.10.3-1. AVERAGE CONTROLLED EMISSION FACTORS FOR THE PRODUCTION OF AMMONIUM PHOSPHATES[a]

EMISSION FACTOR RATING: A

Emission Point	Controlled Emission Factors	
	lb/ton P_2O_5	kg/MT P_2O_5
Reactor/ammoniator-granulator		
Fluoride (as F)	0.05	0.02
Particulates	1.52	0.76
Ammonia	b	b
Dryer/cooler		
Fluoride (as F)	0.03	0.02
Particulates	1.50	0.75
Ammonia	b	b
Product sizing and material transfer		
Fluoride (as F)[c]	0.01	0.01
Particulates[c]	0.06	0.03
Ammonia	b	b
Total plant emissions		
Fluoride (as F)[d]	0.08	0.04
	0	
Ammonia	0.14	0.07

[a] Reference 1, pp. 80-83, 173.

[b] No information available. Although ammonia is emitted from these unit operations, it is reported as a total plant emission.

[c] Represents only one sample.

[d] EPA has promulgated a fluoride emission guideline of 0.03 g/kg P_2O_5 input.

[e] Based on limited data from only 2 plants.

Reference for Section 6.10.3

1. J. M. Nyers, et al., Source Assessment: Phosphate Fertilizer Industry, EPA-600/2-79-019c, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1979.

7. METALLURGICAL INDUSTRY

The metallurgical industry can be broadly divided into primary and secondary metal production operations. Primary refers to the production of metal from ore. Secondary includes the production of alloys from ingots and the recovery of metal from scrap and salvage.

The primary metals industry discussed in this chapter includes both ferrous and nonferrous operations. These processes are characterized by the large quantities of sulfur oxides and particulate emitted. Secondary metallurgical process are also discussed, and the major air contaminant from such activity is particulate in the forms of metallic fumes, smoke and dust.

8.6 PORTLAND CEMENT MANUFACTURING

8.6.1 Process Description

Most of the hydraulic cement produced in the United States is portland cement, a cementitious, crystalline compound composed of metallic oxides. It is produced by a pyroprocess in a rotary kiln from raw materials, such as limestone containing calcium carbonate and aluminum, iron, and silicon oxides, shale, clay and sand. A diagram of this process is shown in Figure 8.6-1. This manufacturing process may be conveniently divided into five stages, correlated with location and temperature of the materials in the rotary kiln.

1. Uncombined water evaporates from raw materials as material temperature increases to 100°C (212°F).
2. As the material temperature increases from 100°C to approximately 430°C (800°F), dehydration and precalcination occur.
3. Between 430°C and 900°C (1650°F), calcination occurs in which CO_2 is liberated from the carbonates.
4. Following calcination, sintering of the oxides occurs in the burning zone of the rotary kiln at temperatures up to 1510°C (2750°F).
5. Following sintering, cement clinker is produced as the temperature of the material decreases from 1510°C to 1370°C (2500°F).

The raw material mix enters the kiln at the elevated end, and the burner is at the opposite end as shown in Figure 8.6-2. The raw materials are then changed into cementitious oxides of metals by a countercurrent heat exchange process. The materials are continuously and slowly moved to the lower end by rotation of the kiln. The fuel burned in the kiln may be natural gas, oil or coal. Many cement plants burn coal, but supplemental fuels such as waste solvents, chipped rubber, shredded municipal garbage, and coke have been used in recent years.

There are three variations in cement manufacturing, wet, dry, and dry preheater/precalciner processes. These processes are essentially identical relative to the manufacture of cement from raw materials. However, the type of process does affect the equipment design, method of operation, and fuel consumption. Fuel combustion differs between the wet and dry processes and the preheater/precalciner process. In the former two, all fuel combustion occurs in the kiln. In the latter, some fuel combustion occurs in a precalcining or calcining vessel before the materials enter the kiln. See Figure 8.6-2. Generally speaking, preheater/precalciner equipment uses less fuel and requires a shorter kiln, and the wet process uses the most fuel and takes the longest kiln, but the relationship is not linear.

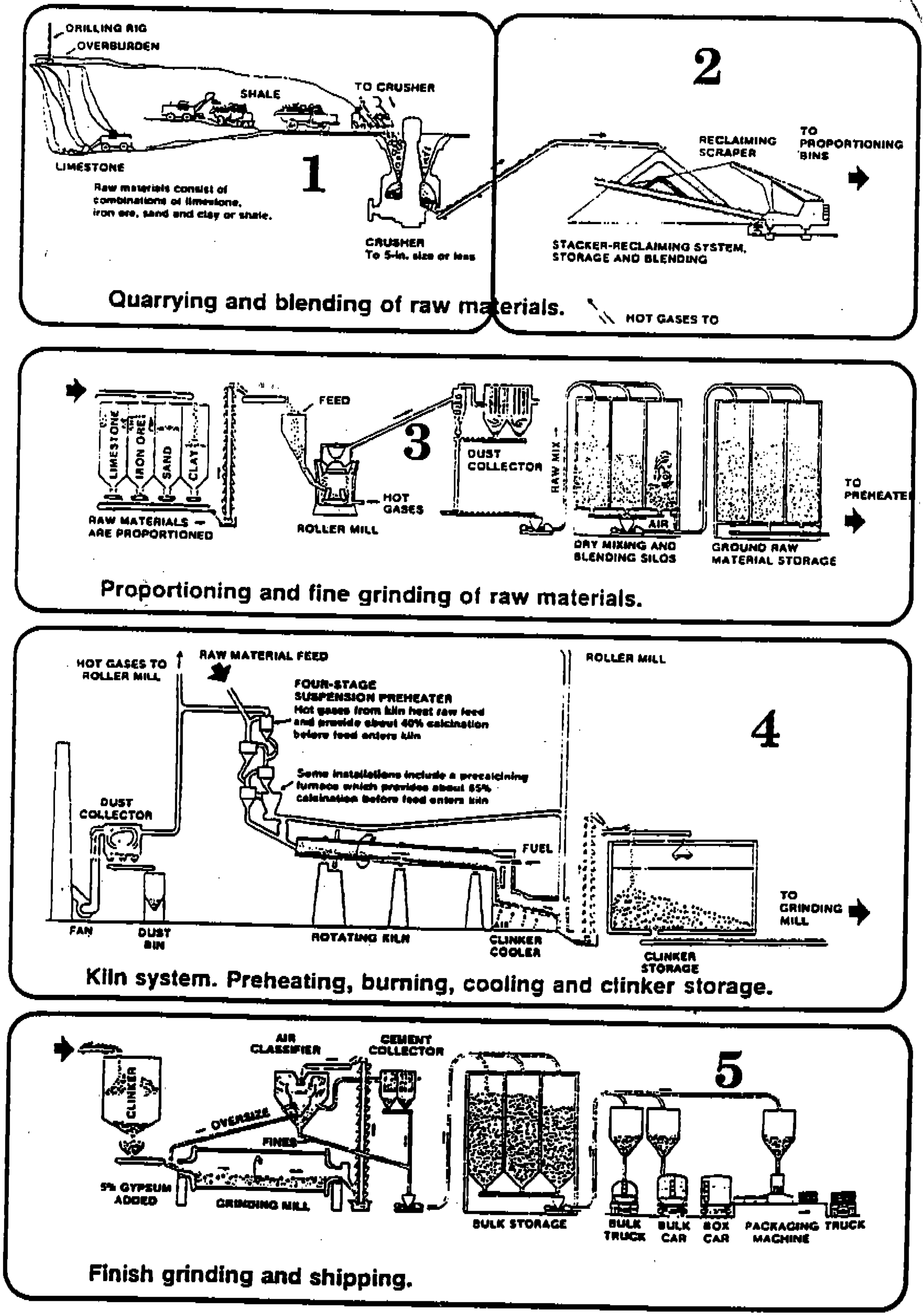

Figure 8.6-1. Steps in the manufacture of portland cement by dry process with preheater.

8.6.2 Emissions And Controls

Particulate NO_x, SO_2, CO and CO_2 are the primary emissions in the manufacture of portland cement, and emissions may also include minute particles from the fuel and raw materials.

Sources of particulate at cement plants include (1) quarrying and crushing, (2) raw material storage, (3) grinding and blending (in the dry process only), (4) clinker production, (5) finish grinding, and (6) packaging. The largest emission source within cement plants is the three units of kiln operation: the feed system, the fuel firing system, and the clinker cooling and handling system. The most desirable method of disposing of the collected dust is injection into the kiln burning zone and production of clinkers from the dust. If the alkali content of the raw materials is too high, however, some of the dust is discarded or leached before returning to the kiln. In many instances, the maximum allowable cement alkali content of 0.6 percent (calculated as sodium oxide) restricts the amount of dust that can be recycled. Additional sources of particulate are raw material storage piles, conveyors, storage silos, and loading/unloading facilities.

The complications of kiln burning and the large volumes of material handled have led to the adoption of many control systems. The industry may use mechanical collectors, electrostatic precipitators, fabric filters (baghouses), or combinations of these devices to control emissions, depending on the material emitted, the temperature of plant effluents, and applicable particulate emission standards and community practices.

