



EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT - SECTION 313

Guidance for Reporting Hydrochloric Acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size)

Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) requires certain facilities manufacturing, processing, or otherwise using listed toxic chemicals to report their environmental releases of such chemicals annually. Beginning with the 1991 reporting year, such facilities also must report pollution prevention and recycling data for such chemicals, pursuant to section 6607 of the Pollution Prevention Act, 42 U.S.C. 13106. When enacted, EPCRA section 313 established an initial list of toxic chemicals that was comprised of more than 300 chemicals and 20 chemical categories. EPCRA section 313(d) authorizes EPA to add chemicals to or delete chemicals from the list, and sets forth criteria for these actions.

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Section 1. Introduction

On July 25, 1996 (61 FR 38600), EPA modified the listing for hydrochloric acid (HCl) (Chemical Abstracts Service Registry Number 7647-01-0) on the list of toxic chemicals subject to the reporting requirements under section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) (17). EPA modified the listing by deleting non-aerosol forms of hydrochloric acid from the section 313 list based on the conclusion that they cannot reasonably be anticipated to cause adverse effects on human health or the environment. EPA added a modifier to the listing for hydrochloric acid to exclude the non-aerosol forms. The listing now reads **A**Hydrochloric acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size).@ Therefore, beginning with the 1995 reporting year, facilities are no longer required to include non-aerosol forms of hydrochloric acid in threshold and release determinations. In this document we will use the term **A**hydrochloric acid aerosols@ to indicate airborne forms of hydrochloric acid as listed under section 313 of EPCRA.

The purpose of this document is to assist facilities in determining the sources and amounts of hydrochloric acid aerosols that are to be included in threshold and release determinations under EPCRA section 313. This document is not meant to be exhaustive, but rather provides some guidance to help facilities in their determination of threshold and release quantities. Threshold and release determinations for hydrochloric acid aerosols are highly dependent on site specific conditions and equipment. Therefore, this document can only provide general information concerning the possible formation and release of hydrochloric acid aerosols. Guidance documents are available for some industry sectors subject to EPCRA section 313 and these documents should be consulted for additional information (see <http://www.epa.gov/tri>).

Section 1.1. Who Must Report

A plant, factory, or other facility is subject to the provisions of EPCRA section 313, if it meets all three of the following criteria:

- C It is included in the primary Standard Industrial Classification (SIC) codes 20 through 39 or is in one of the following industries: Metal Mining, SIC code 10 (except SIC codes 1011, 1081, and 1094); Coal Mining, SIC code 12 (except SIC code 1241); Electric Utilities, SIC codes 4911, 4931, or 4939 (each limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce); Commercial Hazardous Waste Treatment, SIC code 4953 (limited to facilities regulated under the Resource Conservation and Recovery Act, subtitle C, 42 U.S.C. section 6921 *et seq.*); Chemicals and Allied Products-Wholesale, SIC code 5169; Petroleum Bulk Terminals and Plants, SIC code 5171; and, Solvent Recovery Services, SIC code 7389 (limited to facilities primarily engaged in solvent recovery services on a contract or fee basis); and

- C It has 10 or more full-time employees (or the equivalent of 20,000 hours per year); and
- C It manufactures (includes imports), processes or otherwise uses any of the toxic chemicals listed on the EPCRA section 313 list in amounts greater than the threshold quantities specified below.

In addition, pursuant to Executive Order 12856 entitled "Federal Compliance with Right-to-Know Laws and Pollutant Prevention Requirements," federal facilities are required to comply with the reporting requirements of EPCRA Section 313 beginning with calendar year 1994. This requirement is mandated regardless of the facility's SIC code.

Section 1.2. Thresholds

Thresholds are specified amounts of toxic chemicals manufactured, processed, or otherwise used during the calendar year that trigger reporting requirements. Reporting is required for hydrochloric acid aerosols if the following thresholds are exceeded.

- C If a facility *manufactures* or *imports* 25,000 pounds of hydrochloric acid aerosols over the calendar year.
- C If a facility *processes* 25,000 pounds of hydrochloric acid aerosols over the calendar year.
- C If a facility *otherwise uses* 10,000 pounds of hydrochloric acid aerosols over the calendar year.

The quantities of hydrochloric acid aerosols included in threshold determinations are not limited to the amounts of hydrochloric acid aerosols released to the environment. All hydrochloric acid aerosols manufactured, processed, or otherwise used are to be counted toward threshold determinations. This includes any amount of hydrochloric acid aerosols that may be generated in closed systems, storage tanks, or that are generated in stacks prior to or after being treated by scrubbers.

Section 1.3. What Constitutes Aerosol Forms of Hydrochloric Acid and Their Manufacture, Processing, or Otherwise Use

For the purposes of the reporting requirements under EPCRA section 313, hydrochloric acid aerosols include mists, vapors, gas, fog, and other airborne forms of any particle size. Since hydrochloric acid is a gas under ordinary conditions, it should be especially noted that the gaseous form of hydrochloric acid, commonly referred to as hydrogen chloride, is included under the EPCRA section 313 hydrochloric acid aerosols listing. Also note that there is no size limit for particles that must be

included under the EPCRA section 313 hydrochloric acid aerosols listing. Although the qualifier includes the terms mists, vapors, gas, and fog these terms are not specifically defined for EPCRA section 313 since the last part of the qualifier "other airborne forms of any particle size" makes it clear that any airborne form is covered by the listing. The specific terms mists, vapors, gas, and fog are included to make it clear that hydrochloric acid that is identified as being in one of these forms would be covered by the hydrochloric acid aerosols listing.

If hydrochloric acid is present in the form of a gas, fog, vapor, mist or any other airborne form, then hydrochloric acid is considered to be in the aerosol form and is covered by the EPCRA section 313 hydrochloric acid aerosols listing. Solutions of hydrochloric acid which do not become airborne are not covered by the EPCRA section 313 hydrochloric acid aerosols listing but such solutions may generate hydrochloric acid aerosols during their manufacture, processing or use. In general, *hydrochloric acid aerosols are manufactured any time a solution of hydrochloric acid is made to become airborne such as when it evaporates, is sprayed or distilled.* However if gaseous HCl is absorbed into atmospheric water forming a mist, fog or aerosol, no additional aerosol hydrochloric acid is produced since the gas is already considered a reportable aerosol form. If the generation of hydrochloric acid aerosols through spraying or other means is intentional (i.e., it is intended that the hydrochloric acid aerosol be generated for a particular use activity) then, in addition to manufacturing the hydrochloric acid aerosol, such aerosols are also being otherwise used. Thus, spraying of hydrochloric acid aerosols on to an item for cleaning, etching, or other purposes constitutes the manufacture and otherwise use of hydrochloric acid aerosols. Similarly, during pickling or cleaning of metals, if hydrogen gas is liberated and sweeps hydrochloric acid into the air, then hydrochloric acid aerosols are generated. If hydrochloric acid aerosols are used in a process in which any part of the hydrochloric acid becomes incorporated into a product which is then distributed in commerce then, under EPCRA section 313, the hydrochloric acid aerosols are considered to have been processed. Examples of processes in which hydrochloric acid aerosols are manufactured, processed or otherwise used are given below.

Hydrochloric acid aerosols are generally *manufactured* when:

- C evaporation of HCl occurs from a tank containing hydrochloric acid solution;
- C volatilization of HCl occurs during loading and unloading;
- C when HCl is entrained in hydrogen emanating from a metal cleaning or pickling tank;
- C when HCl is distilled (including distillation for reclamation);
- C when material containing chlorine is burned;
- C when HCl gas is formed as a result of a chemical reaction; or
- C when solutions of hydrochloric acid are sprayed into the air.

Hydrochloric acid aerosols are generally *processed* when:

- C any part of the hydrochloric acid aerosol becomes incorporated into a product that is distributed in commerce.

Hydrochloric acid aerosols are generally *otherwise used* when:

- C HCl is applied as a spray for surface treatment.

Section 2.0. Guidance On Hydrochloric Acid Aerosols For Certain Specific Activities That Generate Aerosols Forms

EPA has provided the following guidance for specific activities that generate hydrochloric acid aerosols. The guidance in sections 2.1, 2.2, and 2.3 is intended to apply only to the specific situations discussed in these sections. If you are not sure whether this guidance applies to the situation at your facility, then EPA should be consulted before using this guidance.

