[Note: with the publication of the Fifth Edition of AP-42, the Chapter and Section number for Chlor-Alkali changed to 8.11.]

BACKGROUND REPORT

AP-42 SECTION 5.5

CHLOR-ALKALI INDUSTRY

Prepared for

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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 test reports to support revision of emission factors for chlor-alkali production.

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

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 AP-42 Section 5.5.

2.0 INDUSTRY DESCRIPTION

2.1 GENERAL[1-2]

The chlor-alkali electrolysis process results in the manufacture of chlorine, hydrogen and sodium hydroxide (caustic) solution. Of these three, the primary product is chlorine. Chlorine is one of the more abundant chemicals produced by industry and has a wide variety of industrial uses. Chlorine was first used to produce bleaching agents for the textile and paper industries and for general cleaning and disinfecting. Since 1950, chlorine has become increasingly important as a raw material for synthetic organic chemistry. Chlorine is an essential component of a multitude of end products including materials of construction, solvents, and insecticides, to name a few.

In 1991, 52 chlor-alkali plants were in operation in 23 states around the country. Louisiana and Texas have the largest number of plants operating within their borders (9 and 6, respectively). Annual production from facilities in the U.S. was 9.9 million megagrams (10.9 million tons) in 1990 after peaking at 10.4 million megagrams (11.4 million tons) in 1989.

2.2 PROCESS DESCRIPTION[1-3]

The three basic processes for the electrolytic production of chlorine are 1) the diaphragm cell process (Griesheim cell, 1885), 2) the mercury cell process (Castner-Kellner cell, 1892), and 3) the membrane cell process (1970). In each process, a salt solution is electrolyzed by the action of direct electric current which converts chloride ions to elemental chlorine.

The overall process reaction is:

$$2\,NaCl + 2\,H_2O \rightarrow Cl_2 + H_2 + 2\,NaOH \qquad (1)$$

Each process represents a different method of keeping the chlorine (Cl_2) produced at the positive electrode (anode) separate from the caustic soda (NaOH) and hydrogen (H_2) produced, directly or indirectly, at the negative electrode (cathode). Of the chlorine produced in the U.S. in 1989, 94 percent was produced either by the diaphragm cell or mercury cell process. Therefore, these will be the only two processes discussed in detail.

Diaphragm Cell Process

Figure 2.2-1 shows a simplified block diagram for the diaphragm cell process.Water and sodium chloride salt are first combined to create the starting brine solution. The brine next undergoes precipitation and filtration steps to remove any impurities. After the addition of heat and more salt, the nearly saturated, purified brine is heated again before entering the electrolysis portion of the process where direct electric current is applied. The anode area is separated from the cathode by a permeable asbestos-based diaphragm
to prevent the reaction of caustic soda with chlorine. The chlorine produced at the anode is removed as the saturated brine flows through the diaphragm to the cathode chamber. The chlorine, which contains oxygen, is purified by liquefaction and evaporation to yield a dry, liquified product.

The caustic brine produced at the cathode is freed from salt and concentrated in an elaborate evaporative process to produce commercial caustic soda. The salt separated from the caustic brine is recycled to saturate the dilute brine. The hydrogen removed in the cathode chamber is cooled and purified by removal of oxygen, then used in other plant processes or sold.

Mercury Cell Process

Figure 2.2-2 shows a simplified block diagram for the mercury cell process. The recycled brine from the electrolysis process (anolyte) first is dechlorinated and then purified by a straightforward precipitation-filtration process. The brine and liquid mercury (which is used as the cathode) enter the cell flowing concurrently. The electrolysis process creates chlorine at the anode and elemental sodium at the cathode. The chlorine is taken off to be cooled, dried, and compressed for sales. The sodium combines with mercury to form sodium amalgam. The amalgam is further reacted with water in a separate reactor called the decomposer to produce hydrogen gas and caustic soda solution. The caustic and hydrogen are then separately cooled and the mercury removed before proceeding to storage, sales or other processes.