Oxides of nitrogen (NO_x) are generated during fuel combustion by oxidation of chemically bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. As flame temperature increases, the amount of thermally generated NO_x increases, and the amount of NO_x generated from fuel increases with the quantity of nitrogen in the fuel. In the cement manufacturing process, there are two areas which may generate NO_x, the burning zone of the kiln and the burning zone of a precalcining vessel. Fuel use will affect the quantity and type of NO_x generated. Natural gas combustion with a high flame temperature and low fuel nitrogen may generate a different quantity of NO_x than would oil or coal, which have higher fuel nitrogen but lower flame temperatures.

Fuel use varies in the cement manufacturing process. Generally, natural gas is used only in the kiln, while coal and oil are used in the kiln and precalcining vessel. Therefore, the generation and emission of NO_x relate to the type of fuel burned and to the extent to which fuel affects flame temperature and contains chemically bound nitrogen.

Currently, there are data to support only two types of reduction of NO_x in the cement industry. First, for conventional wet and dry process kilns, NO_x emissions are reduced by fuel conversion, with coal producing the least NO_x. For new construction, the data are not yet clear. Some preheater/precalciner systems have low emissions and others have high.

There are at least ten different preheater/precalciner systems used in the cement industry, and each appears to have unique emission properties. However, it is evident that for a single system, burning oil in the calciner produces less NO_x than coal. The NO_x emissions from the preheater/precalciner appear to relate to design. Some have very low emissions and others have emissions in a mid range of some conventional or wet processes.

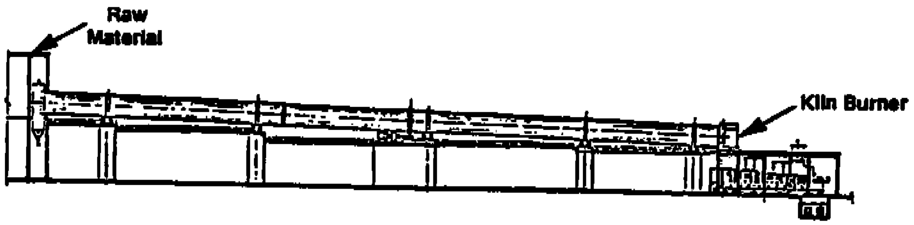

Figure 8.6-2. Conventional portland cement kiln.

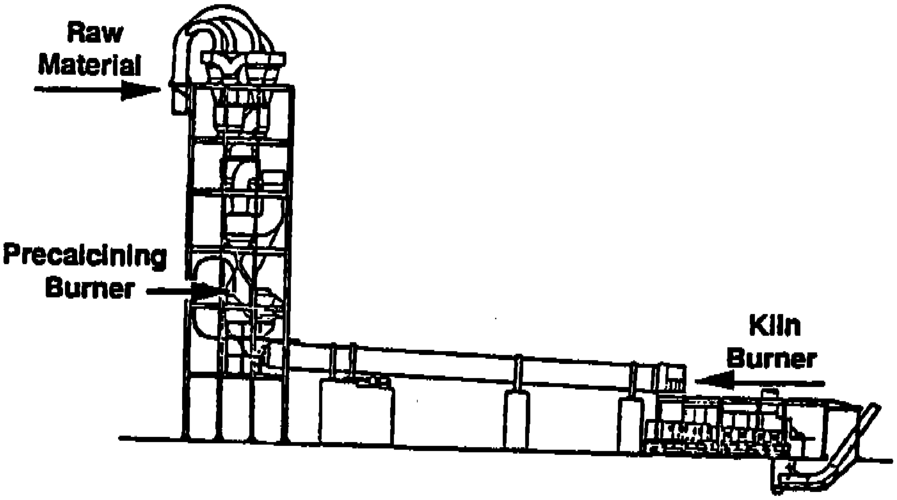

Figure 8.6-3. Typical portland cement preheater/precalciner.

Sulfur dioxide may be generated both from the sulfur compounds in the raw materials, and from sulfur in the fuel. The sulfur content of both raw materials and fuels will vary from plant to plant and with geographic location. The alkaline nature of the cement, however, provides for direct absorption of SO_2 into the product. Using a baghouse that allows the SO_2 to come in contact with the cement dust provides inherent reduction of 75 percent or more of the raw material and fuel sulfur content. The percent reduction, of course, will vary with the alkali and sulfur content of the raw materials and fuel.

CO emissions are associated with the efficiency of the combustion process, and the CO_2 is generally a release of 33 percent of the weight of the limestone in the calcining process. Currently, there are no methods available for reducing CO or CO_2 except process control for CO and reduced production for CO_2.

Tables 8.6-1 through 8.6-4 give emission factors for cement manufacturing, including factors based on particle size. Size distributions for particulate emissions from controlled and uncontrolled kilns and clinker coolers are also shown in Figures 8.6-4 and 8.6-5.

NOTICE

The revised information in this Section involves only SO_2 and NO_x. The Emission Inventory Branch intends to update material on particulate and to add CO information in the future. Toward this end, we would welcome any emissions data, comments or suggestions from the reader.

Table 8.6-1. UNCONTROLLED EMISSION FACTORS FOR COAL COMBUSTION IN PORTLAND CEMENT MANUFACTURING[a]

Process	Particulate[b]		Sulfur dioxide		Nitrogen oxide		Lead	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Dry process Kiln	128	256	3.5^c	7.0^c	2.9^c	5.7^c	0.06	0.12
Dryer[d]	48	96	-	-	-	-	0.02	0.04
Wet process Kiln	120	240	3.0^e	6.0^e	4.1^e	8.2^e	0.05	0.10
Dryer[d]	16	32	-	-	-	-	0.01	0.02
Clinker cooler[f]	4.6	9.2	-	-	-	-	-	-
Preheater kiln	-	-	0.4^e	0.8^e	2.8^c	5.5^c	-	-
Precalciner kiln	-	-	0.5^c	1.0^c	2.4^c	4.8^c	-	-

[a] References 1-2. Factors are expressed as units of clinker produced, assuming 5% gypsum in finished cement. Includes fuel combustion emissions, which should not be calculated separately. Assumes that 1.33 Mg raw materials makes 1 Mg clinker, and 1 Mg clinker and 0.05 Mg gypsum make 1.05 Mg of cement. Dash = No data.

[b] Emission Factor Rating: B.

[c] Reference 13. Emission Factor Rating: B.

[d] Expressed as units of cement produced.

[e] Reference 13. Emission Factor Rating: C.

[f] Reference 8. Emission Factor Rating: D.

Table 8.6-2. CONTROLLED PARTICULATE EMISSION FACTORS FOR CEMENT MANUFACTURING[a]

Type of source	Control	Particulate kg/Mg clinker	Particulate lb/ton clinker	Emission Factor Rating
Wet process kiln	Baghouse	0.57	1.1	C
	ESP	0.39	0.78	C
Dry process kiln	Multiclone	130[b]	260[b]	D
	Multicyclone + ESP	0.34	0.68	C
	Baghouse	0.16	0.32	B
Clinker cooler	Gravel bed filter	0.16	0.32	C
	ESP	0.048	0.096	D
	Baghouse	0.010	0.020	C
Primary limestone crusher[c]	Baghouse	0.00051	0.0010	D
Primary limestone screen[c]	Baghouse	0.00011	0.00022	D
Secondary limestone screen and crusher[c]	Baghouse	0.00016	0.00032	D
Conveyor transfer[c]	Baghouse	0.000020	0.000040	D
Raw mill system[c,d]	Baghouse	0.034	0.068	D
Finish mill system[e]	Baghouse	0.017	0.034	C

[a] Factors are for kg particulate/Mg (lb particulate/ton) of clinker produced, except as noted. ESP = electrostatic precipitator.

[b] Based on a single test of a dry process kiln fired with a combination of coke and natural gas. Not generally applicable to a broad cross section of the cement industry.

[c] Expressed as mass of pollutant/mass of raw material processed.

[d] Includes mill, air separator and weigh feeder.

[e] Expressed as units of cement produced. Includes mill, air separator(s) and one or more material transfer operations.

Table 8.6-3 SIZE SPECIFIC PARTICULATE EMISSION FACTORS FOR CEMENT KILNS[a]

EMISSION FACTOR RATING: D

	Cumulative mass % < stated size[b]						Cumulative emission factor < stated size[c]													
	Uncontrolled		Baghouse				Uncontrolled								Baghouse					
Particle size (μm)	Wet process kiln	Dry process kiln	Dry process kiln with multiclone	Wet process kiln with ESP	Wet process kiln	Dry process kiln	Wet process		Dry process		Dry process with multiclone[d]		Wet process with ESP		Wet process		Dry process			
							kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton		
2.5	7.0	18.0	3.8	64.0	NA	45.0	8.4	17.0	23.0	46.0	5.0	10.0	0.25	0.50	NA	NA	0.073	0.15		
5.0	20.0	NA	14.0	83.0	NA	77.0	24.0	48.0	-	-	19.0	38.0	0.32	0.64	NA	NA	0.13	0.26		
10.0	24.0	42.0	24.0	85.0	NA	84.0	29.0	58.0	54.0	108.0	32.0	64.0	0.33	0.66	NA	NA	0.14	0.28		
15.0	35.0	44.0	31.0	91.0	NA	89.0	43.0	86.0	57.0	114.0	41.0	82.0	0.36	0.72	NA	NA	0.15	0.30		
20.0	57.0	NA	38.0	98.0	NA	100.0	68.0	136.0	-	-	49.0	98.0	0.39	0.78	NA	NA	0.16	0.32		
Total mass emission factor							120[e]	240[e]	128[e]	256[e]	130[f]	260[f]	0.39[f]	0.78[f]	0.57[f]	1.1[f]	0.16[f]	0.32[f]		

[a] Reference 8. ESP = electrostatic precipitator. NA = not available. Dash = no data.

