BACKGROUND REPORT

AP-42 SECTION 8.6

HYDROCHLORIC ACID PRODUCTION

Prepared for

U.S. Environmental Protection Agency
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AP-42 Background Report

TECHNICAL SUPPORT DIVISION

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
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1.0 INTRODUCTION

The document "Compilation of Air Pollutant Emission Factors" (AP-42) has been published by the U.S. Environmental Protection Agency (the EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by the EPA to respond to new emission factor needs of the EPA, State, and local air pollution control programs and industry.

An emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source. The uses for the emission factors reported in AP-42 include:

1. Estimates of area-wide emissions;
2. Emission estimates for a specific facility; and
3. Evaluation of emissions relative to ambient air quality.

The purpose of this report is to provide background information from process information obtained from industry comment and hydrochloric acid production test reports to support revision of the process description and/or emission factors for hydrochloric acid production.

Including the introduction (Chapter 1), this report contains four chapters. Chapter 2 gives a description of the hydrochloric acid production industry. It includes a characterization of the industry, an overview of the different process types, a description of emissions, a description of the technology used to control emissions resulting from hydrochloric acid production, and a review of specific data sets.

Chapter 3 is a review of emissions data collection and analysis procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Chapter 4 details criteria and noncriteria pollutant emission factor development. It includes the review of specific data sets and the results of data analysis. Particle size determination and particle size data analysis methodology are described when applicable. Appendix A presents a copy of the revised AP-42 Section 8.6.

2.0 INDUSTRY DESCRIPTION

2.1 GENERAL[1,4]

Hydrochloric acid (HCl) is a versatile chemical that has a number of different industrial uses. Some examples are hydrometallurgical processing (e.g., production of alumina and/or titanium dioxide), chlorine dioxide synthesis, hydrogen production, activation of petroleum wells, and miscellaneous cleaning/etching operations including metal cleaning (e.g., steel pickling). Also known as muriatic acid, HCl is used by masons to clean finished brick work. Hydrochloric acid is also a common ingredient in many reactions and is the preferred acid for catalyzing organic processes. One example is a carbohydrate reaction promoted by hydrochloric acid, analogous to those in the digestive tracts of mammals.

Hydrochloric acid may be manufactured by several different processes, however, over 90 percent of the HCl produced in the U.S. is a byproduct of the chlorination reaction. Some examples of chlorination reactions are the production of dichloromethane, trichloroethylene, perchloroethylene, and vinyl chloride.

The 1990 Directory of Chemical Producers lists 80 facilities in the U.S. that produce HCl. These facilities produce approximately 2.3 million megagrams (2.5 million tons) of HCl annually, a slight decrease from the 2.5 million megagrams (2.8 million tons) produced in 1985. The majority of these facilities are located in the Gulf Coast and Northeast portions of the country. Fourteen of the facilities are located in Louisiana, the most of any State. Texas has the second highest total with nine, followed by West Virginia with seven and New Jersey with five facilities each.

2.2 PROCESS DESCRIPTION[1-3,5]

Hydrochloric acid can be produced by one of the five following processes:

1) Synthesis from elements:

$$H_2 + Cl_2 \rightarrow 2HCl \quad (1)$$

2) Reaction of metallic chlorides, particularly sodium chloride (NaCl), with sulfuric acid (H_2SO_4) or a hydrogen sulfate:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \quad (2)$$

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl \quad (3)$$

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl \quad (4)$$

3) As a byproduct of chlorination, e.g. in the production of dichloromethane, trichloroethylene, perchloroethylene, or vinyl chloride:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \quad (5)$$

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \quad (6)$$

4) By thermal decomposition of the hydrated heavy-metal chlorides from spent pickle liquor in metal treatment:

$$2FeCl_3 + 6H_2O \rightarrow Fe_2O_3 + 3H_2O + 6HCl \quad (7)$$

5) From incineration of chlorinated organic waste:

$$C_4H_6Cl_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O + 2HCl \quad (8)$$