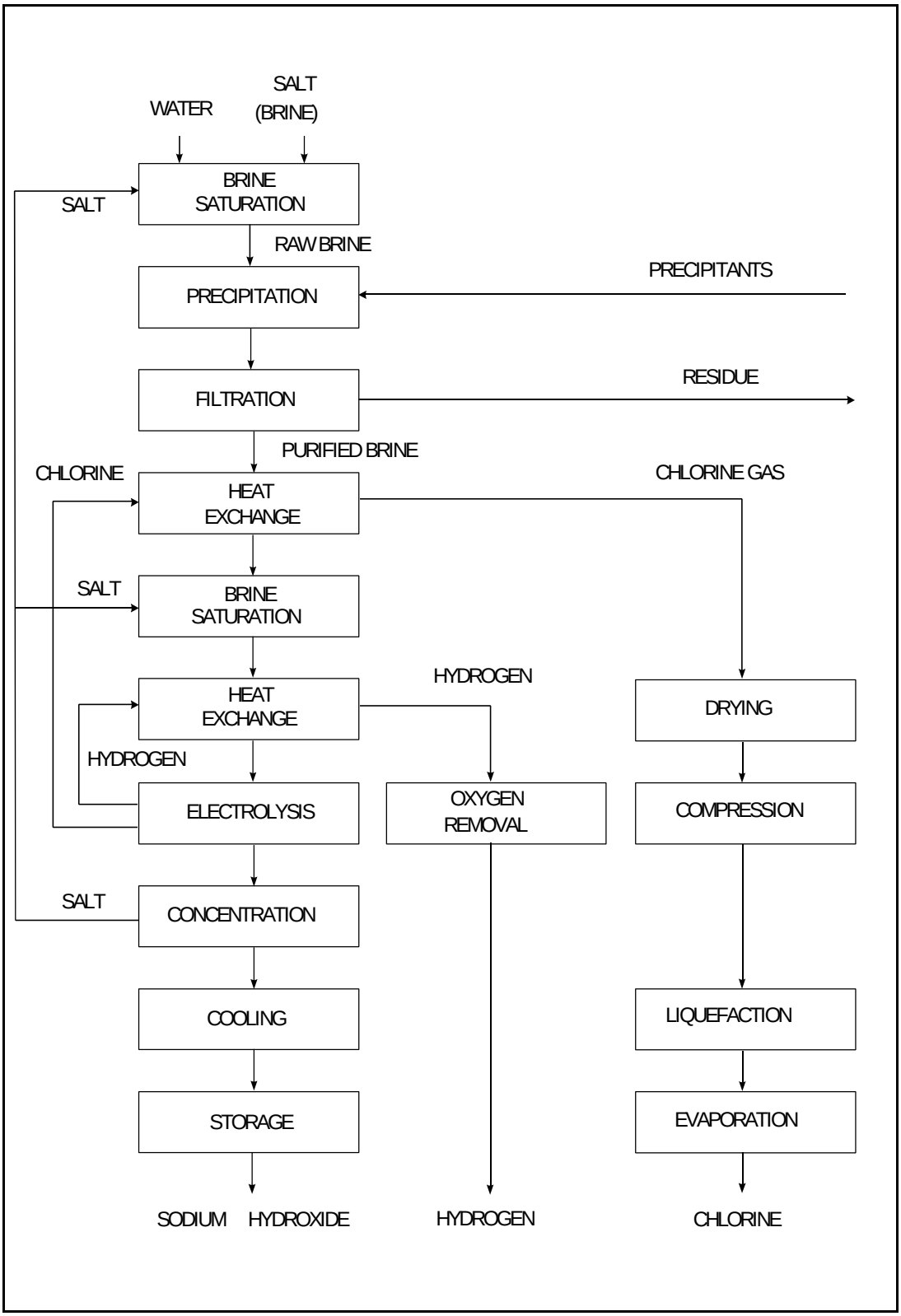

Figure 2.2-1. Simplified diagram of the diaphragm cell process

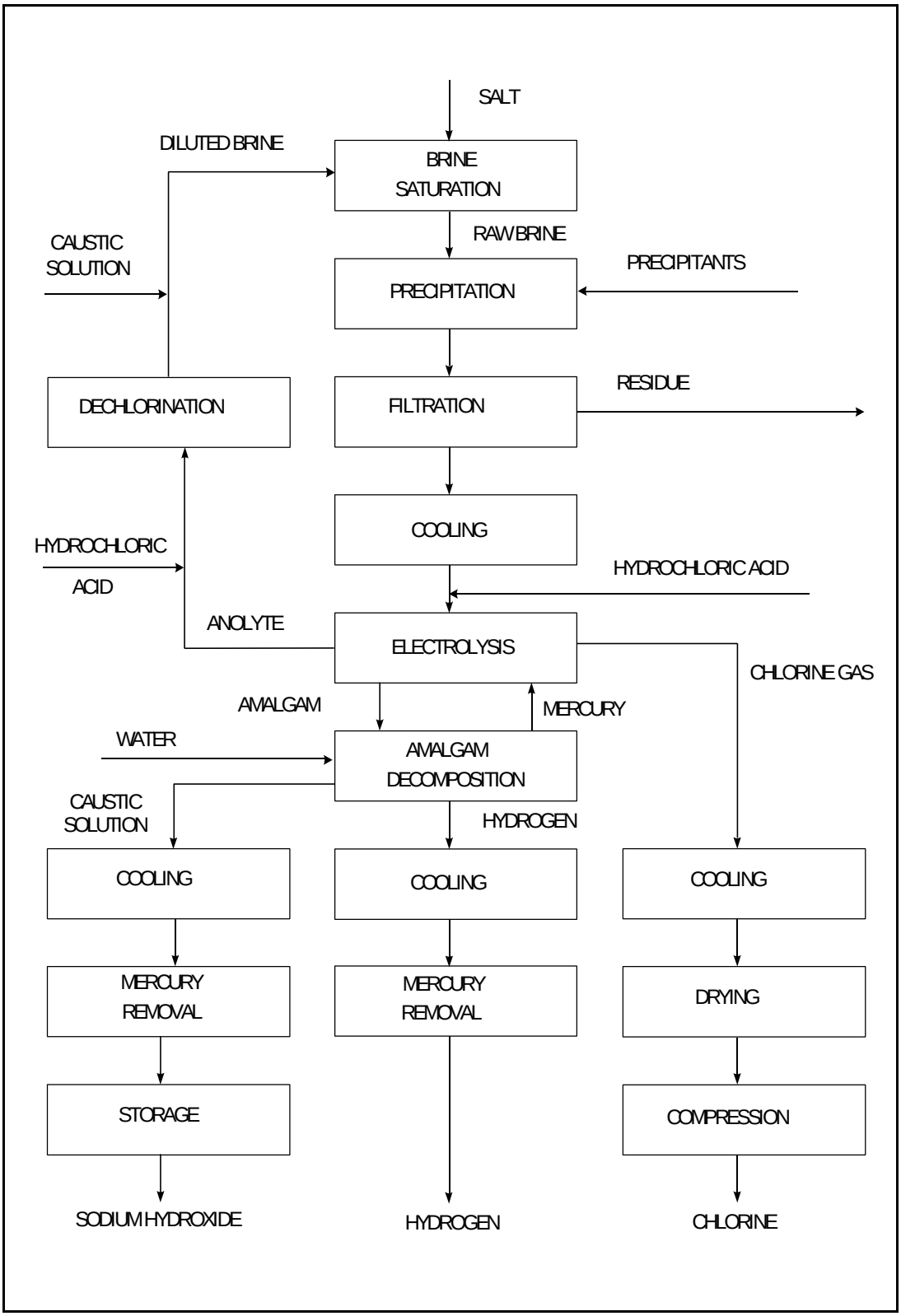

Figure 2.2-2. Simplified diagram of the mercury cell process

2.3 EMISSIONS AND CONTROLS[4]

Emissions from mercury and diaphragm cell plants include chlorine gas, carbon dioxide, carbon monoxide, and hydrogen. Gaseous chlorine is present in the blow gas from liquefaction, from vents in tank cars and tank containers during loading and unloading, and from storage tanks and process transfer tanks. Carbon dioxide emissions result from the decomposition of carbonates in the brine feed when contacted with acid. Carbon monoxide and hydrogen are created by side reactions within the production cell. Other emissions include mercury vapor from mercury cathode cells and chlorine from compressor seals, header seals, and the air blowing of depleted brine in mercury-cell plants. Emissions from these locations are, for the most part, controlled through the use of the gas in other parts of the plant, neutralization in alkaline scrubbers, or recovery of the chlorine from effluent gas streams.

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) Alabama Department of Environmental Management, Montgomery, AL.
2) Dow Chemical Corporation, Freeport, TX.
3) Elf-Atochem North America Inc., Portland, OR, and Tacoma, WA.
4) Florida Department of Environmental Regulation, Tallahassee, FL.
5) Georgia Department of Natural Resources, Atlanta, GA.
6) Kansas Department of Health and Environment, Topeka, KS.
7) Michigan Department of Natural Resources, Lansing, MI.
8) Missouri Department of Natural Resources, Jefferson City, MO.
9) North Carolina Division of Environmental Management, Raleigh, NC.
10) Pennsylvania Department of Environmental Resources, Harrisburg, PA.
11) PPG Industries, Pittsburgh, PA, and New Martinsville, WV.
12) The Chlorine Institute, Washington, DC.

Responses were received from Sources (1), (3), (11) and (12). No responses were received from the remaining sources.

Source (1) provided a source test for mercury emissions that could not be used to update emission factors (See Section 4.1, Reference 2, for details). Sources (3) and (11) provided

general process description information that was useful in confirming industry process descriptions. Source (12) provided a significant amount of both statistical data (production volumes, number of facilities, facility locations) and process description information. PES incorporated the information from these four sources into the AP-42 chapter revision.

PES also travelled to Texas Air Control Board regional offices in Houston and Beaumont, Texas to obtain copies of any compliance test data or reports for chlor-alkali plants. Although a number of facilities are located in this part of the country, no data was available at either location. Although other States, such as Louisiana, may have valid chlor-alkali source tests, the States would not voluntarily review their files and provide PES with copies of the tests. Travel to each State to obtain the information was beyond the project scope of work.