[b] Aerodynamic diameter. Rounded to two significant figures.

[c] Expressed as unit weight of particulate/unit weight of clinker produced, assuming 5% gypsum in finished cement. Rounded to two significant figures.

[d] Based on a single test, and to be used with caution.

[e] From Table 8.6-1.

[f] From Table 8.6-2.

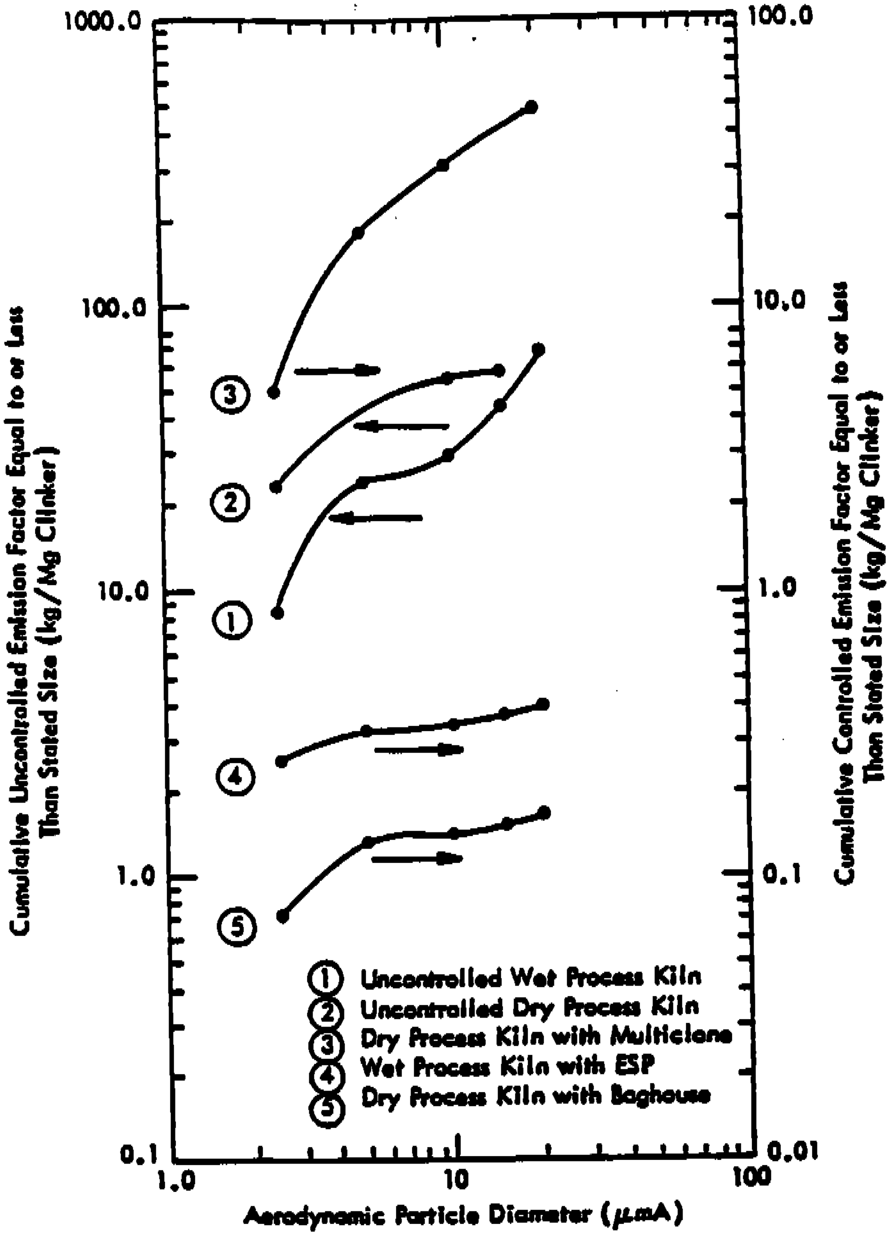

Figure 8.6-4. Size specific emission factors for cement kiln operations.

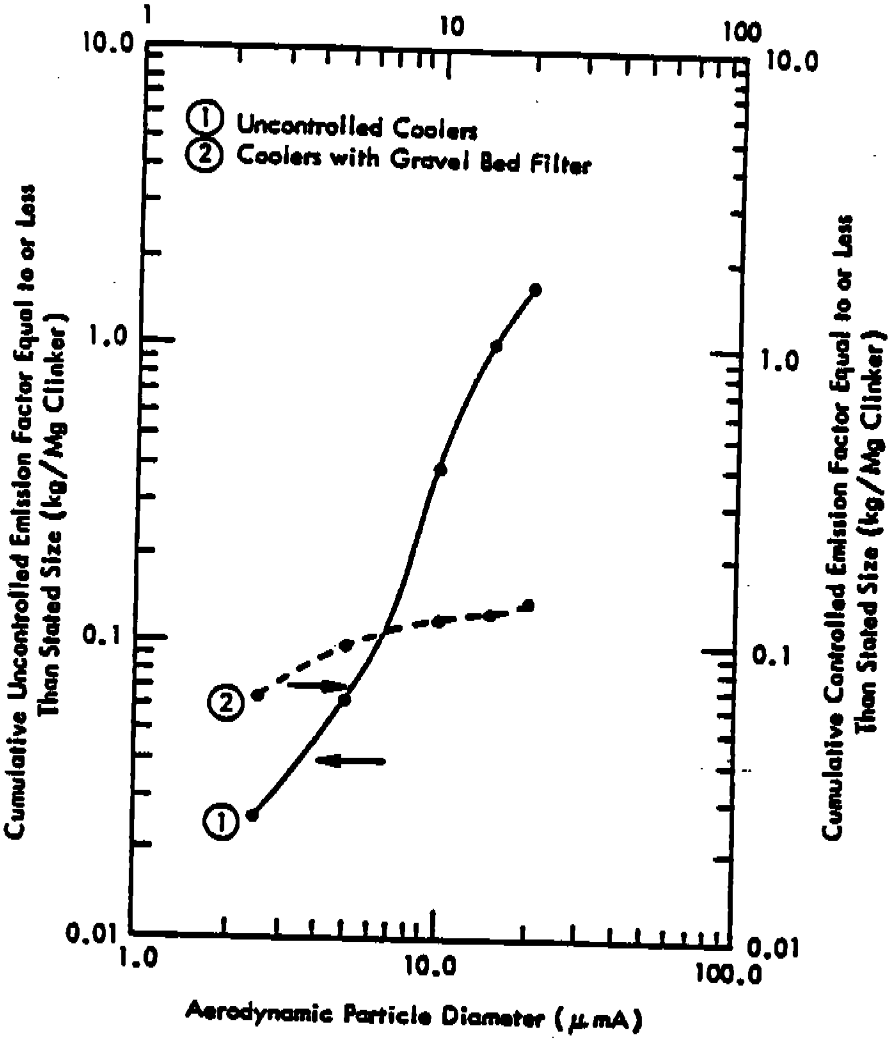

Figure 8.6-5. Size specific emission factors for clinker coolers in a portland cement process.

Table 8.6-4. SIZE SPECIFIC EMISSION FACTORS FOR CLINKER COOLERS[a]

EMISSION FACTOR RATING: E

Particle size[b] (µm)	Cumulative mass % ≤ stated size[c]		Cumulative emission factor ≤ stated size[d]			
	Uncontrolled	Gravel bed filter	Uncontrolled kg/Mg	Uncontrolled lb/ton	Gravel bed filter kg/Mg	Gravel bed filter lb/ton
2.5	0.54	40	0.025	0.050	0.064	0.13
5.0	1.5	64	0.067	0.13	0.10	0.20
10.0	8.6	76	0.40	0.80	0.12	0.24
15.0	21	84	0.99	2.0	0.13	0.26
20.0	34	89	1.6	3.2	0.14	0.28
Total mass emission factor			4.6[e]	9.2[e]	0.16[f]	0.32[f]

[a] Reference 8.

[b] Aerodynamic diameter.

[c] Rounded to two significant figures.

[d] Unit weight of pollutant/unit weight of clinker produced. Rounded to two significant figures.

[e] From Table 8.6-1.

[f] From Table 8.6-2.

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10. M. S. May, et al., "Nitrogen Oxide Emissions From Cement Kiln Exhaust Gases By Process Modification", Proceedings: 1987 Joint Symposium On Stationary Source Combustion NO_x Control, EPA-600/9-88-026a and 026b, U. S. Environmental Protection Agency, Cincinnati, OH, December 1988.