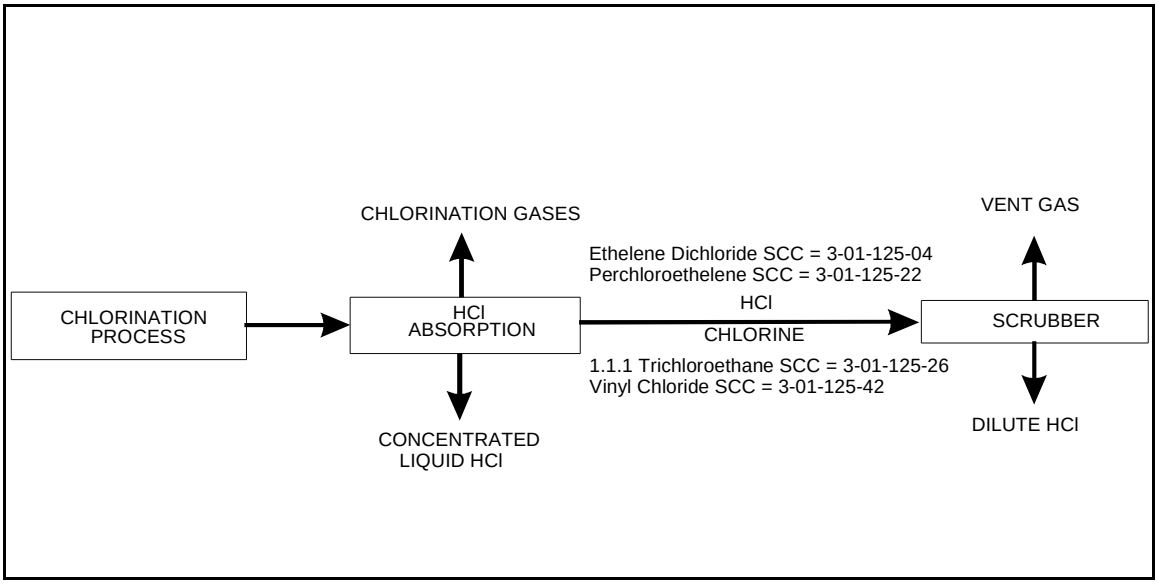

Figure 2.2-1 HCl production from chlorination process

Figure 2.2-1 is a simplified diagram of the steps used for the production of byproduct HCl from the chlorination process.

After leaving the chlorination process, the HCl-containing gas stream proceeds to the absorption column, where concentrated liquid HCl is produced by absorption of HCl vapors into a weak solution of hydrochloric acid. The HCl-free chlorination gases are removed for further

processing. The liquid acid is then either sold or used elsewhere in the plant. The final gas stream is sent to a scrubber to remove the remaining HCl prior to venting.

2.3 EMISSIONS AND CONTROLS[5,6]

Hydrochloric acid is listed as a Title III Hazardous Air Pollutant (HAP) as defined in the 1990 Clean Air Act Amendments. Emissions from hydrogen chloride production result primarily from gas that exits the HCl purification system. The contaminants are HCl gas and chlorine (both HAPs), and chlorinated organic compounds. The type of chlorinated organic compounds emitted are dependent on the type process that produces the HCl as a byproduct.

According to a 1985 emission inventory, over 89 percent of all HCl emitted to the atmosphere resulted from the combustion of coal. Less than one percent of the HCl emissions came from the direct production of HCl.

Tailgas concentrations of the various contaminants emitted from typical byproduct acid plants are often reduced by being scrubbed with water in a packed tower located after the final process tower. Venturi scrubbers are also used. These systems are usually designed for reducing a single contaminant but may often remove other gases. For instance, a phosgene decomposition tower which allows the phosgene to contact water or a caustic solution will at the same time absorb traces of hydrogen chloride which are present. Another method of preventing atmospheric emissions is to use a closed system. The materials are then never emitted to the atmosphere, but are simply recycled.

The removal of organics is a specific design problem for each tailgas compound. In some cases, a decomposition system is necessary; in others, an absorption system properly sized and designed is needed. If needed, the absorption medium can be changed and the efficiency will be increased so that all the organics are removed. The use of a properly designed gas scrubber will also remove organics.

2.4 REVIEW OF SPECIFIC DATA SETS

Pacific Environmental Services (PES) contacted the following sources to obtain the most up-to-date information on process descriptions and emissions for this industry:

1) Allied-Signal, Inc., Baton Rouge, Louisiana and Danville, Illinois.

2) BASF Chemicals Corp., Geismar, Louisiana.

3) Borden Chemicals and Plastics, Geismar, Louisiana.

4) Dow Chemical, Midland, Michigan.

5) Elf-Atochem N.A., Inc., Calvert City, Kentucky and King of Prussia, Pennsylvania.

6) Formosa Plastics Corp., Baton Rouge, Louisiana.

7) Hanlin Group (LCP Chemicals), Orrington, Maine and Reigelwood, North Carolina.

8) Pioneer Chlor-Alkali, Henderson, Nevada.

9) PPG Industries, Lake Charles, Louisiana.