Section 2.1. Hydrochloric Acid Aerosols Generated In Acid Reuse Systems

When solutions of hydrochloric acid volatilize, the **Amanufacture@** of a listed chemical (hydrochloric acid aerosols as defined in section 1.3) has occurred. This is a result of the qualifier to the hydrochloric acid listing, which excludes non-aerosol forms and limits the reporting to aerosol forms only. The addition of the acid aerosol qualifier has an impact on certain processes that, prior to the addition of the qualifier, would not have been considered to be **Amanufacturing@** a listed chemical. Acid reuse systems that use aqueous solutions of hydrochloric acid to generate acid aerosols, use the acid aerosols, condense them back into solution, and then reuse the acid solution again and again are impacted by the addition of the acid aerosol qualifier. In such processes, the continuous reuse of the acid solutions generates very large quantities of acid aerosols that technically should be counted towards the **Amanufacture@** [the generation of the acid aerosol is the **Amanufacture@** of hydrochloric acid (acid aerosol)] and **Aotherwise use@** thresholds. This may result in many facilities greatly exceeding the **Amanufacture@** and **Aotherwise use@** reporting thresholds that, prior to the addition of the qualifier, would not have exceeded thresholds.

While it is technically correct to apply all of the quantities of acid aerosols generated in such systems towards the **Amanufacture@** and **Aotherwise use@** reporting thresholds, EPA did not intend to increase the reporting burden as a result of addition of the hydrochloric acid aerosol qualifier. In addition, under EPA's general approach to reuse systems, a toxic chemical is not counted toward thresholds each time it is reused but only once per reporting period, and that approach would apply to hydrochloric acid reuse systems were it not for the aerosol qualifier. Therefore, EPA is providing the

following guidance to reduce the reporting burden for facilities that operate such processes and to bring the treatment of such systems into alignment with EPA's general approach to reuse.

Rather than having facilities count all quantities of acid aerosol generated in such systems towards the **Manufacture** and **Otherwise use** thresholds, EPA will allow facilities to apply the total quantity of acid in these systems only once to these thresholds. For example, if an acid reuse system starts the year with 2000 pounds of acid and 500 pounds is added during the year then the total amount applied towards acid aerosol thresholds would be 2500 pounds. This reflects a one time per year counting of all of the acid molecules as being in the acid aerosol form rather than counting them over and over again each time the acid aerosol form is generated and subsequently used. Since in these acid reuse systems the acid aerosols are **Manufactured** and then **Otherwise used** the 10,000 pound **Otherwise use** threshold would be the threshold that would first trigger reporting from such systems.

The guidance in this section applies only to acid reuse systems and the reporting of hydrochloric acid aerosols and sulfuric acid aerosols under EPCRA section 313. This guidance does not apply to any other types of processes or to any other listed chemical.

Section 2.2. Hydrochloric Acid Aerosols Removed By Scrubbers

When a scrubber is used to remove hydrochloric acid aerosols prior to or in a stack, the acid aerosols are usually converted to the non-aerosol form. The non-aerosol forms of hydrochloric acid are not reportable under EPCRA section 313 because the qualifier to the hydrochloric acid listing includes only acid aerosol forms. Hydrochloric acid as a discrete chemical has not actually been destroyed by the scrubber, but the form of hydrochloric acid reportable under EPCRA section 313 has been destroyed. Therefore, since hydrochloric acid aerosols removed by scrubbers are converted to a non-reportable form, the quantity removed by the scrubber can be reported as having been treated for destruction.

Section 2.3. Hydrochloric Acid Aerosols Generated In Storage Tanks

Hydrochloric acid aerosols are generated in the empty space (head space) above hydrochloric acid solutions contained in storage tanks. The amounts of acid aerosols generated in such storage tanks are to be applied towards the **Manufacture** threshold for hydrochloric acid aerosols. In such storage tanks the hydrochloric acid molecules are constantly moving between the atmosphere and the solution. EPA does not intend for facilities to count such movement of the acid molecules in and out of the stored acid solution as continuous **Manufacture** of hydrochloric acid aerosols. For such storage tanks the amount of acid aerosol to be applied towards the **Manufacture** threshold is the average amount that existed in the atmosphere above the acid solution during the year.

Each facility should determine the average conditions for their specific storage tank (i.e., the capacity of the tank, the average amount in the tank, the average head space in the tank, the concentration of the acid solution stored, the temperature, and other information that may have an impact on aerosol calculations) and make the appropriate calculation of the amount of acid aerosol to apply towards the Amanufacture@threshold. Any amounts of hydrochloric acid aerosols that may be released from the storage tank through venting or fugitive releases must also be included in the threshold determination. If the storage tank is refilled and drawn down several times during the year then the calculations should be based on all of the acid that was stored in the tank. For example, if a 10,000 pound capacity tank is refilled and drawn down 6 times during the year (such that 60,000 pounds of acid were stored in the tank during the year) then the tank calculations, based on the average condition for one 10,000 pound tank of acid, should be multiplied by 6.

EPA has an AP-42 document that presents models for estimating air emissions for organic liquid storage tanks (26). These models can be adapted to estimate emissions of hydrochloric acid aerosols. EPA also has software programs for estimating the losses of volatile organic chemicals (VOCs) from storage and treatment facilities which can be adapted to hydrochloric acid aerosols. TANKS, a DOS-based computer software program, is useful for estimating emissions from fixed- and floating-roof storage tanks. WATER8 (Wastewater Treatment Compound Property Processor and Air Emissions Estimator program) is another DOS-based computer software program that is useful for estimating chemical-specific emissions from wastewater collection and treatment systems.

The TANKS 3.0 program requires certain information about a storage tank and the liquid it contains to calculate the tank's air emissions. This information is entered and stored in tank records. There are four categories of information in a tank record: tank information (e.g., construction type, and physical characteristics); fitting information (for floating roof tanks only); site information (e.g., ambient temperature, wind speed); and liquid information. Information on the chemical composition and vapor pressure of the stored hydrochloric acid must be provided. Information has been provided in Appendix 1 to assist in such calculations.

WATER8 is an analytical model for estimating chemical-specific emissions from wastewater collection and treatment systems. It can be used for estimating emissions from open tanks and agitated systems. Both of the above software estimation programs can be downloaded from the EPA web site at <http://www.epa.gov/ttn/chief/software.html>

Section 3.0. Properties of Hydrochloric Acid

HCl is a gas at normal temperature and pressure with a normal boiling point of -85 EC. The gas is generally referred to as hydrogen chloride, while the solution is more commonly referred to as hydrochloric acid, however the terms are often used interchangeably. HCl gas is readily absorbed by water. Therefore, gaseous HCl will partition into atmospheric water such as fog, mist, and cloud water (the very small aerosol droplets of water of which clouds are composed).

The solubility of HCl in water at atmospheric pressure is 42% by weight at 20 EC. It is essentially totally ionized in solution. Hydrochloric acid solutions deviate widely from Henry's law¹ at all concentrations. Concentrated hydrochloric acid solutions (~37%) fume readily in moist air.

Under EPCRA section 313, hydrochloric acid aerosols are reported as 100% HCl so the amount of releases reported is independent of whether HCl is present as a gas or in atmospheric water (e.g., mist or fog) containing fractional amounts of HCl.

Hydrogen chloride and water form a constant boiling mixture (azeotropic mixture or azeotrope); at atmospheric pressure, 101 kiloPascals (kPa), the mixture boils at 108.584 EC and has a composition of 20.222 wt % HCl (2). As the pressure increases, the boiling point increases and the azeotropic composition decreases (see Appendix 1). At HCl concentrations below the azeotropic concentration, the vapor has a higher water concentration than the solution with which it is in equilibrium. At concentrations higher than the azeotropic concentration, the vapor is enriched in HCl relative to the liquid. Above 35 wt % HCl, the vapor has very little water content.

An equation of state for hydrochloric acid for mole fractions (x) up to 0.23 at temperatures up to 780 K and pressures up to 150 bar has been developed and describes the behavior in the single phase (vapor) region to about 1% (20). In the equation below the pressure (p) is in kPa² and the temperature (T) in degrees Kelvin.

$$\log_{10} p = 7.515 - 2056 T^{-1} + x_{\text{HCl}} (2.064 - 888 T^{-1})$$

Commercial reagent grade hydrochloric acid normally contains 36.5 to 38.0 wt % hydrochloric acid with the remainder being water. A vapor-liquid phase diagram (Figure A1), vapor composition data (Figure A3 and Table A1), and vapor pressure data (Table A2) as a function of temperature and composition for aqueous hydrochloric acid appear in Appendix 1. Conversion factors for pressure and

¹Henry's law states that the partial pressure of a component becomes proportional to its mole fraction in the limit of zero concentration.