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12. Methodology For Development Of SO_x/NO_x Emission Factor, PSM International, Inc., Dallas, TX, July 26, 1990.

13. F. Bergman, Review Of Proposed Revision To AP-42 Section 8.6, Portland Cement Manufacturing, EPA Contract No. 68-02-4395, Midwest Research Institute, Kansas City, MO, September 30, 1990.

TABLE 8.19.1-1. UNCONTROLLED PARTICULATE EMISSION FACTORS FOR SAND AND GRAVEL PROCESSING PLANTS[a]

Uncontrolled Operation	Emissions by Particle Size Range (aerodynamic diameter)[b]				Emission Factor Rating
	Total Particulate	TSP ($\leq$ 30 μm)	PM_{10} ($\leq$ 10 μm)	Units	
Process Sources[c]					
Primary or secondary crushing (wet)	NA	0.009 (0.018)	NA	kg/Mg (lb/ton)	D
Open Dust Sources[c]					
Screening[d]					
Flat screens (dry product)	NA	0.08 (0.16)	0.06 (0.12)	kg/Mg (lb/ton)	C
Continous drop[c]					
Transfer station	0.014 (0.029)	NA	NA	kg/Mg (lb/ton)	E
Pile formation - stacker	NA	0.065 (0.13)	0.03 (0.06)[e]	kg/Mg (lb/ton)	E
Batch drop[c]					
Bulk loading	0.12 (0.24)	0.028 (0.056)[f]	0.0012 (0.0024)[f]	kg/Mg (lb/ton)	E
Active storage piles[g]					
Active day	NA	14.8 (13.2)	7.1 (6.3)[e]	kg/hectare/day[h] (lb/acre/day)	D
Inactive day (wind erosion only)	NA	3.9 (3.5)	1.9 (1.7)[e]	kg/hectare/day[h] (lb/acre/day)	D
Unpaved haul roads					
Wet materials	[i]	[i]	[i]		D

[a] NA = not available. TSP = total suspended particulate. Predictive emission factor equations, which generally provide more accurate estimates of emissions under specific conditions, are presented in Chapter 11. Factors for open dust sources are not necessarily representative of the entire industry or of a "typical" situtation.

[b] Total particulate is airborne particles of all sizes in the source plume. TSP is what is measured by a standard high volume sampler (see Section 11.2).

[c] References 5-9.

[d] References 4-5. For completely wet operations, emissions are likely to be negligible.

[e] Extrapolation of data, using k factors for appropriate operation from Chapter 11.

[f] For physical, not aerodynamic, diameter.

[g] Reference 6. Includes the following distinct source operations in the storage cycle: (1) loading of aggregate onto storage piles (batch or continuous drop operations), (2) equipment traffic in storage areas, (3) wind erosion of pile (batch or continuous drop operations). Assumes 8 to 12 hours of activity/24 hours.

[h] Kg/hectare (lb/acre) of storage/day (includes areas among piles).

[i] See Section 11.2 for empirical equations.

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5. "Crushed Rock Screening Source Test Reports on Tests Performed at Conrock Corp., Irwindale and Sun Valley, CA Plants", Engineering-Science, Inc., Arcadia, CA, August 1984.

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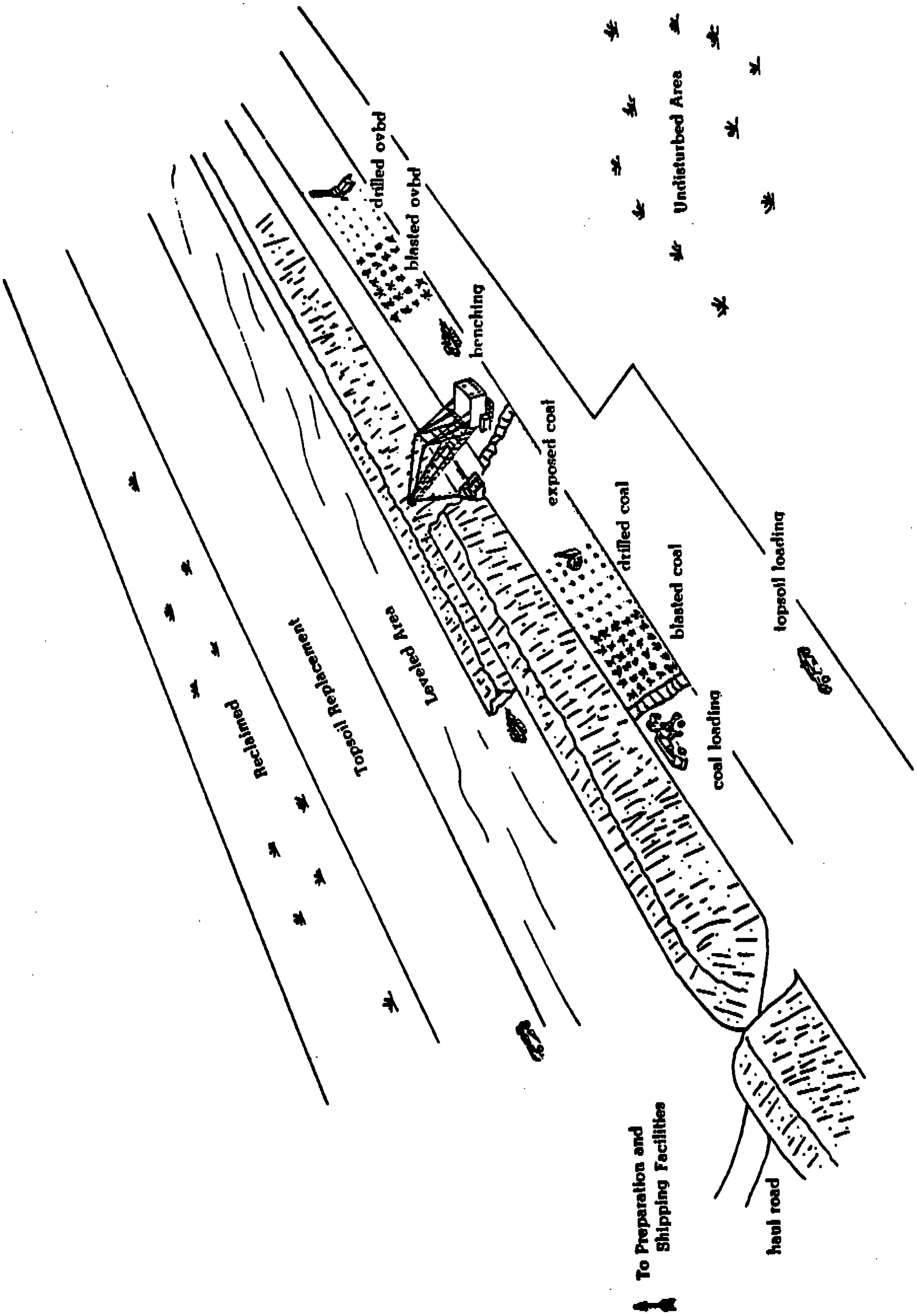

Figure 8.24-2. Operations at typical western surface coal mines.

TABLE 8.24-1. EMISSION FACTOR EQUATIONS FOR UNCONTROLLED OPEN DUST SOURCES AT WESTERN SURFACE COAL MINES (METRIC UNITS)[a]

Operation	Material	Emissions by particle size range (aerodynamic diameter)[b,c]				Units	Emission Factor Rating
		TSP ≤ 30 um	≤ 15 um	≤ 10 um[d]	<2.5 um/TSP[e]		
Blasting	Coal or overburden	$0.00022^{1.5}$	NA	0.52[e]	NA	kg/blast	C
Truck loading	Coal	$\frac{0.580}{(M)^{1.2}}$	$\frac{0.0596}{(M)^{0.9}}$	0.75	0.019	kg/Mg	B
Bulldozing	Coal	$\frac{35.6\ (s)^{1.2}}{(M)^{1.3}}$	$\frac{8.44\ (s)^{1.5}}{(M)^{1.4}}$	0.75	0.022	kg/hr	B
	Overburden	$\frac{2.6\ (s)^{1.2}}{(M)^{1.3}}$	$\frac{0.45\ (s)^{1.5}}{(M)^{1.4}}$	0.75	0.105	kg/hr	B
Dragline	Overburden	$\frac{0.0046\ (d)^{1.1}}{(M)^{0.3}}$	$\frac{0.0029\ (d)^{0.7}}{(M)^{0.3}}$	0.75	0.017	kg/m^3	B
Scraper (travel mode)		$9.6 \times 10^{-6}\ (s)^{1.3}\ (W)^{2.4}$	$2.2 \times 10^{-6}\ (s)^{1.4}\ (W)^{2.5}$	0.60	0.026	kg/VKT	A
Grading		$0.0034\ (S)^{2.5}$	$0.0056\ (S)^{2.0}$	0.60	0.031	kg/VKT	B
Vehicle traffic (light/medium duty)		$\frac{1.63}{(M)^{4.0}}$	$\frac{1.05}{(M)^{4.3}}$	0.60	0.040	kg/VKT	B
Haul truck		$0.0019\ (w)^{3.4}\ (L)^{0.2}$	$0.0014\ (w)^{3.5}$	0.60	0.017	kg/VKT	A
Active storage pile (wind erosion and maintenance)	Coal	1.8 u	NA	NA	NA	$\frac{kg}{(hectare)(hr)}$	C[f]

---

[a] Reference 1, except for coal storage pile equation from Reference 4. TSP = total suspended particulate. VKT = vehicle kilometers traveled. NA = not available.