10) Rubicon Inc., Geismar, Louisiana.

11) Vulcan Inc., Geismar, Louisiana.

No source tests or emissions data related to hydrochloric acid production were received from any of the companies contacted. The general discussion, process description, and emissions chapters of Section 8.6 were updated utilizing the following references PES obtained through a literature search for information on HCl manufacturing.

Reference 1: *Encyclopedia of Chemical Technology*

Reference 2: *Ullmann's Encyclopedia of Industrial Chemistry*

Reference 3: *Encyclopedia of Chemical Processing and Design*

Process descriptions and the block flow diagram were updated using information from these three references.

Reference 4: *1990 Directory of Chemical Producers*

Reference 4 was used to determine industrial capacity and regional statistics for the general industry description section.

Reference 5: *Hydrogen Chloride and Hydrogen Fluoride Emission Factors for the NAPAP Emission Inventory*

The quote related to HCl emissions from the combustion of coal found in the Emissions chapter was obtained from Reference 5.

Reference 6: *Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes*

The information from Reference 6 in the emissions chapter was left unchanged from the previous Section 8.6 update (February 1972).

2.5 REFERENCES FOR CHAPTER 2

1. Encyclopedia of Chemical Technology, Third Edition, Volume 12, John Wiley and Sons, New York, 1978.

2. Ullmann's Encyclopedia of Industrial Chemistry, Volume A, VCH Publishers, New York, 1989.

3. Encyclopedia of Chemical Processing and Design, Marcel Dekker, Inc., New York, 1987.

4. 1990 Directory of Chemical Producers. United States of America. Menlo Park, California: Chemical Information Services, Stanford Research Institute, 1990.

5. Hydrogen Chloride and Hydrogen Fluoride Emission Factors for the NAPAP (National Acid Precipitation Assessment Program) Emission Inventory, U.S. EPA, PB86-134040. October 1985.

6. Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes. U.S. DHEW, PHS, CPEHS, National Air Polluting Control Administration. Durham, N.C. Publication Number AP-54. September 1969.

3.0 GENERAL EMISSION DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING SOURCE TESTS

The first step in the investigative process involved a search of available literature relating to criteria and noncriteria pollutant emissions associated with hydrochloric acid production. This search included, but was not limited to the following references:

1) AP-42 background files maintained by the Emission Factor and Methodologies Section.
2) Files maintained by the Emission Standards Division.
3) Handbook of Emission Factors, Parts I and II, Ministry of Health and Environmental Protection, The Netherlands, 1980/1983.
4) The EPA databases, including but not limited to the *VOC/Particulate Matter* (PM) *Speciation Database Management System* (SPECIATE), the *Crosswalk/Air Toxic Emission Factor Data Base Management System* (XATEF), and the Emission Measurement Technical Information Center's *Test Methods Storage and Retrieval System* (TSAR).

To reduce the amount of literature collected to a final group of references pertinent to this report, the following general criteria were used:

1. Emissions data must be from a primary reference, i.e. the document must constitute the original source of test data. For example, a technical paper was not included if the original study was contained in the previous document.
2. The referenced study must contain test results based on more than one test run.
3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions (e.g., one-page reports were generally rejected).

If no primary data was found and the previous update utilized secondary data, this secondary data was still used and the Emission Factor Rating lowered, if needed. A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria. The final set of reference materials is given in Chapter 4.0.

3.2 EMISSION DATA QUALITY RATING SYSTEM

As part of Pacific Environmental Services' analysis of the emission data, the quantity and quality of the information contained in the final set of reference documents were evaluated. The following data were always excluded from consideration:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods (i.e., comparison of the EPA Method 5 front-half with the EPA Method 5 front- and back-half);
3. Test series of controlled emissions for which the control device is not specified;
4. Test series in which the source process is not clearly identified and described; and
5. Test series in which it is not clear whether the emissions were measured before or after the control device.

Data sets that were not excluded were assigned a quality rating. The rating system used was that specified by the OAQPS for the preparation of AP-42 sections. The data were rated as follows:

A Rating

Multiple tests performed on the same source using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the methodology specified in either the inhalable particulate (IP) protocol documents or the EPA reference test methods, although these documents and methods were certainly used as a guide for the methodology actually used.