²To obtain the pressure in other units, add the following constant to the right hand side of the equation: bars, -2.000; torr, 0.875; atm, -2.006; psi, -0.839.

concentration units appear in Tables A3 and A4 of Appendix 1. Nomograms³ are available which allow you to determine the partial pressure of HCl, the partial pressure of water, the total pressure, and the vapor composition of the vapor as a function of concentration of aqueous hydrochloric acid and temperature (19). The information in Appendix 1 and the guidance in sections 2.3 can be used to assist in determining if significant amounts of hydrochloric acid aerosols are present in storage tanks.

Section 3.1. Industrial Sources of Hydrochloric Acid Aerosols

In 1995 there were 1976 facilities that reported for hydrochloric acid aerosols under EPCRA section 313 (18). In order to analyze the more significant industrial sources of hydrochloric acid aerosols, this document focuses on the 326 facilities that reported releases of 25,000 pounds or more to air. The number of these facilities in each of the covered 2-digit SIC codes is shown in Table 1, as well as the prominent types of industries within each SIC code that have reported hydrochloric acid emissions to air. The industries shown in italics include 50 facilities that are in the 97.4th percentile (over 326,000 pounds per year) for hydrochloric acid releases to air. These 50 facilities= air emissions are almost entirely from point sources, and 34 of them report producing hydrochloric acid as a byproduct.

Table 1. Industrial Categories of 326 Facilities Emitting over 25,000 lbs/yr of Hydrochloric Acid Aerosols in 1995 and Top 50 Emitters.

| 2-Digit SIC Code | Category | No. Sites* | | Major Industries in Category** |
|------------------|---------------------------------|------------|------|---|
| | | (326) | (50) | |
| 26 | Paper and Allied Products | 236 | 46 | <i>Paper, pulp and paperboard mills</i> |
| 28 | Chemicals and Allied Products | 161 | 30 | <i>Plastics and resins; industrial inorganic chemicals; organic fibers; pharmaceuticals; alkalis and chlorine</i> |
| 33 | Primary Metal Industries | 54 | 6 | <i>Blast furnaces and steel mills; aluminum sheet; secondary nonferrous metals; cold finishing of steel; steel wire; aluminum rolling and drawing</i> |
| 37 | Transportation Equipment | 20 | 1 | <i>Motor vehicle bodies; motor vehicle parts; space propulsion units and parts</i> |
| 32 | Stone, Clay, and Glass Products | 19 | 3 | <i>Cement, hydraulic; minerals, ground or treated; glass; lime; bricks</i> |

³A nomogram is a graphic representation that consists of several lines marked off to scale and arranged in such a way that by using a straightedge to connect known values on two lines an unknown value can be read at the point of intersection with another line.

| 2-Digit SIC Code | Category | No. Sites* | | Major Industries in Category** |
|------------------|---------------------------------------|------------|------|--|
| | | (326) | (50) | |
| 20 | Food and Kindred Products | 12 | 1 | Malt beverages, <i>wet corn milling</i> , soybean oil mills |
| 24 | Lumber and Wood Products | 11 | 1 | Sawmills and planing mills; <i>reconstituted wood products</i> ; softwood veneer and plywood |
| 30 | Rubber and Misc. Plastics Products | 8 | | Plastic products |
| 29 | Petroleum and Coal Products | 7 | 1 | Petroleum refining; <i>petroleum and coal products</i> |
| 34 | Fabricated Metal Products | 7 | 1 | <i>Metal coatings</i> |
| 22 | Textile Mill Products | 5 | 1 | <i>Non-woven fabrics</i> |
| 49 | Electric, Gas, and Sanitary Services | 4 | 3 | <i>Electric services, combination utilities, refuse systems</i> |
| 21 | Tobacco Products | 4 | 1 | <i>Cigarettes</i> |
| 35 | Industrial Machinery and Equipment | 4 | | Construction machinery |
| 36 | Electronic & Other Electric Equipment | 3 | | |
| 38 | Instruments and Related Products | 1 | 1 | <i>Photographic equipment and supplies</i> |
| 27 | Printing and Publishing | 1 | | |

*A site may list more than one SIC code.

**The industries shown in italics are among the top 50 facilities for hydrochloric acid releases to air. Other industries are those more frequently occurring among the 326 facilities emitting more than 25,000 pounds of HCl to air.

The industrial breakdown does not necessarily indicate that emissions result from processes unique to the industry. For example, combustion of chlorine-containing organic waste or fuels may result in emissions of hydrochloric acid aerosols. This may occur at Electric Utilities burning coal (SIC codes 4911) or at a Commercial Hazardous Waste Treatment facility (SIC code 4953) burning chlorine-containing waste.

Section 3.1.1 Pulp and Paper Mills

The kraft pulping process involves the digesting of wood chips at elevated temperature in **Awhite liquor**, an aqueous solution of sodium sulfide and sodium hydroxide, to dissolve the lignin that binds the cellulose fibers of the wood together. The spent liquor used to digest wood chips, called **Ablack liquor**, is combusted in recovery furnaces to recover heat and cooking chemicals. Black liquors can contain significant levels of chlorides which during combustion undergo both transformation and partitioning. A small fraction of the chlorides can be converted to hydrochloric acid and be released to the atmosphere in stack gases. Kraft recovery furnace flue gas is the largest source of hydrochloric acid emissions from pulp and paper mills. It is released from recovery furnaces of both the direct contact evaporator (DCE) and non-direct contact evaporator (NDCE) types. In a DCE, the flue gas comes in contact with the

black liquor, whereas in a NDCE, it does not. Chlorides in black liquor originate primarily from the wood chips used for pulping and the caustic used as makeup during white liquor preparation. Mill process water may also contribute significant chloride. The chloride component of black liquor may end up either in the smelt or deposited particulate phase as inorganic alkali salts or in the emitted gas phase as mostly hydrochloric acid. The smelt is dissolved in water to form green liquor, which is transferred to a causticizing tank where quicklime is added to convert the solution back to white liquor for return to the digester. A lime mud precipitates from the causticizing tank. This is calcined in a lime kiln to regenerate quicklime. HCl aerosols are emitted from the causticizing area/lime kilns. However in most studies, these emissions are included with those from the recovery furnaces.

In developing National Emission Standards for Hazardous Air Pollutants (NESHAP), EPA analyzed data from their 5 Mill Study, a Texas Mill Study, and International Paper reports (24). The Agency looked at emissions from processes connected with kraft pulp mills and derived average HCl emission factors for these processes. No HCl emissions were indicated for acid sulfite, and neutral sulfite semi-chemical (NSSC) pulping and soda mills. EPA emission data and emission factors for kraft pulp mills appear in Table 2.

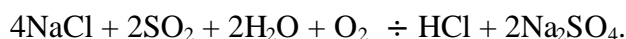
Table 2. Emissions and Emission Factors from Kraft Pulp Mills *

| Process Unit | Example Kraft Mill Emission Estimates (Mg/yr) (based on 1000 TODP per day) | | Typical HCl Emission Factors (lb/TODP) |
|------------------------|---|-------------------|--|
| | Range | Typical Emissions | |
| Causticizing area | 0.81-6.6 | 2.5 | 0.0159 |
| DCE Recovery furnaces | 9.2-85 | 58 | 0.362 |
| NDCE Recovery furnaces | NA | (59) | 0.365 |
| Bleach plant air vents | NA | 0.63 | 0.0396 |
| Boilers | NA | (3.0) | 0.0192 |

*Source: Reference 24. Emissions and emissions factors based on tons of oven-dried pulp (TODP) are derived from data on methanol and HCl to methanol ratios. Boiler data is based on average of industry test data reports. NA = not available.

While the formation of HCl in the combustion of coal, municipal solid waste, and other chloride-containing fuels is due to the direct conversion of organic chlorides to HCl during combustion, HCl

formed in a kraft recovery furnace, where the bulk of the chlorides are in the inorganic form, is believed to result from an entirely different mechanism involving SO₂, namely



The reaction may involve KCl in addition to NaCl shown above. The discovery of this reaction mechanism followed the observation that the mole percent chlorine in the gas phase increased with the sulfur content of the liquor.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) tested fourteen recovery furnaces, 10 of the non-direct contact type and 4 of the direct contact type for HCl emissions (5). In the study, emissions of SO₂ and pertinent information on furnace operating conditions was collected to ascertain whether there was a relation between HCl emissions and other factors. Stack emissions were measured according to EPA Method 26. A prototype continuous monitoring system for HCl gave unacceptably low results compared with the standard method. HCl emissions for the mills were very variable. The results of the study appear in Table 3. NCASI also compiled results of recent HCl emission tests for 17 kraft recovery furnaces (11 NDCE and 6 DCE) from other mills. These data also appear in Table 3. Results are reported in lbs of HCl per ton of black liquor solids (BLS) or lbs of HCl per ton of air-dried pulp (ADTP).