[b] TSP denotes what is measured by a standard high volume sampler (see Section 11.2).

[c] Symbols for equations:

A = horizontal area, with blasting depth $\leq$ 21 m.
Not for vertical face of a bench.
M = material moisture content (%)
s = material silt content (%)
u = wind speed (m/sec)
d = drop height (m)
W = mean vehicle weight (Mg)
S = mean vehicle speed (kph)
w = mean number of wheels
L = road surface silt loading (g/m^2)

[d] Multiply the $\leq$15 um equation by this fraction to determine emissions.

[e] Multiply the TSP predictive equation by this fraction to determine emissions in the $\leq$2.5 um size range.

[f] Rating applicable to Mine Types I, II and IV (see Tables 8.24-5 and 8.24-6).

9. PETROLEUM INDUSTRY

The petroleum industry involves the refining of crude petroleum and the processing of natural gas into a multitude of products.

In discussing prescribed burning, the combustion process is divided into preheating, flaming, glowing and smoldering phases. The different phases of combustion greatly affect the amount of emissions produced.[5-7] The preheating phase seldom releases significant quantities of material to the atmosphere. Glowing combustion is usually associated with burning of large concentrations of woody fuels such as logging residue piles. The smoldering combustion phase is a very inefficient and incomplete combustion process that emits pollutants at a much higher ratio to the quantity of fuel consumed than does the flaming combustion of similar materials.

The amount of fuel consumed depends on the moisture content of the fuel.[8-9] For most fuel types, consumption during the smoldering phase is much greatest when the fuel is driest. When lower layers of the fuel are moist, the fire usually is extinguished rapidly.[10]

The major pollutants from wildland burning are particulate, carbon monoxide and volatile organics. Nitrogen oxides are emitted at rates of from 1 to 4 grams per kilogram burned, depending on combustion temperatures. Emissions of sulfur oxides are negligible.[11-12]

Particulate emissions depend on the mix of combustion phase, the rate of energy release, and the type of fuel consumed. All of these elements must be considered in selecting the appropriate emission factor for a given fire and fuel situation. In some cases, models developed by the U. S. Forest Service have been used to predict particulate emission factors and source strength.[13] These models address fire behavior, fuel chemistry, and ignition technique, and they predict the mix of combustion products. There is insufficient knowledge at this time to describe the effect of fuel chemistry on emissions.

Table 11.1-3 presents emission factors from various pollutants, by fire and fuel configuration. Table 11.1-4 gives emission factors for prescribed burning, by geographical area within the United States. Estimates of the percent of total fuel consumed by region were compiled by polling experts from the Forest Service. The emission factors are averages and can vary by as much as 50 percent with fuel and fire conditions. To use these factors, multiply the mass of fuel consumed per hectare by the emission factor for the appropriate fuel type. The mass of fuel consumed by a fire is defined as the available fuel. Local forestry officials often compile information on fuel consumption for prescribed fires and have techniques for estimating fuel consumption under local conditions. The Southern Forestry Smoke Management Guidebook[5] and the Prescribed Fire Smoke Management Guide[15] should be consulted when using these emission factors.

The regional emission factors in Table 11.1-4 should be used only for general planning purposes. Regional averages are based on estimates of the acreage and vegetation type burned and may not reflect prescribed burning activities in a given state. Also, the regions identified are broadly defined, and the mix of vegetation and acres burned within a given state may vary considerably from the regional averages provided. Table 11.1-4 should not be used to develop emission inventories and control strategies.

To develop state emission inventories, the user is strongly urged to contact that state's federal land management agencies and state forestry agencies that conduct prescribed burning to obtain the best information on such activities.

Table 11.1-3. EMISSION FACTORS FOR PRESCRIBED BURNING[a]

Fire/fuel configuration	Phase	Pollutant (g/kg)						Fuel mix (%)	Emission Factor Rating
		Particulate			Carbon Monoxide	Volatile Organics			
		PM-2.5	PM-10	Total		Methane	Nonmethane		
Broadcast logging slash									
Hardwood[b]	F	6	7	13	44	2.1	3.8	33	A
	S	13	14	20	146	8.0	7.7	67	A
	Fire	11	12	18	112	6.1	6.4		A
Conifer									
Short needle[c]	F	7	8	12	72	2.3	2.1	33	A
	S	14	15	19	226	7.2	4.2	67	A
	Fire	12	13	17	175	5.6	3.5		A
Long needle[d]	F	6	6	9	45	1.5	1.7	33	B
	S	16	17	25	166	7.7	5.4	67	B
	Fire	13	13	20	126	5.7	4.2		B
Logging slash debris									
Dozer piled conifer									
No mineral soil[d]	F	4	4	5	28	1.0	-	90	B
	S	6	7	14	116	8.7	-	10	B
	Fire	4	4	6	37	1.8	-		B
10-30% mineral soil[e]	S	-	-	25	200	-	-	-	D
25% organic soil[e]	S	-	-	35	250	-	-	-	D
Range fire									
Juniper slash[f]	F	7	8	11	41	2.0	2.7	8.2	B
	S	12	13	18	125	10.3	7.8	15.6	B
	Fire[k]	9	10	14	82	6.0	5.2	12.5	B
Sagebrush[f]	F	15	16	23	78	3.7	3.4		B
	S	13	15	23	106	6.2	7.3		B
	Fire[k]	13	15	23	103	6.2	6.9		B
Chaparral shrub communities[m]	F	7	8	16	56	1.7	8.2		A
	S	12	13	23	133	6.4	15.6		A
	Fire	10	11	20	101	4.5	12.5		A

Table 11.1-3. EMISSION FACTORS FOR PRESCRIBED BURNING (cont.)[a]

Fire/fuel configuration	Phase	Pollutant (g/kg) Particulate PM-2.5	Particulate PM-10	Particulate Total	Carbon Monoxide	Volatile Organics Methane	Volatile Organics Nonmethane	Fuel mix (%)	Emission Factor Rating
Line fire									
Conifer									
Long needle (pine)	Heading[g]	-	40	50	200	-	-		D
	Backing[h]	-	20	20	125	-	-		D
Palmetto/gallberry[g]	Heading	-	15	17	150	-	-		D
	Backing	-	15	15	100	-	-		D
	Fire	-	8 to 22	-	-	-	-		D
Chaparral[h]	Heading	8	9	15	62	2.8	3.5		C
Grasslands[g]	Fire	-	10	10	75	-	0		D

[a] References 7-8. Unless otherwise noted, determined by field testing of fires ≥ 1 acre size. F = flaming. S = smoldering. Fire = weighted average of F and S. Dash = no data.

[b] For PM-10, Reference 7. Emission Factor Rating: C.

[c] For PM-10, References 3,7. Emission Factor Rating: C.

[d] For PM-10, References 3,7. Emission Factor Rating: D.

[e] Reference 12. Determined using laboratory combustion hood.

[f] Reference 16.

[g] References 13-14. Determined using laboratory combustion hood.

[h] References 13-14.

[j] Reference 7.

[k] Fuel mix uncertain, because of short, intense flaming phase. Use fire average for emission inventory purposes.

[m] References 17-18.

TABLE 11.1-4. EMISSION FACTORS FOR PRESCRIBED BURNING BY U. S. REGION

Regional configuration and fuel type[a]	Percent of fuel[b]	Pollutant[c]			
		Particulate (g/kg)			CO
		$PM_{2.5}$	PM_{10}	PM	
Pacific Northwest					
Logging slash					
Piled slash	42	4	5	6	37
Douglas fir/ Western hemlock	24	12	13	17	175
Mixed conifer	19	12	13	17	175
Ponderosa pine	6	13	13	20	126
Hardwood	4	11	12	18	112
Underburning pine	5	30	30	35	163
Average for region	100	9.4	10.3	13.3	111.1
Pacific Southwest					
Sagebrush	35		9	15	62
Chaparral	20	8	9	15	62
Pinyon/Juniper	20		13	17	175
Underburing pine	15		30	35	163
Grassland	10		10	10	75
Average for region	100		13.0	17.8	101.0
Southeast					
Palmetto/gallberry	35		15	16	125
Underburning pine	30		30	35	163
Logging slash	20		13	20	126
Grassland	10		10	10	75
Other	5		17	17	175
Average for region	100		18.8	21.9	134
Rocky Mountain					
Logging slash	50		4	6	37
Underburning pine	20		30	35	163
Grassland	20		10	10	75
Other	10		17	17	175
Average for region	100		11.9	13.7	83.4
North Central and Eastern					
Logging slash	50		13	17	175
Grassland	30		10	10	75
Underburning pine	10		30	35	163
Other	10		17	17	175
Average for region	100		14	16.5	143.8

[a] Regional areas are generalized, e. g., the Pacific Northwest includes Oregon, Washington and parts of Idaho and California. Fuel types generally reflect the ecosystems of a region, but users should seek advice on fuel type mix for a given season of the year. An average factor for Northern California could be more accurately described as chaparral, 25%; underburning pine, 15%; sagebrush, 15%; grassland, 5%; mixed conifer, 25%; and Douglas fir/Western hemlock, 15%. Dash = no data.