Pacific Environmental Services obtained information from References 1 through 3 through a literature search of the chlor-alkali industry. Reference 4 was obtained from the AP-42 Background File. Each reference was used to update Section 5.5 as discussed below.

Reference 1: *Ullmann's Encyclopedia of Industrial Chemistry*

Process diagrams and descriptions were updated utilizing Reference 1, which was obtained from a literature search.

Reference 2: Pamphlets provided by *The Chlorine Institute*

Reference 2 was obtained from Source (12) above. Data from this reference was used to update production volumes and define facility count and regional facility distribution.

Reference 3: *1991 Directory of Chemical Producers: United States of America*

Reference 3 was obtained from a literature search and used to confirm the statistical data obtained from Reference 2.

Reference 4: *Atmospheric Emissions from Chlor-Alkali Manufacture*.

Reference 4 was used to develop chlor-alkali emission factors as was done in the April 1981 Section 5.5 revision.

2.5 REFERENCES FOR CHAPTER 2

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

2. Pamphlets provided by Arthur E. Dungan of The Chlorine Institute, Inc., Washington, D.C. January 1991.

3. 1991 Directory of Chemical Producers: United States of America. Menlo Park, California: Chemical Information Services, Stanford Research Institute, 1991.

4. Atmospheric Emissions from Chlor-Alkali Manufacture. U.S. EPA, Air Pollution Control Office. Research Triangle Park, N.C. Publication Number AP-80. January 1971.

3.0 GENERAL EMISSION DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING

The first step of this investigation involved a search of available literature relating to criteria and noncriteria pollutant emissions associated with chlor-alkali production. This search included 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).
5) The mercury NESHAP background report and docket, as well as the 1987 Review of National Emission Standards for Mercury.

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

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

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

C

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

D

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: *Atmospheric Emissions from Chlor-Alkali Manufacture*

Reference 1 is a comprehensive study of the chlor-alkali industry from 1971 that provided the only acceptable source of emissions data to develop chlorine emission factors for Section 5.5. Reference 1 was also the only study used to generate emission factors for the April 1981 update of AP-42 Section 5.5.

The reference has well-documented test procedures but no actual source tests to confirm the results. The numbers quoted in the April 1981 update are a combination of quotes from the text of Reference 1 and summary source test data contained in tables. Comments within the text and appendices of Reference 1 generally agree with the numbers quoted in the April 1981 update, but there is little data to back up the quoted ranges. Some factors are based on engineering judgement; others are based on telecons with industry representatives. The table below summarizes the data taken from the text and used in Section 5.5. The last column compares the factors found in this update with those used in the April 1981 update.

Category	Chlorine Emission Factor (except as noted)	Reference 1 Page #	Source	April 1981 Section 5.5 Update
Diaphragm cell	1000 - 5000 kg/100 Mg (2000 - 10000 lb/100 ton)	19	Unknown	No change
Mercury cell	2000 - 8000 kg/100 Mg (4000 - 16000 lb/100 ton)	19	Unknown	No change
Returned tank car vents	4.1 kg/Mg (8.2 lb/ton)	20	Telecon	2.25 kg/Mg (4.5 lb/ton)
Air blowing of mercury brines	2.7 kg/Mg (5.4 lb/ton)	22	Engineering Estimate	2.5 kg/Mg (5.0 lb/ton)

The first two categories have remained unchanged. The last two were changed due to errors in transfer of the data from Reference 1. New emission factors for mercury cell losses are discussed in Chapter 4.3.

The emission factors for the remaining three emission categories found in Section 5.5 were based on the source test results tabulated in Reference 1. Average emission factors for these three categories are calculated below:

Water absorber

[(0.0003 + 0.0008 + 2.49)/3)] = 0.83 kg/Mg (1.66 lbs/ton)

Caustic scrubbers

[(0.0052 + 0.0002 + 0.0042 + 0.002 + 0.0027 + 0.0011 + 0.0038 + 0.034 + 0.0016 + 0.004)/10]= 0.006 kg/Mg (0.012 lb/ton)

Shipping container vents (based on 19 sources)

[(8.25 + 0.555 + 0.665 + 4.00 + 1.43 + 15.4 + 11.1 + 7.50 + 0.87 + 19.0 + 4.00 + 30.0 + 17.86 + 3.94 + 4.51 + 7.25 + 12.79 + 3.00 + 12.23)/19] = 8.66 kg/Mg
(17.3 lb/ton)

The average water absorber emission factor (0.83 kg/Mg) was used for this revision, versus an estimated range (0.125 to 5 kg/Mg; 0.25 to 10 lb/ton) quoted in the April 1981 update. Similarly, the caustic/lime scrubber value is now an average of the test results shown above. The emission factor was previously 0.5 kg/Mg (1 lb/ton), a number that PES was unable to verify. The "shipping container vents" category is now an average of 19 tests and was renamed (from "storage tank vents") to more closely represent the data. The April 1981 version quoted an emission factor of 6 kg/Mg (12 lbs/ton) for this category. This has been changed to 8.66 kg/Mg.