Table 3. Kraft Mill Emission Factors from NCASI Study and 17 Individual Mill Study*

| Study/Mill Type/Number | HCl Emissions in lb/ton BLS | | HCl Emissions in lb/ADTP | |
|---------------------------|-----------------------------|---------|---------------------------|---------|
| | Range | Average | Range | Average |
| NCASI - 10 NDCE | 0.00 to 0.84 | 0.29 | | 0.47 |
| NCASI - 4 DCE | 0.06 - 0.52 | 0.25 | | 0.37 |
| NCASI - 14 Mill SUMMARY | 8×10^{-4} - 0.84 | 0.28 | 1×10^{-3} - 1.36 | 0.44 |
| 17 Mill Study - 11 NDCE | ND - 1.23 | 0.24 | | |
| 17 Mill Study - 6 DCE | ND - 0.36 | 0.14 | | |
| 17 Mill Study - SUMMARY | ND - 1.23 | 0.20 | ND - 2.00 | 0.33 |
| 21 NDCE Recovery Furnaces | ND - 1.23 | 0.26 | | |
| 10 DCE Recovery Furnaces | ND - 0.52 | 0.18 | | |

* Source: Reference 5. Abbreviations: BLS = black liquor solids; ND = not detected; DCE = direct contact evaporator; NDCE = non-direct contact evaporator.

The chlorine content of the as-fired black liquor solids averaged 0.85% (range 0.36 to 1.35%). Material balances showed that only a very small amount of the chloride present in the as-fired black

liquor solids (1.4% on the average) is released through the stack as HCl; the rest is captured in the precipitated dust (24-34%) or retained in the smelt (64-75%). The results showed that stack HCl concentrations correlated strongly only with SO₂ concentrations in kraft recovery stacks. In the case of NDCE furnaces for stack SO₂ concentrations ranging from 0-500 parts per million (ppm), the stack

Install Equation Editor and double-click here to view equation.

HCl concentration could be best expressed as a Langmuir-type absorption isotherm

where the concentrations of HCl and SO₂ are expressed as ppm dry stack O₂. The rate-controlling step involved the adsorption of SO₂ by the salt. For DCE furnaces, there was no clear correlation between stack HCl and stack SO₂ levels. However, NCASI data and recent tests at individual mills showed HCl emissions from DCE furnaces to be significantly lower than for NDCE furnaces.

NCASI also analyzed the chloride inputs to kraft liquor cycles for 8 of the mills because it might shed some light on the emission behavior of HCl. They found that the average chloride input for mills that used reagent grade caustic was 0.48 lb Cl/ADTP whereas those that used diaphragm-grade caustic was 0.94 lb/ADTP. Similarly, NCASI found that the chloride content of the wood chips ranged from 12 to 93 ppm, averaging 35.5 ppm (45.7 and 29.8 for hard and soft woods, respectively) dry basis. However, emission factors were not developed that reflected these differences in chloride inputs.

The average hydrochloric acid emissions from the direct contact and non-direct contact evaporator recovery furnaces can be used to estimate hydrochloric acid emissions. For example, a kraft mill using 1100 tons of air dried pulp (ADTP) per day and generating 0.62 tons of BLS per ADTP while operating two DCE furnaces for 365 days per year has determined that an appropriate HCl emission factor for their furnaces is 0.18 lb/ton BLS. Therefore, the pounds of HCl, H, emitted during the year will be:

$$H = 1100 \text{ ADTP/day} \times 365 \text{ days/year} \times 0.62 \text{ ton BLS/ADTP} \times 0.18 \text{ lb HCl/ton BLS} = 44,800$$

HCl emission factors for recovery furnaces vary widely as the data provided in Tables 2 and 3 indicates. In the absence of site-specific emission factors, use an emission factor from these tables that best approximates your facility.

The pounds of hydrochloric acid aerosols produced in recovery furnaces on site should be combined with that produced from the bleach plant and from waste wood combustion and coal combustion in boilers which are used for steam and power generation. Generally, bark is the major type of waste burned in pulp mills and either a mixture of wood and bark waste or wood waste alone is burned most frequently in the lumber and plywood industries. An average emission factor for 'chlorine' from wood waste combustion is 7.8×10^{-3} lb/ton (7). Assuming the emissions to be HCl, this emission

factor is equivalent to 8.0×10^{-3} lb of HCl/ton. However the factor was based on data from one source test. Guidance on the production of HCl in coal-fired boilers is given in Section 3.1.6.1.

Sludge from the waste water treatment plant where bleaching waste water is sent may be burned and release HCl to air. Hydrochloric acid emissions may also occur from the bleach plant where SO_2 is used to treat vent gas for controlling Cl_2 and ClO_2 emissions (6). The following reactions indicate that HCl is released in the process.



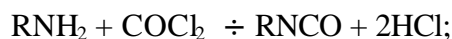
Section 3.1.2 Acid Aerosols from Hydrochloric Acid Manufacture

Over 90% of hydrochloric acid is produced as a byproduct from the production of chlorinated solvents, fluorocarbons, isocyanates, organics, magnesium, and vinyl chloride monomer (2,13,14). Examples of these include (15):

C Vinyl chloride from dehydrochlorination of 1,2-dichloroethane



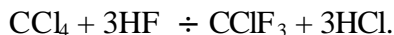
C Isocyanates from amine phosgenation



C Chlorination of aliphatic hydrocarbons



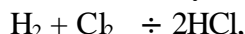
C Fluorocarbons from alkyl chlorides



Much of the vinyl chloride monomer and chlorinated solvents byproduct acid is recycled into the production process. If HCl is recycled in a closed system no HCl aerosol emissions are likely to occur. After the chlorination process, the HCl-containing gas stream goes to an absorption tower where concentrated hydrochloric acid is produced by absorption of HCl gas into a weak solution of hydrochloric acid. The final gas stream may be sent through a scrubber to remove any remaining HCl before it is vented to the atmosphere.

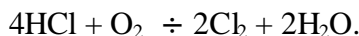
Another process for producing byproduct HCl is from magnesium metal recovery using electrolytic reduction of magnesium chloride from seawater to form magnesium and chlorine. The magnesium chloride hexahydrate is dehydrated stepwise; the further dehydration of the dihydrate results in some hydrolysis with the concurrent formation of hydrogen chloride (16).

Less than 10% of U.S. HCl production is made by the direct reaction of hydrogen and chlorine,



generally referred to as the thermal method. This reaction is highly exothermic and when a stoichiometric mixture is used produces a very pure product after cooling. The 'burner gas' that is produced is sent into an absorber to produce hydrochloric acid solutions.

Hydrochloric acid is also recovered from the disposal of chlorinated hydrocarbons by incineration (1). The combustion of these wastes ideally produce hydrogen chloride, water, and carbon dioxide. Excess oxygen must be present to insure complete combustion. However, the hydrogen chloride gas formed can also react with this oxygen to form chlorine and water,



The reaction has a negative enthalpy and entropy of reaction. With increasing temperature, the equilibrium shifts to the left, favoring the formation of HCl. A temperature greater than 1000 EC is necessary to keep the chlorine at an acceptable level. For this reason and to prevent nitrogen oxides from forming, incineration is carried out between 1000 and 1200 EC.

Anhydrous hydrochloric acid may be recovered from aqueous acid. If the aqueous acid is more concentrated than the azeotropic concentration, simple distillation is adequate. Any recovery or manufacturing process in which vapor phase hydrochloric acid is produced from the aqueous acid is considered as the production of hydrochloric acid aerosols according to section 313 of EPCRA. An old method of HCl production based on the reaction of a metal chloride, particularly sodium chloride, with sulfuric acid or a hydrogen sulfate salt is not used presently in the United States.

Nearly all the hydrochloric acid aerosols emitted from hydrochloric acid manufacturing plants come from the exit gases of the absorber or the purification system (12). The purification system for byproduct anhydrous HCl is dictated by the level and type of contaminants originating from the primary process and the end use of the acid. Common methods of purification include absorption, adsorption, distillation, or chemical reactions. In many cases the HCl can be utilized internally without further purification. An example is in vinyl chloride manufacturing where byproduct HCl from the 1,2-dichloroethane cracking step can be used directly in the oxychlorination unit. According to a 1985 emission inventory, less than one percent of HCl emissions came from direct production of HCl (12). EPA analyzed emission data and estimated emission factors for byproduct HCl manufacture of 0.15 lb/ton (0.08 kg/Mg) HCl produced with a final scrubber and 1.8 lb/ton (0.90 kg/Mg) HCl without a

scrubber. However the data are weak, being based on few and relatively old data, and at best provide only an estimate of emissions from this industry.