[b] Based on the judgment of forestry experts.

[c] Adapted from Table 11.1-3 for the dominant fuel types burned.

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11.4 WET COOLING TOWERS

11.4.1 General[1]

Cooling towers are heat exchangers which are used to dissipate large heat loads to the atmosphere. They are used as an important component in many industrial and commercial processes needing to dissipate heat. Cooling towers may range in size from less than $5.3(10)^6$ kilojoules ($5(10)^6$ British Thermal Units per hour) for small air conditioning cooling towers to over $5275(10)^6$ kilojoules per hour ($5000(10)^6$ Btu/h) for large power plant cooling towers.

Although cooling towers can be classified several ways, the primary classification is into dry towers or wet towers. However, some hybrid wet-dry combinations exist. Subclassifications can include the type of draft and/or the location of the draft relative to the heat transfer medium, the type of heat transfer medium, the relative direction of air movement, and the type of distribution system.

When water is used as the heat transfer medium, wet or evaporative cooling towers may be used. Wet cooling towers rely on the latent heat of water evaporation to exchange heat between the process and the air passing through the cooling tower. The cooling water may be an integral part of the process or provide cooling via heat exchangers.

In wet cooling towers, the heat transfer is measured by the decrease in the process temperature and a corresponding increase in the moisture content and wet bulb temperature of the air passing through the cooling tower. (There may also be a change in the sensible, or dry bulb, temperature; however, its contribution to the heat transfer process is very small and is typically ignored when designing wet cooling towers.) Wet cooling towers typically have a wetted media called "fill" to promote evaporation by providing a large surface area and/or by creating many water drops with a large cumulative surface area.

Cooling towers can be categorized by: the type of heat transfer; the type of draft and location of the draft relative to the heat transfer medium; the type of heat transfer medium; the relative direction of air and water contact; and the type of water distribution system. Since evaporative cooling towers are the dominant type, and they also generate air pollutants, this Section will address only that type of tower. Diagrams of the various tower configurations are shown in Figures 11.4-1 and 11.4-2.

11.4.2 Emissions And Controls[1]

Because wet cooling towers have direct contact between the cooling water and the air passing through the tower, some of the liquid water may be entrained in the air stream and be carried out of the tower as "drift" droplets. Therefore, the constituents of the drift droplets, i. e., particulate matter, may be classified an emission.

The magnitude of drift loss is influenced by the number and size of droplets produced within the cooling tower, which in turn are determined by the fill design, the air and water patterns, and other interrelated factors. Tower maintenance and operation can also influence the formation of drift droplets. For example, excessive water flow, excessive air flow, and water bypassing the tower drift eliminators can promote and/or increase drift emissions.

Since the drift droplets generally have the same water chemistry as the water circulating through the tower, they may compose airborne emissions. Large drift droplets settle out of the tower exhaust air stream and deposit near the tower. This can lead to wetting, icing, salt deposition, and related problems such as damage to equipment or vegetation. Since other drift droplets may evaporate before being deposited in the area surrounding the tower, they can also result in PM-10 emissions. PM-10 is generated when the drift droplets evaporate leaving fine particulate matter formed by crystallization of dissolved solids. Dissolved solids found in cooling tower drift can consist of mineral matter, chemicals for corrosion inhibition, etc.

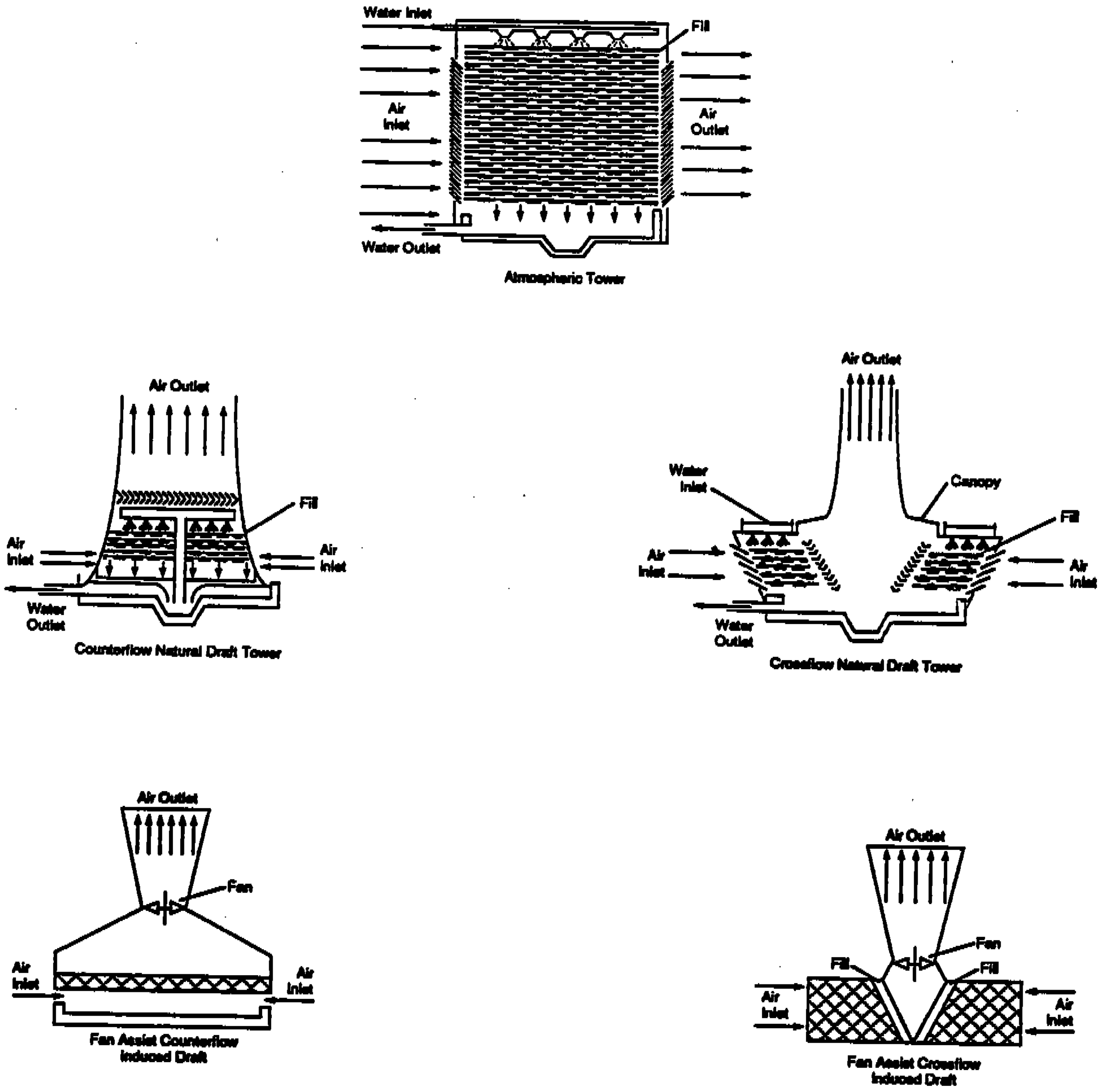

Figure 11.4-1. Atmospheric and natural draft cooling towers.