B Rating

Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

C Rating

Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D Rating

Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented In the report. The source was operating within typical parameters during the test.
2. Sampling procedures. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent such alternative procedures could influence the test results.
3. Sampling and process data. Adequate sampling and process data are documented in the report. Many variations can occur unnoticed and without warning during testing. Such variations can induce wide deviations in sampling results. If a large spread between test results cannot be explained by information contained in the test report, the data are suspect and were given a lower rating.
4. Analysis and calculations. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by the EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM

The quality of the emission factors developed from analysis of the test data was rated utilizing the following general criteria:

A (Excellent)

Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B (Above average)

Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

C (Average)

Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

D (Below average)

The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E (Poor)

The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always noted.

The use of these criteria is somewhat subjective and depends to an extent on the individual reviewer.

3.4 REFERENCES FOR CHAPTER 3

1. Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections. U.S. Environmental Protection Agency, Emissions Inventory Branch, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 27711, April, 1992. [Note: this document is currently being revised at the time of this printing.]

2. AP-42, Supplement A, Appendix C.2, "Generalized Particle Size Distributions." U.S. Environmental Protection Agency, October, 1986.

4.0 POLLUTANT EMISSION FACTOR DEVELOPMENT

4.1 REVIEW OF SPECIFIC DATA SETS

Reference 1

Reference 1 is a comprehensive study undertaken in 1969 to determine emissions from the manufacture of HCl. Although the test procedures are well documented in Reference 1, no individual source tests were available to confirm the test results. The data is also over 20 years old and may not be representative of the industry today. The rating of the study was therefore dropped from "A," in the previous AP-42 update (February 1972), to "C."

The study contains data from 21 facilities that were tested, of which two utilized closed systems, nine had uncontrolled emission sources, and the remaining 10 were controlled. The data is very questionable, however, since the average uncontrolled emission factor is 0.15 kg/Mg (0.30 lb/ton), but the average controlled emission factor is 0.675 kg/Mg (1.35 lb/ton), a higher value.

PES feels that the average of the tests is not representative of actual HCl emissions since any reading of 0.5 percent HCl or less in the exit gases was considered negligible and reported as zero. This was the case for 16 of the 21 facilities tested. No further information was found in the study to indicate the minimum detectable level of HCl so that the "zero" data could be utilized. Consequently, the data reported as zero emissions could not be used.

If all of the tests reported as zero emissions are ignored and the remaining five non-zero test results are utilized, this technique results in a more reasonable uncontrolled emission factor of 0.90 kg/Mg (1.8 lb/ton) and a controlled emission factor of 0.08 kg/Mg (0.15 lb/ton). Since this is the only data available for hydrochloric acid production, this technique was used to update the emission factors for Section 8.6. The specific calculations utilizing the data in Table 4.3-1 are shown below:

Uncontrolled Emission Factor Calculation

$[(0.5 + 1.3)/2] = 0.9$ kg/Mg

Controlled Emission Factor Calculation

[(0.004 + 0.2 + 0.025)/3] = 0.08 kg/Mg

Note that the new emission factors are lower than those quoted in the previous update and that the quality ratings have been lowered as well. The previous emission factors appear to have been based on the results of a single test. This update utilizes the average of several tests to develop the emission factors. The emission factor ratings were lowered to provide a more realistic appraisal of the quality of the data. Both of the changes made for this update are a result of more closely following the emission factor development procedures outlined in Chapter 3.0 of this background report.

4.2 CRITERIA POLLUTANT EMISSIONS DATA

Volatile organic compounds.

No data on emissions of these pollutants were found for the hydrochloric acid production process. The presence and quantity of these pollutants is entirely dependent on the specific process used to produce the byproduct HCl.

Lead.

No data on emissions of these pollutants were found for the hydrochloric acid production process. The presence and quantity of these pollutants is entirely dependent on the specific process used to produce the byproduct HCl.

Sulfur dioxide.

No data on emissions of these pollutants were found for the hydrochloric acid production process. The presence and quantity of these pollutants is entirely dependent on the specific process used to produce the byproduct HCl.

Nitrogen oxides.

No data on emissions of these pollutants were found for the hydrochloric acid production process. The presence and quantity of these pollutants is entirely dependent on the specific process used to produce the byproduct HCl.

Carbon monoxide.

No data on emissions of these pollutants were found for the hydrochloric acid production process. The presence and quantity of these pollutants is entirely dependent on the specific process used to produce the byproduct HCl.

Total Suspended Particulate.

No data on emissions of these pollutants were found for the hydrochloric acid production process. The presence and quantity of these pollutants is entirely dependent on the specific process used to produce the byproduct HCl.

4.3 NONCRITERIA POLLUTANT EMISSIONS DATA

Hazardous Air Pollutants.