Section 3.1.3. Secondary Metal Production

Hydrochloric acid emissions from secondary metal production and foundries arise from chlorine-containing components in the feed (e.g., lacquer) or flux. Therefore, HCl emissions would be highly dependent on the feed, the type and amount of fluxing agent required, as well as the type and efficiency of pollution control equipment used. In secondary lead production, the feed is primarily spent lead acid batteries. HCl emissions in secondary lead production arise from the PVC cell separators used in the batteries. However, PVC is being replaced by a material that does not contain chlorine and the proportion of batteries containing PVC separators will decline as these batteries are removed from service (25). In 1994, less than 0.1% of batteries contained PVC. Therefore, secondary lead production would no longer be a major source of HCl emissions in the future and EPA withdrew proposed Cl₂/HCl emission standards for the industry (25).

In secondary aluminum operations, chlorine or other chlorinating agents (e.g., anhydrous aluminum chloride, chlorinated organics) may also be introduced as fluxes in demagging operations. Excess chloride combines with aluminum to form aluminum chloride which is a vapor at furnace temperatures and readily combines with water vapor to form hydrochloric acid. A few emission factors, reported in the FIRE database (9), are listed for reference in Table 4.

Table 4. Emission Factors for Secondary Metal Production.

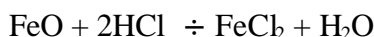
| Source | Feed | Emission Factor | Pollution Control Device | Reference Date |
|-------------------------------|-----------------------------------|---|---|----------------|
| Secondary lead production | spent lead batteries | 2.5 x 10 ⁻³ lb/ton lead produced | Afterburner, baghouse, ammonia scrubber | 1994 |
| Secondary lead production | spent lead batteries | 2.7 lb/ton lead produced | Afterburner, baghouse | 1994 |
| Secondary aluminum production | aluminum cans, de-laquering plant | 1.6 x 10 ⁻³ lb/lb cans | Multiple cyclones | 1991 |

Section 3.1.4. Steel Pickling

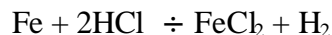
During the hot forming or heat treating of steel, oxygen from the air reacts with the iron to form iron oxides or scale on the surface of the steel. This scale must be removed before the iron is subsequently shaped or coated. One method of removing this scale is pickling with hydrochloric acid.

Pickling is conducted by continuous, semi-continuous or batch modes depending on the form of metal processed. In developing a National Emission Standard for the Steel Pickling industry, EPA recently surveyed the industry and produced a background information document containing detailed information concerning the various processes in the industry, pollution control devices, and emissions (21).

When iron oxides dissolve in hydrochloric acid, ferrous chloride is formed according to the following reactions:



Since Fe_3O_4 is $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$, the reaction for Fe_3O_4 is the sum of the two reactions. Some of the base metal is consumed in the first reaction as well as in the following reaction:



An inhibitor is usually added to lessen the acid's attack on the base metal while permitting it to act on the iron oxides. The rate of pickling increases with temperature and concentration of HCl. As pickling continues, HCl is depleted and ferrous chloride builds up in the pickling liquid to a point where pickling is no longer effective. At this point, the old liquid is discharged and the pickling tank replenished with fresh acid. Typical HCl concentrations in a batch pickling process are 12 wt % for a fresh solution and 4 wt % before acid replenishment. At these concentrations, the concentration of HCl in the vapor phase increases rapidly with temperature.

Hydrochloric acid aerosols are produced and released into the air during the pickling process as HCl volatilizes and steam and hydrogen gas with entrained acid fumes rise from the surface of the pickling tank and from the pickled material as it is transferred from the pickling tank to the rinse tank. Pickling and rinse tanks are covered and the acid fumes are generally collected and treated by control devices (e.g., packed tower scrubbers) to remove HCl. Emissions from many batch operations are uncontrolled. Pickling is sometimes accomplished in vertical spray towers. In this process, *all* the HCl in the pickling solution produces hydrochloric acid aerosols that is also used. Acid storage tanks and loading and unloading operations are also potential sources of HCl emissions. Uncontrolled HCl emissions from a storage tank may be on the order of 0.07 to 0.4 tons per year (tpy) of HCl per tank, depending on tank size and usage. For each million tons of steel processed at continuous coil or push-pull coil model facilities, storage tank losses are estimated to amount to 0.39 tpy. For other types of pickling facilities, storage tank losses are estimated to be about 11.19 tpy of HCl per million tons of steel processed.

The guidance for acid storage tanks in section 2.3 is applicable to storage tanks used in conjunction with the pickling process and may be extended to apply to the pickling process itself. For storage tanks, one applies the amount of hydrochloric acid aerosol generated from a tank under average

capacity and other conditions to the manufacturing threshold and multiplies that by the number of times the tank has been drawn down and refilled. The amount of acid aerosol manufactured during the pickling process can be similarly determined by the amount of HCl generated from the pickling tanks during the processing of a certain amount of material and scaling that figure up to apply to all the material processed by the same process and under the same conditions. The amount of hydrochloric acid aerosols lost from the pickling tanks are counted towards the material released to air unless the aerosol is collected and removed before exiting the stack. The hydrochloric acid aerosol collected in a scrubber is converted to the non-aerosol form, not reportable under EPCRA section 313; the hydrochloric acid aerosol removed by the scrubber is considered to have been treated for destruction (see Section 2.2).

Hydrochloric acid may be recovered from the waste pickling liquid (WPL) in an acid regeneration process. This process has the potential of emitting significant amounts of hydrochloric acid aerosols. Of ten acid regeneration plants surveyed by EPA (21), annual capacities ranged from 3.2 to 39.8 million gallons per year for a single facility. The spray roasting acid regeneration process is the dominant one presently employed. One older facility used a fluidized bed roasting process.

In the spray roasting acid regeneration process, WPL at 2-4% HCl comes into contact with hot flue gas from the spray roaster which vaporizes some of the water in the WPL. The WPL then becomes concentrated pickling liquor (CPL). The CPL is then sprayed on the spray roaster where ferrous chloride in the droplets falling through the rising hot gases react with oxygen and water to form ferric oxide and HCl,



Flue gas containing HCl goes to a venturi preconcentrator and an absorption column. The regenerated acid contains approximately 18% HCl by weight. Emissions from acid regeneration plants range from about 1 to more than 10 tpy from existing facilities with and without pollution control devices (controlled and uncontrolled facilities). The amount of hydrochloric acid regenerated as an aerosol should be applied towards the EPCRA section 313 "manufacturing" threshold.

Acid regeneration plants have storage tanks for spent and regenerated acid and these tanks are potential sources of HCl emissions. Emission estimates for uncontrolled and controlled storage tanks at acid regeneration facilities are 0.0126 and 0.008 tpy per 1,000 gallons of storage capacity, respectively.

Acid recovery systems are used to recover the free acid in the WPL. They are not employed in larger facilities because they recover only the 2-4% free HCl in the spent acid, but leave the FeCl_2 in the solution which must be processed or disposed of separately. These acid recovery systems are generally closed-loop processes that do not emit HCl. However, any acid aerosols generated in these types of recovery systems should be applied towards the EPCRA section 313 "manufacturing" threshold.

In their survey, EPA compiled data from different types of pickling operations and their estimated emissions (21). This information is reproduced in the Table 5.

Table 5. Annual Emission Estimates from Steel Pickling Operations

| Type of Facility | No. of Facilities | No. of Operations | Uncontrolled emission (Mg/yr) | Controlled emissions (Mg/yr) |
|---------------------|-------------------|-------------------|-------------------------------|------------------------------|
| Continuous coil | 36 | 64 | 22,820 | 2,640 |
| Push-pull coil | 19 | 22 | 815 | 29 |
| Continuous rod/wire | 20 | 55 | 6,524 | 4,252 |
| Continuous tube | 4 | 11 | 100 | 52 |
| Batch | 26 | 59 | 2,632 | 1,943 |
| Acid regeneration | 10 | 13 | 5,662 | 393 |
| Storage tanks | 99 | 369 (est) | 41 | 24 |

Source: Reference 21, page 3-32.

In order to estimate emissions from pickling facilities, EPA developed seventeen model plants to represent five types of pickling operations and one acid regeneration process (21). The model plants include one or more size variation for each process model. The model plants were developed from information obtained from a survey of steel pickling operations and control technologies. EPA estimated emissions rates for model facilities. Using these emission rates and the production and hours of operation for the model pickling plants, emission factors were calculated. These appear in Table 6.