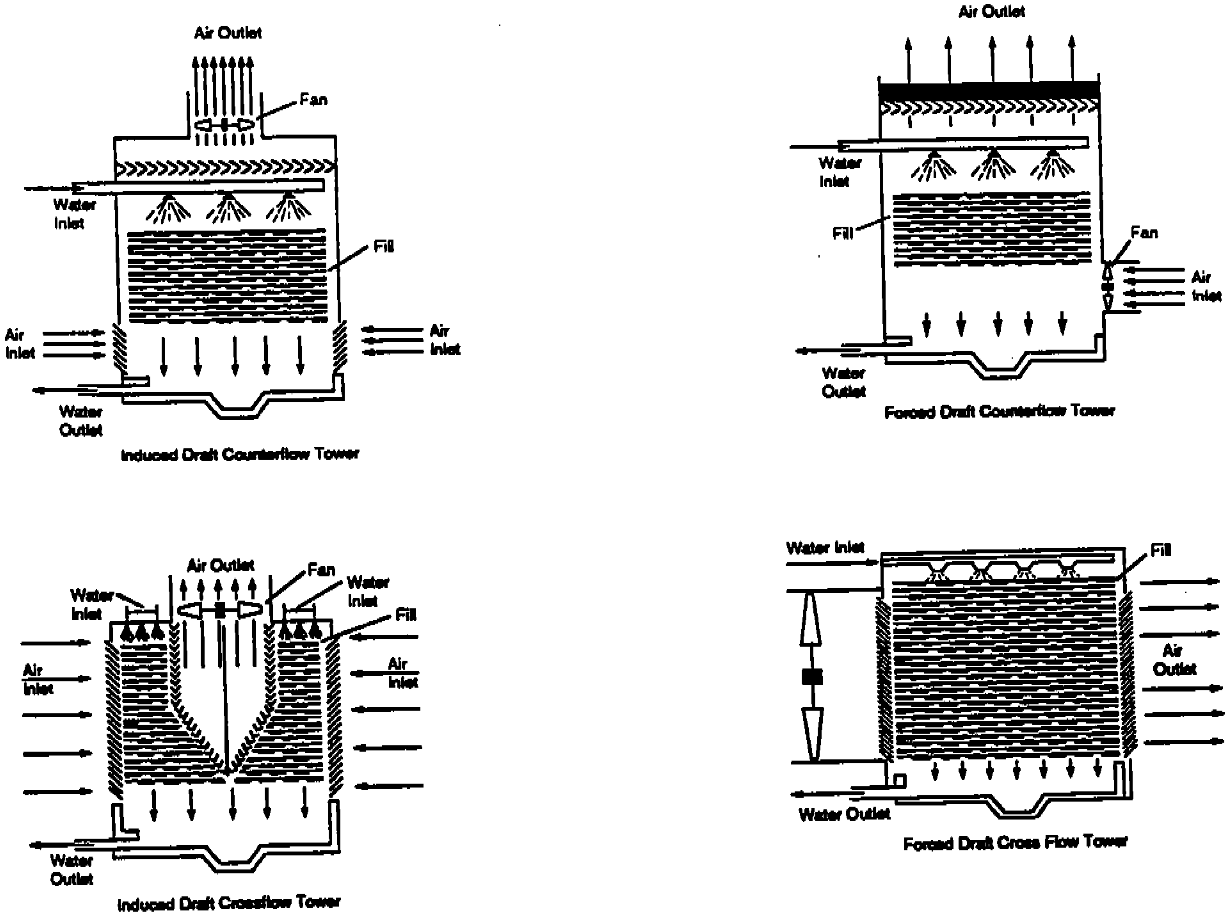

Figure 11.4-2. Mechanical draft cooling towers.

In order to reduce the drift from cooling towers, drift eliminators are usually incorporated into the cooling tower design to remove as many droplets as practical from the air stream before exiting the tower. The drift eliminators used in cooling towers rely on inertial separation caused by direction changes while passing through the eliminators. Drift eliminator configurations include herringbone (blade-type), wave form, and cellular (or honeycomb) designs, with the cellular units generally being most efficient.

Like cooling tower fill materials, drift eliminators may include various materials such as ceramic, fiber reinforced cement, fiberglass, metal, plastic, and wood installed or formed into closely spaced slats, sheets, honeycomb assemblies, or tiles. The materials may have other features such as corrugations and water removal channels to enhance the drift removal further.

Table 11.4-1 provides available particulate emission factors for wet cooling towers. Separate emission factors are given for induced draft and natural draft cooling towers. Also note that the factors shown in Table 11.4-1 most closely represent older towers with less efficient mist elimination.

Table 11.4-1. PARTICULATE EMISSIONS FACTORS FOR WET COOLING TOWERS[a]

	Total Liquid Drift Factor[b]				Apparent Factor[c]		
Tower Type[d]	Circulating Water Flow[b]	g/dkL	lb/10^3 gal	Emission Factor Rating	g/dkL[e]	lb/10^3 gal	Emission Factor Rating
Induced draft	0.020	2.0	1.7	D	0.023	0.019	E
Natural draft	0.00088	0.088	0.073	E	NA	NA	

[a] References 1-17. Numbers are given to two significant figures. NA = not available.

[b] Total liquid drift is water droplets entrained in the cooling tower exit air stream. Factors expressed as % of circulating water flow (10^{-2} L drift/L [10^{-2} gal drift/gal] water flow) and g drift/dkL (lb drift/10^3 gal) circulating water flow. 0.12 g/dkL = 0.1 lb/10^3 gal; 1 dkL = 10^1 L. References 2, 5-7, 9-10, 12-13, 15-16.

[c] Insufficient data to develop a true emission factor for wet cooling towers. Apparent emission factor calculated for each source using total drift emission factor and total dissolved solids (TDS) in circulating water, assuming TDS in circulating water = TDS in drift; and 100% conversion of TDS to PM-10 in the atmosphere. Based on available test data. Near-source deposition of large droplets is unaccounted. Includes only solid PM-10 particles. References 2, 4, 8, 11-14.

[d] See Figures 11.4-1 and 11.4-2.

[e] Expressed as g PM-10/dkL (lb PM-10/10^3 gal) circulating water flow.

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11.5 INDUSTRIAL FLARES

11.5.1 General

Flaring is a high temperature oxidation process used to burn combustible components, mostly hydrocarbons, of waste gases from industrial operations. Natural gas, propane, ethylene, propylene, butadiene and butane constitute over 95 percent of the waste gases flared. In combustion, gaseous hydrocarbons react with atmospheric oxygen to form carbon dioxide (CO_2) and water. In some waste gases, carbon monoxide (CO) is the major combustible component. Presented below, as an example, is the combustion reaction of propane.

$$C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$$

During a combustion reaction, several intermediate products are formed, and eventually, most are converted to CO_2 and water. Some quantities of stable intermediate products such as carbon monoxide, hydrogen and hydrocarbons will escape as emissions.

Flares are used extensively to dispose of 1) purged and wasted products from refineries, 2) unrecoverable gases emerging with oil from oil wells, 3) vented gases from blast furnaces, 4) unused gases from coke ovens, and 5) gaseous wastes from chemical industries. Gases flared from refineries, petroleum production, chemical industries, and to some extent, from coke ovens, are composed largely of low molecular weight hydrocarbons with high heating value. Blast furnace flare gases are largely of inert species and CO, with low heating value. Flares are also used for burning waste gases generated by sewage digesters, coal gasification, rocket engine testing, nuclear power plants with sodium/water heat exchangers, heavy water plants and ammonia fertilizer plants.

There are two types of flares, elevated and ground flares. Elevated flares, the more common type, have larger capacities than ground flares. In elevated flares, a waste gas stream is fed through a stack anywhere from 10 to over 100 meters tall and is combusted at the tip of the stack. The flame is exposed to atmospheric disturbances such as wind and precipitation. In ground flares, combustion takes place at ground level. Ground flares vary in complexity, and they may consist either of conventional flare burners discharging horizontally with no enclosures or of multiple burners in refractory-lined steel enclosures.

The typical flare system consists of 1) a gas collection header and piping for collecting gases from processing units, 2) a knockout drum (disentrainment drum) to remove and store condensables and entrained liquids, 3) a proprietary seal, water seal, or purge gas supply to prevent flash-back, 4) a single or multiple burner unit and a flare stack, 5) gas pilots and an ignitor to ignite the mixture of waste gas and air, and if required, 6) a provision for external momentum force (steam injection or forced air) for smokeless flaring. Natural gas, fuel gas, inert gas or nitrogen can be used as purge gas. Figure 11.5-1 is a diagram of a typical steam-assisted elevated smokeless flare system.

Complete combustion requires sufficient combustion air and proper mixing of air and waste gas. Smoking may result from combustion, depending upon waste gas components and the quantity and distribution of combustion air. Waste gases containing methane, hydrogen, CO and ammonia usually burn without smoke. Waste gases containing heavy hydrocarbons, such as paraffins above methane, olefins and aromatics, cause smoke. An external momentum force, such as steam injection or blowing air, is used for efficient air/waste gas mixing and turbulence, which promotes smokeless flaring of heavy hydrocarbon waste gas. Other external forces may be used for this purpose, including water spray, high velocity vortex action or natural gas. External momentum force is rarely required in ground flares.

Steam injection is accomplished either by nozzles on an external ring around the top of the flare tip or by a single nozzle located concentrically within the tip. At installations where waste gas flow varies, both are used. The internal nozzle provides steam at low waste gas flow rates, and the external jets are used with large waste gas flow rates. Several other special purpose flare tips are commercially available, one of which is for injecting both steam and air. Typical steam usage ratio varies from 7:1 to 2:1, by weight.

Waste gases to be flared must have a fuel value of at least 7500 to 9300 kilojoules per cubic meter (200 to 250 British Thermal Units per cubic foot) for complete combustion, otherwise fuel must be added. Flares providing supplemental fuel to waste gas are known as fired, or endothermic, flares. In some cases, flaring waste gases even having the necessary heat content will also require supplemental heat. If fuel bound nitrogen is present, flaring ammonia with a heating value of 13,600 kJ/m^3 (365 Btu/ft^3) will require higher heat to minimize nitrogen oxide (NO_x) formation.