The Reference 1 study has been rated "C"; the AP-42 emission factors using this data were downgraded to from "B" to "E." The drop in emission factor rating is due to the lack of primary source test data needed to confirm the study results.

Reference 2: *Stationary Source Sampling Report, Reference No. 5593*

Reference 2 is a mercury emissions source test report for the Linden Chemicals and Plastics, Inc. chlor-alkali plant located in Riegelwood, North Carolina. Based on the criteria set forth in Chapter 3.0 of this background report, the test was rejected for the following reasons:

1) Velocity measurements have conflicting documentation.

2) No calibration curve is reported.
3) Pitot tube documentation was not found.
4) No thermometer calibration data was found.
5) There is no record of a post-test calibration.

Table 4.3-1 contains a summary of the test data. It has been included for information purposes only.

Reference 3: B.F. Goodrich Chemical Company

Reference 3 contains mercury emissions source tests for the B.F. Goodrich chlor-alkali plant in Calvert City, Kentucky. The tests were used to substantiate the 1973 mercury NESHAP. The tests have been rated "C" due to the use of non-standard methods to obtain the results as well as no calibration documentation. The data is contained in Table 4.3-1.

Reference 4: Diamond Shamrock Corporation

Reference 4 contains mercury emissions source tests for the Diamond Shamrock chlor-alkali plant in Delaware City, Delaware. The tests were used to substantiate the 1973 mercury NESHAP. The tests have been rated "C" due to the lack of calibration documentation as well as the use of non-standard methods to obtain the test results. The data is contained in Table 4.3-1.

4.2 CRITERIA POLLUTANT EMISSIONS DATA

No data on emissions of volatile organic compounds, lead, sulfur dioxide, nitrogen oxides, or total suspended particulate and PM_{10} were found or expected for the chlor-alkali process.

Carbon monoxide.

Carbon monoxide (CO) is generated due to side reactions that occur in the chlor-alkali production cells. No test data were found to elaborate on these reactions or to quantify the emissions. Reference 1 estimates CO emissions in the blow gas to be 0.4 percent by volume.

4.3 NONCRITERIA POLLUTANT EMISSIONS DATA

Hazardous Air Pollutants.

Hazardous Air Pollutants (HAPs) are defined in the 1990 Clean Air Act Amendments. Both mercury and chlorine are HAPs and are known emissions from the chlor-alkali process. See Chapter 4.1 for a detailed discussion of the source tests included in Table 4.3-1.

Mercury emission factors for mercury cell plants were calculated using the data from References 3 and 4. No other mercury emission data was found. The results utilizing the "B" and "C" data only, are shown below.

Hydrogen Vent (Uncontrolled)

[(0.003 + 0.0003)/2] = 0.0017 kg mercury/Mg chlorine produced (0.0033 lbs/ton)

Hydrogen Vent (Controlled)

[(0.001 + 0.0002)/2] = 0.0006 kg mercury/Mg chlorine produced (0.0012 lbs/ton)

End Box

[(0.004 + 0.006)/2] = 0.005 kg mercury/Mg chlorine produced (0.010 lbs/ton)

These factors have replaced the previous engineering estimate of mercury cell loses (0.175 kg/Mg) quoted in the previous AP-42 Section 5.5.

TABLE 4.3-1 (METRIC UNITS)
HAZARDOUS AIR POLLUTANTS: MERCURY EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 2. Hydrogen vent[d]						
None	D	102	1	130	0.037	0.0003
			2	130	0.047	0.0004
			3	130	0.044	0.0003
			Average	130	0.043	0.0003
Facility 2. End Box[d]						
None	D	102	1	130	0.015	0.0001
			2	130	0.020	0.0002
			3	130	0.020	0.0002
			Average	130	0.018	0.0001
Facility 3. Hydrogen Vent						
None	C	Unknown	1	272	0.869	0.003
			2	272	0.950	0.003
			3	272	0.607	0.002
			Average	272	0.809	0.003
Facility 3. Hydrogen Vent						
Demister	C	Unknown	1	272	0.282	0.001
			2	272	0.374	0.001
			3	272	0.508	0.002
			Average	272	0.388	0.001
Facility 3. End Box						
None	C	Unknown	1	272	1.44	0.005
			2	272	1.08	0.004
			3	272	0.802	0.003
			Average	272	1.107	0.004

[a]Units in Mg chlorine/day.
[b]Units in kg mercury/day.
[c]Units in kg/Mg.
[d]Reference 2.