Table 6. Emissions and Emission Factors for Model Pickling Plants

| Type Facility | Production | Hours of Operation | Uncontrolled HCl Emissions | Control Efficiency | Emission Factor | |
|-------------------------|------------|--------------------|----------------------------|--------------------|-----------------|-----|
| | (tpy)* | (hr) | (lb/hr) | % | (U) | (C) |
| Continuous Coil (S) | 450,000 | 6,300 | 111 | 93 | 1.6 | 0.1 |
| Continuous Coil (M) | 1,000,000 | 6,300 | 179 | 92 | 1.1 | 0.1 |
| Continuous Coil (L) | 2,700,000 | 7,000 | 347 | 92 | 0.9 | 0.1 |
| Push-pull coil (S) | 300,000 | 5,000 | 12 | 98 | 0.2 | 0.0 |
| Push-pull coil (M) | 550,000 | 4,400 | 27 | 98 | 0.2 | 0.0 |
| Push-pull coil (L) | 1,300,000 | 8,760 | 42 | 95 | 0.3 | 0.0 |
| Continuous rod/wire (S) | 10,000 | 5,100 | 46 | 98 | 23.5 | 0.5 |
| Continuous rod/wire (M) | 55,000 | 7,800 | 119 | 84 | 16.9 | 2.7 |

| | | | | | | |
|-------------------------|---------|-------|------|------|----------|--------|
| Continuous rod/wire (L) | 215,000 | 7,200 | 413 | C | 13.8 | C |
| Continuous tube (S) | 80,000 | 6,400 | 73 | 95 | 5.8 | 0.3 |
| Continuous tube (L) | 420,000 | 6,700 | 312 | 95 | 5.0 | 0.2 |
| Batch (S) | 15,000 | 4,400 | 16 | 94 | 4.7 | 0.3 |
| Batch (M) | 75,000 | 4,600 | 65 | 90 | 4.0 | 0.4 |
| Batch (L) | 170,000 | 5,700 | 147 | 81 | 4.9 | 0.9 |
| Acid Regeneration (S) | 4 | 8,200 | 7 | 98 | 14350.0 | 287.0 |
| Acid Regeneration (M) | 13.5 | 7,700 | 28 | 98 | 15970.4 | 319.4 |
| Acid Regeneration (L) | 30 | 8,760 | 1064 | 98.5 | 310688.0 | 4660.3 |

Source: Based on information in Reference 21.

Abbreviations: S = small; M = medium; L = large; U = uncontrolled; C = controlled.

*Units of production for acid regeneration facilities are in millions of gallons/yr.

**Emission factor units for acid regeneration facilities are in lbs of HCl per million gallons of HCl produced.

A National Emission Standard for Hazardous Air Pollutants (NESHAP) for new and existing hydrochloric acid process steel pickling lines and HCl regeneration plants pursuant to section 112 of the Clean Air Act as amended in November 1990 has been proposed (62 FR 49051, September 18, 1997). The purpose of this rulemaking is to reduce emissions of HCl by about 8360 megagrams per year.

Section 3.1.5. Stone, Clay, and Glass Products

Mineral products invariably contain chloride impurities which may be emitted as hydrochloric acid aerosols during processing. Some chloride may also be retained in condensed phases and therefore a mass balance approach to determining the amount of HCl emissions would not be expected to yield accurate results. As with any high-temperature, energy-intensive industrial processes, combustion of fuels to generate process energy may release substantial amounts of HCl. Therefore, emissions from the fuel may contribute to those measured for the process. EPA has reviewed data from emission tests and developed emission factors for brick manufacture, cement kilns, and glass manufacture.

An emission factor (EF) of 0.17 lb/ton (0.65 kilogram per Megagram (kg/Mg)) was estimated for uncontrolled HCl emissions from natural gas-fired kilns used in brick manufacture (11). The EFs were developed using A-rated (excellent) data from one test, B-rated (above average) data from two tests, and C-rated (average) data from 2 tests, but because of the wide range of the data, 0.018 lb/ton to 0.41 lb/ton, the average emission factor developed is D-rated (below average).

Emission factors of 0.049 lb/ton (0.025 kg/Mg) and 0.14 lb/ton (0.073 kg/Mg) of clinker production have been developed for portland cement kilns using electrostatic precipitators and fabric filters, respectively. The ratings for these EFs are E (poor) and D (below average), respectively, in part because the small number of facilities used in developing the factors may not be representative of the industry. All emission tests used were for coal-fired kilns. Hazardous wastes are often added to

cement kilns both as a subsidiary fuel or to dispose of the waste. Emission factors cannot be developed for such kilns because emission characteristics would be a function of the amount and chemical constitution of the waste used and therefore could not be used in estimating emissions from other kilns in the industry.

For container and pressed and blown glass, hydrogen chloride is reported to be emitted during surface treatment process at a rate of < 0.2 lb/ton (8).

The emission factors for stone, clay and glass products are summarized in Table 7.

Table 7. Emission Factors for Stone, Clay and Glass Products

| Industry | Pollution Control | Emission Factors | |
|------------------------------------|----------------------------|------------------|---------------|
| | | lbs/ton product | kg/Mg product |
| Brick Manufacture | uncontrolled | 0.17 | 0.65 |
| Portland Cement | electrostatic precipitator | 0.049 | 0.025 |
| Portland Cement | fabric filter | 0.14 | 0.073 |
| Container, Pressed and Blown Glass | not reported | <0.2 | |

Section 3.1.6. Hydrochloric Acid Aerosol Formation from Combustion Processes

EPCRA section 313-covered facilities that combust chlorine-containing fuel or other material have the potential for manufacturing and releasing hydrochloric acid aerosols. Facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce and facilities that combust or incinerate solid waste and that are regulated under RCRA subtitle C are examples of such facilities.

Section 3.1.6.1 Coal Combustion

Hydrochloric acid aerosols are produced in boilers during coal combustion. According to a 1985 inventory, over 89% of all HCl emitted to the atmosphere resulted from coal combustion (12). While most of the chlorine contained in the coal is released in the form of hydrogen chloride, lesser amounts of chlorine gas may also be emitted and a portion of the chlorine content of the fuel may be absorbed onto fly ash or bottom ash (10). If HCl aerosols are produced during or after combustion, the amount must be applied to the manufacturing threshold. In the absence of better data, facilities can use the HCl emission factors presented in Table 8. These factors are more appropriate than those AP-42 factors, which are averages of factors for each type of coal (10). Use the emission factor that corresponds to the type of coal being combusted. If a facility combusts a mixture of coal types, and knows the mixture ratio, it may apply this ratio to the emission factors in Table 8. Facilities that do not

know the type of coal they use should assume the coal is bituminous or subbituminous, since these types are commonly used. Hydrochloric acid aerosols may also be manufactured during plant maintenance from the evaporation of boiler cleaning wastes.

Table 8. Emission Factors for HCl Manufactured during the Combustion of Coal

| Source | Emission Factor (lbs/ton coal) |
|--------------------|-----------------------------------|
| Anthracite Coal | 0.91 |
| Bituminous Coal | 1.9 |
| Subbituminous Coal | 1.9 |
| Lignite | 0.01 |

If a facility combusts 1 million tons of bituminous coal the amount of HCl manufactured can be calculated will be:

$$1.9 \text{ lb HCl/ton coal} \times 1,000,000 \text{ tons coal} = 1,900,000 \text{ lbs HCl}$$

This exceeds the 25,000 lb manufacturing threshold and Form R reporting for HCl aerosols is required. The amount of HCl aerosols released to air from the stack will be the amount manufactured minus amounts removed by air control devices and will depend of the efficiency of the device for removing HCl. (See also, EPCRA section 313 Industry Guidance for Electric Generating Facilities, January 1999, EPA 745-B-99-003)

Section 4. Measurement Methods

For source sampling, EPA has specified extractive sampling trains and analytical procedures for the determination of hydrogen chloride emissions from stationary sources (3). An error was noticed in the procedure for Method 26, for which changes were promulgated on April 22, 1994. In section 4.1.2, the word ~~not~~ should be removed from the phrase ~~But~~ not greater than 120 EC. ~~to~~ read ~~But~~ greater than 120 EC (4).