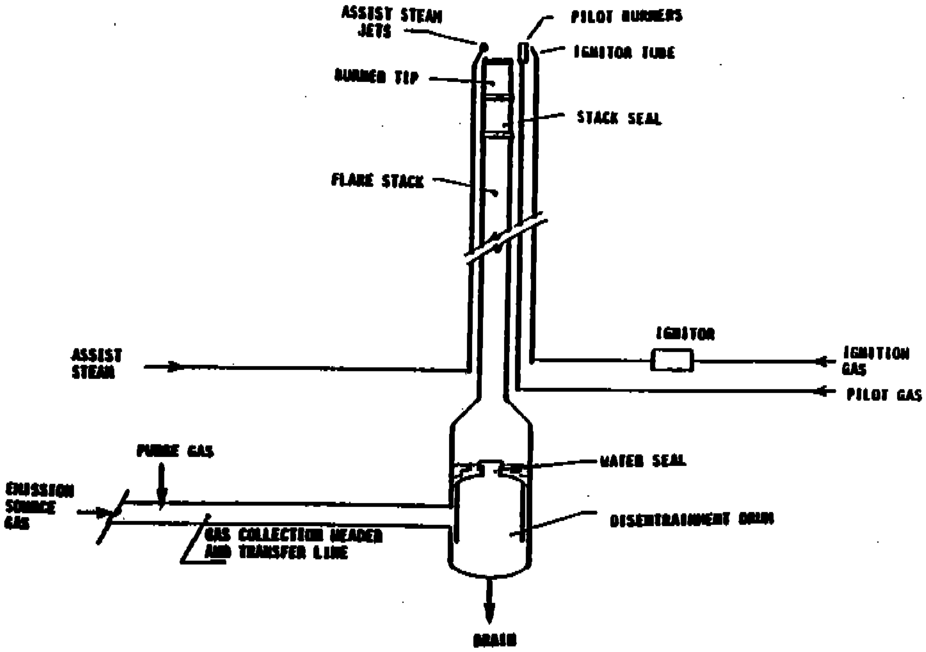

Figure 11.5-1. Diagram of a typical steam-assisted smokeless elevated flare.

At many locations, flares normally used to dispose of low volume continuous emissions are designed to handle large quantities of waste gases which may be intermittently generated during plant emergencies. Flare gas volumes can vary from a few cubic meters per hour during regular operations up to several thousand cubic meters per hour during major upsets. Flow rates at a refinery could be from 45 to 90 kilograms per hour (100 - 200 pounds per hour) for relief valve leakage but could reach a full plant emergency rate of 700 megagrams per hour (750 tons per hour). Normal process blowdowns may release 450 to 900 kg/hr (1000 - 2000 lb/hr), and unit maintenance or minor failures may release 25 to 35 Mg/hr (27 - 39 tons/hr). A 40 molecular weight gas typically of 0.012 cubic nanometers per second (25 standard cubic feet per minute) may rise to as high as 115 cubic nanometers per second (241,000 scfm). The required flare turndown ratio for this typical case is over 15,000 to 1.

Many flare systems have two flares, in parallel or in series. In the former, one flare can be shut down for maintenance while the other serves the system. In systems of flares in series, one flare, usually a low-level ground flare, is intended to handle regular gas volumes, and the other, an elevated flare, to handle excess gas flows from emergencies.

11.5.2 Emissions

Noise and heat are the most apparent undesirable effects of flare operation. Flares are usually located away from populated areas or are sufficiently isolated, thus minimizing their effects on populations.

Emissions from flaring include carbon particles (soot), unburned hydrocarbons, CO, and other partially burned and altered hydrocarbons. Also emitted are nitrogen oxides (NO_x) and, if sulfur-containing material such as hydrogen sulfide or mercaptans is flared, sulfur dioxide (SO_2). The quantities of hydrocarbon emissions generated relate to the degree of combustion. The degree of combustion depends largely on the rate and extent of fuel-air mixing and on the flame temperatures achieved and maintained. Properly operated flares achieve at least 98 percent combustion efficiency in the flare plume, meaning that hydrocarbon and CO emmissions amount to less than 2 percent of hydrocarbons in the gas stream.

The tendency of a fuel to smoke or make soot is influenced by fuel characteristics and by the amount and distribution of oxygen in the combustion zone. For complete combustion, at least the stoichiometric amount of oxygen must be provided in the combustion zone. The theoretical amount of oxygen required increases with the molecular weight of the gas burned. The oxygen supplied as air ranges from 9.6 units of air per unit of methane to 38.3 units of air per unit of pentane, by volume. Air is supplied to the flame as primary air and secondary air. Primary air is mixed with the gas before combustion, whereas secondary air is drawn into the flame. For smokeless combustion, sufficient primary air must be supplied, this varying from about 20 percent of stoichiometric air for a paraffin to about 30 percent for an olefin. If the amount of primary air is insufficient, the gases entering the base of the flame are preheated by the combustion zone, and larger hydrocarbon molecules crack to form hydrogen, unsaturated hydrocarbons and carbon. The carbon particles may escape further combustion and cool down to form soot or smoke. Olefins and other unsaturated hydrocarbons may polymerize to form larger molecules which crack, in turn forming more carbon.

The fuel characteristics influencing soot formation include the carbon-to-hydrogen ratio and the molecular structure of the gases to be burned. All hydrocarbons above methane, i. e., those with a C-to-H ratio of greater than 0.33, tend to soot. Branched chain paraffins smoke more readily than corresponding normal isomers. The more highly branched the paraffin, the greater the tendency to smoke. Unsaturated hydrocarbons tend more toward soot formation than do saturated ones. Soot is eliminated by adding steam or air, hence most industrial flares are steam assisted and some are air assisted. Flare gas composition is a critical factor in determining the amount of steam necessary.

Since flares do not lend themselves to conventional emission testing techniques, only a few attempts have been made to characterize flare emissions. Recent EPA tests using propylene as flare gas indicated that efficiencies of 98 percent can be achieved when burning an offgas with at least 11,200 kJ/m^3 (300 Btu/ft^3). The tests conducted on steam-assisted flares at velocities as low as 39.6 meters per minute (130 feet per minute) to 1140 m/min (3750 ft/min), and on air-assisted flares at velocities of 180 m/min (617 ft/min) to 3960 m/min (13,087 ft/min) indicated that variations in incoming gas flow rates have no effect on the combustion efficiency. Flare gases with less than 16,770 kJ/m^3 (450 Btu/ft^3) do not smoke.

Table 11.5-1 presents flare emission factors, and Table 11.5-2 presents emission composition data obtained from the EPA tests.[1] Crude propylene was used as flare gas during the tests. Methane was a major fraction of hydrocarbons in the flare emissions, and acetylene was the dominant intermediate hydrocarbon species. Many other reports on flares indicate that acetylene is always formed as a stable intermediate product. The acetylene formed in the combustion reactions may react further with hydrocarbon radicals to form polyacetylenes followed by polycyclic hydrocarbons.[2]

In flaring waste gases containing no nitrogen compounds, NO is formed either by the fixation of atmospheric nitrogen with oxygen or by the reaction between the hydrocarbon radicals present in the combustion products and atmospheric nitrogen, by way of the intermediate stages, HCN, CN, and OCN.[2] Sulfur compounds contained in a flare gas stream are converted to SO_2 when burned. The amount of SO_2 emitted depends directly on the quantity of sulfur in the flared gases.

Table 11.5-1. EMISSION FACTORS FOR FLARE OPERATIONS[a]

EMISSION FACTOR RATING: B

Component	Emission Factor (lb/10^6 Btu)
Total hydrocarbons[b]	0.14
Carbon monoxide	0.37
Nitrogen oxides	0.068
Soot[c]	0 to 274

[a] Reference 1. Based on tests using crude propylene containing 80 % propylene and 20 % propane.

[b] Measured as methane equivalent.

[c] Soot in concentration values: nonsmoking flares, 0 µg/liter; lightly smoking flares, 40 µg/l; average smoking flares, 177 µg/l; and heavily smoking flares, 274 µg/l.

Table 11.5-2. HYDROCARBON COMPOSITION OF FLARE EMISSION[a]

Composition	Average (range), Volume %	
Methane	55	(14 - 83)
Ethane/Ethylene	8	(1 - 14)
Acetylene	5	(0.3 - 23)
Propane	7	(0 - 16)
Propylene	25	(1 - 65)

[a] Reference 1. Ranges in parentheses. The composition presented is an average of a number of test results obtained under the following sets of test conditions: steam-assisted flare using high Btu content feed; steam-assisted using low Btu content feed; air-assisted flare using high Btu content feed; and air-assisted flare using low Btu content feed. In all tests, "waste" gas was a synthetic gas consisting of a mixture of propylene and propane.

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16. ABSTRACT

In this Supplement to the Fourth Edition of AP-42, new or revised emissions data are presented for Natural Gas Combustion; Residential Fireplaces, Residential Wood Stoves; Refuse Combustion; Nonindustrial Surface Coating; Waste Water Collection, Treatment And Storage; Polyvinyl Chloride And Polypropylene; Poly(ethylene terephthalate); Polystyrene; Ammonium Phosphates; Portland Cement Manufacturing; Sand And Gravel Processing; Western Surface Coal Mining; Wildfires And Prescribed Burning; Wet Cooling Towers and Industrial Flares

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Stationary Sources Point Sources Area Sources Emission Factors Emissions		

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