TABLE 4.3-1 (METRIC UNITS)
HAZARDOUS AIR POLLUTANTS: MERCURY EMISSIONS
(Concluded)

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 4. Hydrogen vent						
None	C	Unknown	1	363	0.285	0.0008
			2	363	0.054	0.0002
			3	363	0.080	0.0002
			4	366	0.035	0.0001
			Average	363	0.114	0.0003
Facility 4. Hydrogen Vent						
Carbon Absorber	C	Unknown	1	363	0.094	0.0003
			2	363	0.029	0.0001
			3	363	0.039	0.0001
			4	363	0.089	0.0003
			Average	363	0.063	0.0002
Facility 4. End Box						
None	C	Unknown	1	363	2.20	0.006
			2	363	2.98	0.008
			3	363	1.74	0.005
			4	363	1.82	0.005
			5	363	2.14	0.006
			6	363	1.36	0.004
			Average	363	2.04	0.006

[a]Units in Mg chlorine/day.
[b]Units in kg mercury/day.
[c]Units in kg/Mg.
[d]Reference 2.

TABLE 4.3-1 (ENGLISH UNITS)
HAZARDOUS AIR POLLUTANTS: MERCURY EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 2. Hydrogen vent[d]						
None	D	102	1	143.5	0.082	0.0006
			2	143.5	0.104	0.0007
			3	143.5	0.097	0.0007
			Average	143.5	0.094	0.0007
Facility 2. End Box[d]						
None	D	102	1	143.5	0.033	0.0002
			2	143.5	0.044	0.0003
			3	143.5	0.043	0.0003
			Average	143.5	0.040	0.0003
Facility 3. Hydrogen Vent						
None	C	Unknown	1	300	1.92	0.006
			2	300	2.10	0.007
			3	300	1.34	0.004
			Average	300	1.79	0.006
Facility 3. Hydrogen Vent						
Demister	C	Unknown	1	300	0.622	0.002
			2	300	0.826	0.003
			3	300	1.12	0.004
			Average	300	0.856	0.003
Facility 3. End Box						
None	C	Unknown	1	300	3.17	0.011
			2	300	2.38	0.008
			3	300	1.77	0.006
			Average	300	2.44	0.008

[a]Units in tons chlorine/day.
[b]Units in lb mercury/day.
[c]Units in lb/ton.
[d]Reference 2.

TABLE 4.3-1 (ENGLISH UNITS)
HAZARDOUS AIR POLLUTANTS: MERCURY EMISSIONS
(Concluded)

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 4. Hydrogen vent						
None	C	Unknown	1	400	0.629	0.002
			2	400	0.120	0.0003
			3	400	0.175	0.0004
			4	400	0.077	0.0002
			Average	400	0.333	0.0008
Facility 4. Hydrogen Vent						
Carbon Absorber	C	Unknown	1	400	0.206	0.0005
			2	400	0.065	0.0002
			3	400	0.086	0.0002
			4	400	0.200	0.0005
			Average	400	0.139	0.0004
Facility 4. End Box						
None	C	Unknown	1	400	4.84	0.012
			2	400	6.58	0.016
			3	400	3.84	0.010
			4	400	4.02	0.010
			5	400	4.72	0.012
			6	400	2.98	0.007
			Average	400	4.50	0.011

[a]Units in tons chlorine/day.
[b]Units in lb mercury/day.
[c]Units in lb/ton.
[d]Reference 2.

Chlorine emissions from the previous AP-42 Section 5.5 were based solely on the results of Reference 1. Data for the water absorber and scrubber control devices, and uncontrolled shipping container loading emissions are shown in Table 4.3-2.

The average emission factors are shown below:

Water absorber

0.83 kg/Mg (1.66 lbs/ton)

Caustic scrubbers

0.006 kg/Mg (0.012 lb/ton)

Shipping container vents

8.66 kg/Mg (17.3 lb/ton)

The data from Reference 1 has been rated "C." Each factor is rated "E." See Section 4.1 for a detailed discussion of Reference 1.

TABLE 4.3-2 (METRIC UNITS)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 1.[d] Shipping container vents						
None	C	Unknown	**Average**	218	1814	8.35
Facility 2.[d] Shipping container vents						
None	C	Unknown	**Average**	163	90.7	0.555
Facility 3.[d] Shipping container vents						
None	C	Unknown	**Average**	316	90.7	0.665
Facility 4.[d] Shipping container vents						
None	C	Unknown	**Average**	45	181.4	4.00
Facility 6.[d] Shipping container vents						
None	C	Unknown	**Average**	64	90.7	1.43
Facility 7.[d] Shipping container vents						
None	C	Unknown	**Average**	59	907.2	15.4
Facility 8.[d] Shipping container vents						
None	C	Unknown	**Average**	163	1814.4	11.1
Facility 9.[d] Shipping container vents						
None	C	Unknown	1	45	226.8	5.00
			2	45	453.4	10.00
			Average	45	340.2	7.50
Facility 10.[d] Shipping container vents						
None	C	Unknown	**Average**	209	181.4	0.87
Facility 11.[d] Shipping container vents						
None	C	Unknown	1	72	907.2	12.65
			2	72	1814.4	25.3
			Average	72	1360.8	19.0