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- (3) EPA. 1995. 40 CFR Part 60 - Standards of Performance for New Stationary Sources; Appendix A **B** Test Method 26 - Determination of Hydrogen Chloride Emissions from Stationary Sources; Test Method 26A - Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources **B** Isokinetic Method.
- (4) 59 FR 19306-19323, April 22, 1994. Standards of Performance for New Stationary Sources; Appendix A **B** Test Methods; Revisions to Methods 18 and 26 and Additions of Methods 25D and 26A to Appendix A.
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APPENDIX 1

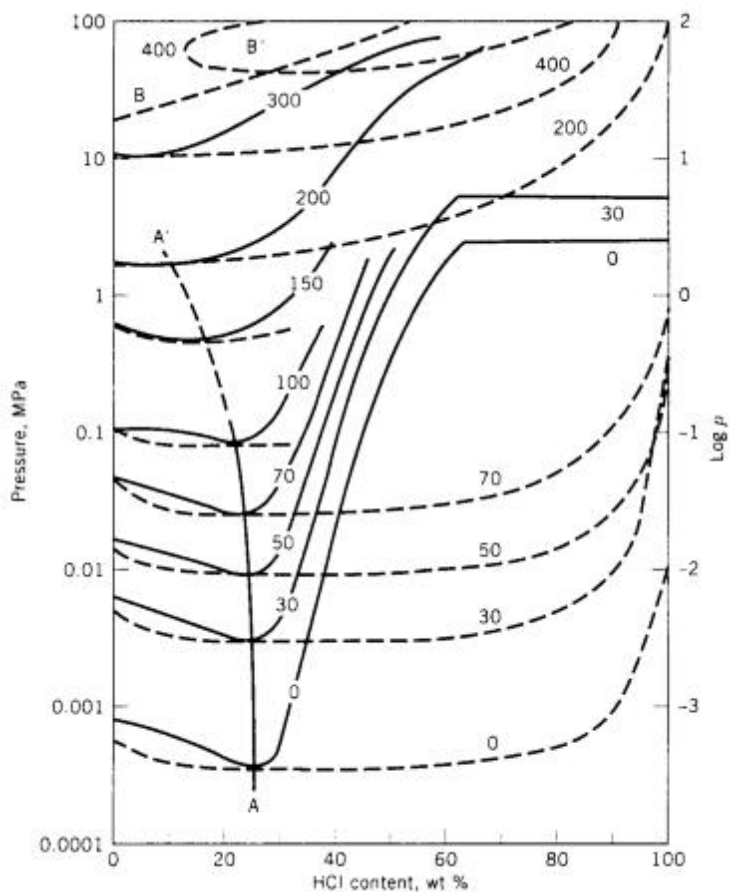


Figure A1. Vapor-liquid phase diagram for the HCl-H₂O system (Reference 2, p. 901). Pressure is in MegaPascals (MPa).

In the vapor-liquid phase diagram for the hydrogen chloride-water system shown in Figure A1, the solid lines separate the two-phase region from the liquid phase and the dashed lines separate the two-phase region from the gas phase. The numbers associated with the curves correspond to the temperature in °C. Line ABA' connects the azeotropic points and BBB' represents the critical segregation curve above the critical point of water. Figure A2 illustrates the use of this diagram.

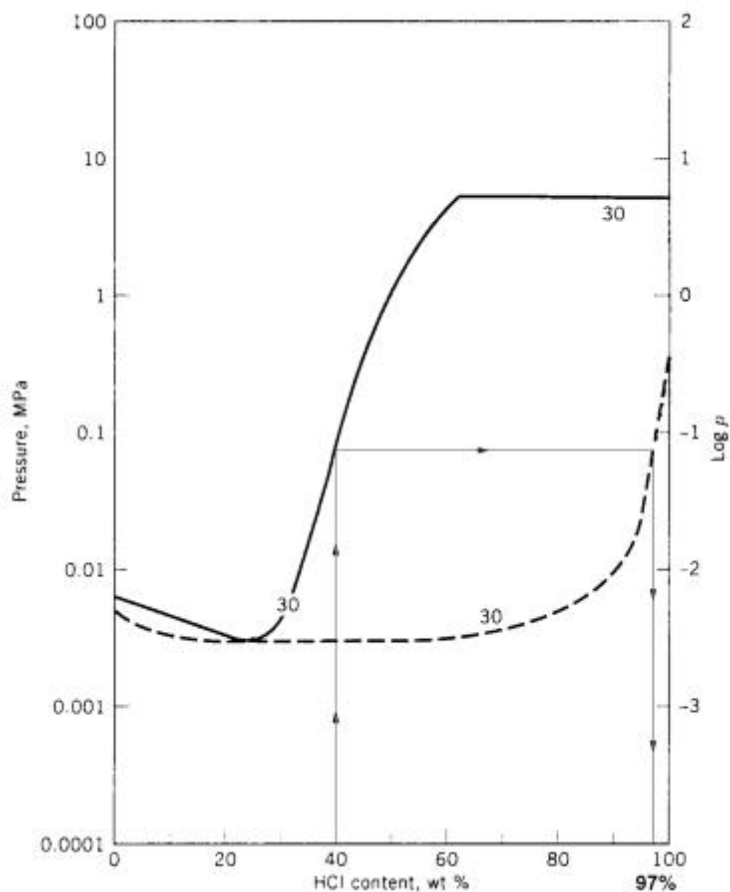


Figure A2. Vapor—liquid phase diagram for HCl–H₂O system at 30 EC.

Figure A2 contains the vapor-liquid phase diagram for 30 EC and has been drawn to illustrate the use of Figure A1. To find the composition of the vapor in equilibrium with a 40 wt % solution of hydrochloric acid, construct a vertical line from 40 wt % on the abscissa. Where this line intersects the solid (liquid) line, construct a horizontal line. Where the horizontal line intersects the dashed (gas) line, read the HCl content of the gas phase off the abscissa (roughly 97 wt % HCl). The total pressure of the solution is found from where the horizontal line intersects the ordinate (roughly 0.1 Mpa).

The composition of the vapor as a function of HCl concentration in the liquid and temperature is shown in Table A1 and Figure A3. They show that for a dilute solution the vapor is essentially water and for solutions above 20 mole % HCl the vapor is over 90 mole % HCl. Table A2 contains the HCl partial pressure and total vapor pressure of the solution (in parenthesis) in the concentration range of 1.0 to 15.88 molal.

TABLE A1. Vapor Composition of HCl-H₂O Systems

| Liquid | | | Vapor, Mole % HCl | | | | | | |
|----------|----------|--------|------------------------|------------------------|------------------------|-----------------------|-----------------------|-----------------------|--|
| Molality | Weight % | Mole % | 0 EC | 10 EC | 20 EC | 30 EC | 40 EC | 50 EC | |
| 1.0 | 3.51 | 1.77 | 4.09x10 ⁻⁴ | 6.01x10 ⁻⁴ | 8.88x10 ⁻⁴ | 12.9x10 ⁻⁴ | 19.0x10 ⁻⁴ | 27.5x10 ⁻⁴ | |
| 2.0 | 6.80 | 3.48 | 2.84x10 ⁻³ | 4.09x10 ⁻³ | 5.87x10 ⁻³ | 8.11x10 ⁻³ | 11.9x10 ⁻³ | 16.3x10 ⁻³ | |
| 3.0 | 9.86 | 5.14 | 11.72x10 ⁻³ | 16.51x10 ⁻³ | 23.12x10 ⁻³ | 32.1x10 ⁻³ | 4.32x10 ⁻² | .0616 | |
| 4.0 | 12.73 | 6.72 | 0.04 | 0.0592 | 0.0808 | 0.109 | 0.145 | .198 | |
| 5.0 | 15.42 | 8.26 | 0.15 | 0.194 | 0.257 | 0.335 | 0.437 | .574 | |
| 6.0 | 17.95 | 9.75 | 0.464 | 0.597 | 0.767 | 0.968 | 1.215 | 1.552 | |
| 7.0 | 20.34 | 11.19 | 1.394 | 1.735 | 2.152 | 2.631 | 3.198 | 3.931 | |
| 8.0 | 22.58 | 12.59 | 3.822 | 4.79 | 5.68 | 6.72 | 7.86 | 9.29 | |
| 9.0 | 24.70 | 13.94 | 10.12 | 11.94 | 13.55 | 15.00 | 17.29 | 19.72 | |
| 10.0 | 26.72 | 15.27 | 23.49 | 25.70 | 28.15 | 30.41 | 32.85 | 35.75 | |
| 11.0 | 28.63 | 16.54 | 43.6 | 46.62 | 48.29 | 50.5 | 52.55 | 55.3 | |
| 12.0 | 30.43 | 17.77 | 65.6 | 67.05 | 68.35 | 69.55 | 70.6 | 71.9 | |
| 13.0 | 32.16 | 18.97 | 82.2 | 82.4 | 82.4 | 83.0 | 83.4 | 83.4 | |
| 14.0 | 33.79 | 20.12 | 91.0 | 91.03 | 90.9 | 90.4 | 91.0 | 91.0 | |
| 15.0 | 35.35 | 21.28 | 95.4 | 95.7 | 95.4 | 95.4 | 94.9 | 95.1 | |
| 15.88 | 36.63 | 24.11 | 97.8 | 97.6 | 97.3 | 97.4 | 97.1 | B | |