Hydrochloric acid is listed as a Title III Hazardous Air Pollutant (HAP) as defined in the 1990 Clean Air Act Amendments. Emissions data for both controlled and uncontrolled manufacturing environments are based solely on the results of the emissions study found in Reference 1. No additional data were found.

Table 4.3-1 contains a listing of the five tests from Reference 1 used to develop emission factors. The controlled emission factor of 0.08 kg/Mg (0.15 lb/ton) and 0.90 kg/Mg (1.8 lb/ton) uncontrolled quoted in the revised AP-42 section are based on this "C" rated data and are therefore rated "E." See Section 4.1 for a more detailed discussion of Reference 1.

Some processes that create byproduct HCl may also produce other HAP emissions. Although both chlorine (a HAP) and chlorinated organic compounds (e.g., dichloromethane, vinyl chloride, etc.) may be emitted during the byproduct production of HCl, the emissions are dependent on the specific processes used to create the byproduct HCl. Emissions data for these compounds should be available within each specific AP-42 section that produces HCl as a byproduct.

Global Warming Gases.

Pollutants such as methane, carbon dioxide, and N_2O have been found to contribute to overall global warming. No data on emissions of these pollutants were found for the hydrochloric acid production process. Although Reference 1 contained HCl emissions data, no corresponding carbon dioxide emissions data were reported.

TABLE 4.3-1 (METRIC UNITS)
HAZARDOUS AIR POLLUTANTS: HYDROCHLORIC ACID

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility #BP-13[d]						
None	C		**Average**	27	13.5	0.5
Facility #BP-18[d]						
Caustic Scrubber	C		**Average**	81.6	0.33	0.004
Facility #BP-19[d]						
Water Scrubber	C		1	54.4	2.7	0.05
			2	54.4	19	0.35
			Average	54.4	10.9	0.2
Facility #BP-20[d]						
Water Scrubber	C		1	127	0.28	0.0022
			2	127	0.24	0.0019
			3	127	8.9	0.07
			Average	127	3.18	0.025
Facility #BP-21[d]						
None	C		**Average**	204	265	1.3

[a]Units are in Mg per day.
[b]Units are in kg per day.
[c]Units are in kg per Mg.
[d]Reference 1.

TABLE 4.3-1 (ENGLISH UNITS)
HAZARDOUS AIR POLLUTANTS: HYDROCHLORIC ACID

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility #BP-13[d]						
None	C		**Average**	30	30	1
Facility #BP-18[d]						
Caustic Scrubber	C		**Average**	90	0.72	0.008
Facility #BP-19[d]						
Water Scrubber	C		1	60	6	0.1
			2	60	42	0.7
			Average	60	24	0.4
Facility #BP-20[d]						
Water Scrubber	C		1	140	0.616	0.0044
			2	140	0.518	0.0037
			3	140	19.6	0.14
			Average	140	6.91	0.049
Facility #BP-21[d]						
None	C		**Average**	225	585	2.6

[a]Units are in tons per day.
[b]Units are in lbs per day.
[c]Units are in lbs per ton.
[d]Reference 1.

Ozone Depletion Gases.

Chlorofluorocarbons have been found to contribute to ozone depletion. No data on emissions of these pollutants were found for the hydrochloric acid production process.

4.4 DATA GAP ANALYSIS

The emissions data for hydrochloric acid manufacturing is weak, at best, and provides only an estimate of emissions from this industry. Although several HCl facilities were contacted, none provided any source test data, only generalizations about emissions. A comprehensive source testing program or access to existing industry data is needed to better define emissions from this industry. The study should begin with emissions from the production of byproduct HCl, the most common production method.

TABLE 4.4-1

LIST OF CONVERSION FACTORS

Multiply:	**by:**	**To obtain:**
mg/dscm	4.37×10^{-4}	gr/dscf
m^2	10.764	ft^2
acm/min	35.31	acfm
m/s	3.281	ft/s
kg/hr	2.205	lb/hr
kPa	1.45×10^{-1}	psia
kg/Mg	2.0	lb/ton
Mg	1.1023	ton

Temperature conversion equations:

Fahrenheit to Celsius:

$$^{\circ}C = \frac{(^{\circ}F - 32)}{1.8}$$

Celsius to Fahrenheit:

$$^{\circ}F = 1.8(^{\circ}C) + 32$$

4.5 REFERENCES FOR CHAPTER 4

1. Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes. U.S. DHEW, PHS, CPEHS, National Air Polluting Control Administration. Durham, N.C. Publication Number AP-54. September 1969.

APPENDIX A.

AP-42 SECTION 8.6

[Not presented here. See instead current AP-42 Section 8.6]