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

TABLE 4.3-2 (METRIC UNITS) (*continued*)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 12.[d] Shipping container vents						
None	C	Unknown	**Average**	227	907.2	4.00
Facility 13.[d] Shipping container vents						
None	C	Unknown	**Average**	91	2721.6	30.00
Facility 14.[d] Shipping container vents						
None	C	Unknown	**Average**	102	1814.4	17.86
Facility 15.[d] Shipping container vents						
None	C	Unknown	**Average**	230	907.2	3.94
Facility 19.[d] Shipping container vents						
None	C	Unknown	**Average**	201	907.2	4.51
Facility 20.[d] Shipping container vents						
None	C	Unknown	**Average**	125	907.2	7.25
Facility 21.[d] Shipping container vents						
None	C	Unknown	**Average**	172	2204.5	12.79
Facility 22.[d] Shipping container vents						
None	C	Unknown	**Average**	163	272.16	3.00
Facility 25.[d] Shipping container vents						
None	C	Unknown	**Average**	415	5080.3	12.23
Facility 1.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	218	1.13	0.0052
Facility 4.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	45	0.0084	0.0002

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

TABLE 4.3-2 (METRIC UNITS) (*continued*)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 7.[d] Liquefaction blow gases						
Water Absorber	C	Unknown	**Average**	59	0.015	0.0003
Facility 9.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	45	0.188	0.0042
Facility 10.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	209	0.408	0.0020
Facility 12.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	236	0.628	0.0027
Facility 13.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	118	0.126	0.0011
Facility 14.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	102	0.387	0.0038
Facility 25.[d] Liquefaction blow gases						
Water Absorber	C	Unknown	**Average**	279	0.211	0.0008
Facility 28.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	336	0.537	0.0016
Facility 29.[d] Liquefaction blow gases						
Caustic scrubber	C	Unknown	**Average**	127	4.33	0.034

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

TABLE 4.3-2 (METRIC UNITS) (*concluded*)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 30.[d]	**Liquefaction blow gases**					
Water absorber	C	Unknown	1	163	1012	6.2
			2	154	298	1.93
			3	135	72	0.53
			4	108	13	0.12
			Average	141	349	2.49
Facility 31.[d]	**Liquefaction blow gases**					
Caustic Scrubber	C	Unknown	**Average**	287	1.17	0.004

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

TABLE 4.3-2 (ENGLISH UNITS)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 1.[d] Shipping container vents						
None	C	Unknown	**Average**	240	4000	16.7
Facility 2.[d] Shipping container vents						
None	C	Unknown	**Average**	180	200	1.11
Facility 3.[d] Shipping container vents						
None	C	Unknown	**Average**	150	200	1.33
Facility 4.[d] Shipping container vents						
None	C	Unknown	**Average**	50	400	8.00
Facility 6.[d] Shipping container vents						
None	C	Unknown	**Average**	70	200	2.86
Facility 7.[d] Shipping container vents						
None	C	Unknown	**Average**	65	2000	30.8
Facility 8.[d] Shipping container vents						
None	C	Unknown	**Average**	180	4000	22.2
Facility 9.[d] Shipping container vents						
None	C	Unknown	1	50	500	10.00
			2	50	1000	20.00
			Average	50	750	15.00
Facility 10.[d] Shipping container vents						
None	C	Unknown	**Average**	230	400	1.74
Facility 11.[d] Shipping container vents						
None	C	Unknown	1	79	2000	25.3
			2	79	4000	50.6
			Average	79	3000	38.0

[a]Units in tons/day.
[b]Units in lb/day.
[c]Units in lb/ton.
[d]Reference 1.

TABLE 4.3-2 (ENGLISH UNITS) (*continued*)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 12.[d] Shipping container vents						
None	C	Unknown	**Average**	250	2000	8.00
Facility 13.[d] Shipping container vents						
None	C	Unknown	**Average**	100	6000	60.00
Facility 14.[d] Shipping container vents						
None	C	Unknown	**Average**	112	4000	35.71
Facility 15.[d] Shipping container vents						
None	C	Unknown	**Average**	254	2000	7.87
Facility 19.[d] Shipping container vents						
None	C	Unknown	**Average**	222	2000	9.01
Facility 20.[d] Shipping container vents						
None	C	Unknown	**Average**	138	2000	14.49
Facility 21.[d] Shipping container vents						
None	C	Unknown	**Average**	190	4860	25.58
Facility 22.[d] Shipping container vents						
			Average	180	600	6.00
Facility 25.[d] Shipping container vents						
None	C	Unknown	**Average**	458	11200	24.45
Facility 1.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	240	2.48	0.0104
Facility 4.[d] Liquefaction blow gases						
Caustic scrubber	C	Unknown	**Average**	50	0.0185	0.0004

[a]Units in tons/day.
[b]Units in lb/day.
[c]Units in lb/ton.
[d]Reference 1.