Source: Reference 19

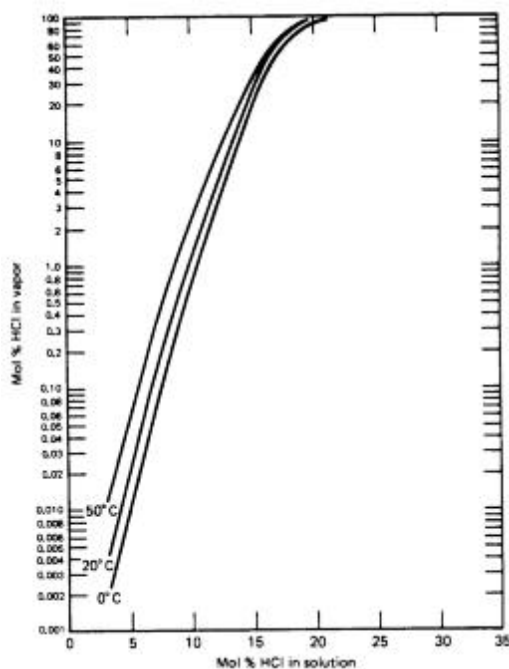


Figure A3. Vapor composition of hydrogen chloride–water systems (Reference 22, p. 988).

| TABLE A2. Partial Pressure of HCl And Total Vapor Pressure of HCl-H ₂ O Systems | | | | | | | | | |
|--|-------|--------|--|---------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|--|
| Liquid | | | HCl Partial Pressure (Total Vapor Pressure) (torr) | | | | | | |
| Molality | Wt % | Mole % | 0 EC | 10 EC | 20 EC | 30 EC | 40 EC | 50 EC | |
| 1.0 | 3.51 | 1.77 | 1.81x10 ⁻⁵ (4.42) | 5.33x10 ⁻⁵ (8.87) | 1.49x10 ⁻⁴ (16.78) | 3.96x10 ⁻⁴ (30.70) | 1.01x10 ⁻³ (53.27) | 2.45x10 ⁻³ (89.18) | |
| 2.0 | 6.80 | 3.48 | 1.20x10 ⁻⁴ (4.22) | 3.45x10 ⁻⁴ (8.44) | 9.44x10 ⁻⁴ (16.08) | 2.43x10 ⁻³ (29.96) | 6.05x10 ⁻³ (50.8) | 0.0143 (87.64) | |
| 3.0 | 9.86 | 5.14 | 4.68x10 ⁻⁴ (3.99) | 1.32x10 ⁻³ (7.95) | 3.51x10 ⁻³ (15.17) | 8.88x10 ⁻³ (27.54) | 0.0211 (48.8) | 0.0497 (80.65) | |
| 4.0 | 12.73 | 6.72 | 1.59x10 ⁻³ (3.69) | 4.36x10 ⁻³ (7.38) | 0.0114 (14.10) | 0.0279 (25.73) | 0.0659 (45.3) | 0.149 (75.4) | |
| 5.0 | 15.42 | 8.26 | 4.89x10 ⁻³ (3.37) | 0.0131 (6.76) | 0.0333 (12.94) | 0.0794 (23.7) | 0.183 (41.9) | 0.401 (69.9) | |
| 6.0 | 17.95 | 9.75 | 0.0141 (3.04) | 0.0366 (6.13) | 0.0903 (11.80) | 0.210 (21.7) | 0.468 (38.5) | 1.001 (64.5) | |
| 7.0 | 20.34 | 11.19 | 0.0382 (2.74) | 0.0964 (5.55) | 0.231 (10.72) | 0.521 (19.8) | 1.132 (35.4) | 2.354 (59.9) | |
| 8.0 | 22.58 | 12.59 | 0.0987 (2.58) | 0.242 (5.05) | 0.563 (9.91) | 1.236 (18.4) | 2.61 (33.2) | 5.27 (56.8) | |
| 9.0 | 24.70 | 13.94 | 0.240 (2.37) | 0.571 (4.78) | 1.295 (9.56) | 2.76 (18.4) | 5.69 (32.9) | 11.20 (56.8) | |
| 10.0 | 26.72 | 15.27 | 0.552 (2.35) | 1.278 (4.97) | 2.83 (10.05) | 5.87 (19.3) | 11.73 (35.7) | 22.6 (63.2) | |
| 11.0 | 28.63 | 16.54 | 1.229 (2.82) | 2.77 (5.94) | 5.86 (12.14) | 11.97 (23.7) | 23.28 (44.3) | 43.9 (79.4) | |
| 12.0 | 30.43 | 17.77 | 2.55 (3.89) | 5.60 (8.35) | 11.75 (17.20) | 23.14 (33.3) | 44.1 (62.5) | 80.9 (112.5) | |
| 13.0 | 32.16 | 18.97 | 5.11 (6.22) | 11.00 (13.36) | 22.25 (27.0) | 43.6 (52.5) | 79.5 (95.7) | 140 (168) | |
| 14.0 | 33.79 | 20.12 | 9.99 (10.97) | 20.75 (22.8) | 41.1 (45.2) | 76.8 (84.5) | 137.4 (152) | 242 (266) | |
| 15.0 | 35.35 | 21.28 | 18.56 (19.39) | 38.0 (39.7) | 72.2 (75.7) | 132.5 (139) | 232 (235) | 400 (421) | |
| 15.88 | 36.63 | 24.11 | 31.0 (31.7) | 61.2 (62.7) | 114.8 (118) | 201.4 (207) | 360 (371) | ----- | |

Source: Reference 23.

The above table contains the partial pressure of hydrochloric acid and total vapor pressure of the solution (in parentheses) over aqueous hydrochloric acid solutions in the concentration range of 1 to 15.88 molality (23). The partial pressure of hydrochloric acid above a hydrochloric acid solution is very low compared to the total vapor pressure at low concentrations; the bulk of the vapor being composed of water. Consequently, when a dilute solution of hydrochloric acid boils, more water than hydrochloric acid is volatilized so that the concentration of the remaining acid increases, and the boiling point of the solution rises. This process continues until the acid concentration reaches 20.222 weight % HCl, when an azeotrope (a mixture of two liquids that boils at constant composition; i.e., the composition of the vapor is the same as that of the liquid) is formed and the concentration of hydrochloric acid in the vapor is the same as that of the solution. Above the azeotropic concentration, the partial pressure of hydrochloric acid increases rapidly with concentration and hydrochloric acid aerosol production will be substantial.

| TABLE A3. Pressure Conversion Factors * | | | | | |
|--|------------|-------------------------|-------------|------------------------|------------------------|
| | kPa | bar | torr | atm | psi |
| 1 kPa | 1.0000 | 1.0000×10^{-2} | 5.501 | 9.869×10^{-3} | 0.1450 |
| 1 bar | 100.00 | 1.0000 | 750.1 | 0.9869 | 14.50 |
| 1 torr | 0.1332 | 1.333×10^{-4} | 1.0000 | 1.316×10^{-2} | 1.934×10^{-2} |
| 1 atm | 101.33 | 1.0133 | 760.0 | 1.0000 | 14.70 |
| 1 psi | 6.895 | 6.895×10^{-2} | 51.71 | 6.805×10^{-2} | 1.0000 |

* To use the table to convert from atm to kPa use the entry in the atm row and the kPa column to obtain 1 atm = 101.33 kPa.

| TABLE A4. HCl Concentration Conversion Factors ** | | | |
|--|------------------------------|-------------------------------|-------------------------------|
| | molal (m) | mole fraction (x) | weight fraction (w) |
| m | 1 | $55.5 x / (1-x)$ | $27.4 w / (1-w)$ |
| x | $m / (m + 55.5)$ | 1 | $18.02 w / (36.45 + 18.43 w)$ |
| w | $36.45 m / (36.45 m + 1000)$ | $36.45 x / (18.02 + 18.43 x)$ | 1 |

* To convert, for example, $x=0.1$ to molality: $m = 55.5 (0.1) / (1-0.1) = 6.17$.