TABLE 4.3-2 (ENGLISH UNITS) (*continued*)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 7.[d] Liquefaction blow gases						
Water Absorber	C	Unknown	**Average**	65	0.0335	0.0005
Facility 9.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	50	0.4154	0.0083
Facility 10.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	230	0.90	0.0039
Facility 12.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	260	1.39	0.0053
Facility 13.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	130	0.277	0.0021
Facility 14.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	112	0.854	0.0076
Facility 25.[d] Liquefaction blow gases						
Water Absorber	C	Unknown	**Average**	308	0.466	0.0015
Facility 28.[d] Liquefaction blow gases						
Caustic Scrubber	C	Unknown	**Average**	370	1.18	0.0032
Facility 29.[d] Liquefaction blow gases						
Caustic scrubber	C	Unknown	**Average**	140	9.56	0.068

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

TABLE 4.3-2 (ENGLISH UNITS) (*concluded*)
HAZARDOUS AIR POLLUTANTS: CHLORINE EMISSIONS

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 30.[d]	**Liquefaction blow gases**					
Water absorber	C	Unknown	1	180	2232	12.4
			2	170	658	3.86
			3	149	158	1.06
			4	119	30	0.25
			Average	155	770	4.98
Facility 31.[d]	**Liquefaction blow gases**					
Caustic scrubber	C	Unknown	**Average**	316	2.58	0.008

[a]Units in tons/day.
[b]Units in lb/day.
[c]Units in lb/ton.
[d]Reference 1.

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 methane and N_2O were found for the chlor-alkali process.

Carbon dioxide emissions were found for Plant 30 in Reference 1 and are listed in Table 4.3-3. The data has been rated "C." Reference 1 contains only CO_2 emission factors from plants that generate CO_2 from the oxidation of graphite anodes and the decomposition of feed brine (as discussed in Section 2.3). Conversations with industry members indicate that graphite anodes are no longer used, making this data obsolete. For this reason, no CO_2 emission factor was shown in the AP-42 update.

TABLE 4.3-3 (METRIC UNITS)
GLOBAL WARMING GASES: CARBON DIOXIDE

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 30.[d]						
None	C	Unknown	1			1.55
			2			2.14
			3			2.17
			4			2.24
			Average			2.03

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

TABLE 4.3-3 (ENGLISH UNITS)
GLOBAL WARMING GASES: CARBON DIOXIDE

Control Equipment	Test Rating	Test Method	Run #	Production Rate[a]	Emission Rate[b]	Emission Factor[c]
Facility 30.[d]						
None	C	Unknown	1			3.10
			2			4.28
			3			4.34
			4			4.48
			Average			4.05

[a]Units in tons/day.
[b]Units in lb/day.
[c]Units in lb/ton.
[d]Reference 1.

4.4 DATA GAP ANALYSIS

As noted in Chapter 4.1, the data for developing emission factors for Section 5.5, Chlor-Alkali Industry is far from ideal. PES was unable to obtain any reliable and/or recent primary source test data for this industrial category. The existing information is out-of-date and, for the most part, unverifiable. A NESHAP is currently under development for this category which will include source testing to quantify current emissions. The results of this work should be available in 1993 and should be used to update the emission factors as well as provide the most up-to-date process descriptions. If source testing is dropped from the NESHAP scope of work, PES recommends that either the chlor-alkali industry be encouraged to supply their most recent source test data so that the emission factors can be updated for this section or a source testing program be undertaken to quantify emissions from the industry. Reliable data is needed to quantify emissions of chlorine, CO_2, CO and mercury. Closer inspection of State files, particularly in Louisiana, may also yield source tests that could be used to improve the quality of the emission factors.

TABLE 4.5-1
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 Chlor-Alkali Manufacture. U.S. EPA, Air Pollution Control Office. Research Triangle Park, N.C. Publication Number AP-80. January 1971.

2. Stationary Source Sampling Report, Reference No. 5593. Entropy Environmentalists Inc., Research Triangle Park, NC. September 1987.

3. B.F. Goodrich Chemical Company Chlor-Alkali Plant Source Tests, Calvert City, Kentucky. Roy F. Weston, Inc., EPA Contract No. CPA 70-132. May 1972.

4. Diamond Shamrock Corporation Chlor-Alkali Plant Source Tests, Delaware City, Delaware. Roy F. Weston, Inc., EPA Contract No. CPA 70-132. June 1972.

APPENDIX A.

AP-42 SECTION 5.5

[Not presented here. See instead current AP-42 Section 8.11.]