



TOXICS RELEASE INVENTORY

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 the annual quantity of such chemicals entering each environmental medium. Such facilities must also report pollution prevention and recycling data for such chemicals, pursuant to section 6607 of the Pollution Prevention Act, 42 U.S.C. 13106. EPCRA section 313 is also known as the Toxics Release Inventory (TRI).

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DISCLAIMER

This guidance document is intended to assist industry with EPCRA section 313 reporting for hydrochloric acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size). In addition to providing an overview of aspects of the statutory and regulatory requirements of the EPCRA section 313 program, this document also provides recommendations and emissions factors to assist industry with EPCRA reporting. These recommendations do not supersede any statutory or regulatory requirements, are subject to change, and are not independently binding on either EPA or covered facilities. Additionally, if a conflict exists between guidance on this site and the statutory or regulatory requirements, the conflict must be resolved in favor of the statute or regulation.

Although EPA encourages industry to consider these recommendations and emissions factors, in reviewing this document, industry should be aware that these recommendations and emissions factors were developed to address common circumstances at typical facilities. The circumstances at a specific facility may significantly differ from those contemplated in the development of this document. Thus, individual facilities may find that the recommendations and emissions factors provided in this document are inapplicable to their processes or circumstances, and that alternative approaches or information are more accurate and/or more appropriate for meeting the statutory and regulatory requirements of EPCRA section 313. To that end, industry should use facility specific information and process knowledge, where available, to meet the requirements of EPCRA section 313. EPCRA section 313 also provides that, in the absence of such readily available data, a reporting facility may make reasonable estimates to meet those EPCRA section 313 requirements. Facilities are encouraged to contact the Agency with any additional or clarifying questions about the recommendations and emissions factors in this document, or if the facility believes that EPA has incorrectly characterized a particular process or recommendation.

Additional guidance documents, including industry specific and chemical specific guidance documents, are also available on TRI's GuideME website:

https://ofmpub.epa.gov/apex/guideme_ext/f?p=guideme:gd-list

SECTION 1.0 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 “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 were no longer required to include non-aerosol forms of hydrochloric acid in threshold and release determinations. In this document we will use the term “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.

Section 1.1 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:

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

Hydrochloric acid aerosols are generally processed when:

- 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:

- HCl is applied as a spray for surface treatment.

Section 1.2 General TRI Reporting Instructions

For general instruction regarding compliance with EPCRA section 313 requirements and form completion, please see the most recent version of the Toxic Chemical Release Inventory Reporting Forms and Instructions, available at: https://ofmpub.epa.gov/apex/guideme_ext/f?p=guideme:rfi-home.

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 Section 2.1, Section 2.2, and Section 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 “manufacture” of a listed chemical (hydrochloric acid aerosols as defined in Section 1.1) 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 “manufacturing” 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 “manufacture” [the generation of the acid aerosol is the “manufacture” of hydrochloric acid (acid aerosol)] and “otherwise use” thresholds. This may result in many facilities greatly exceeding the “manufacture” and “otherwise 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 “manufacture” and “otherwise 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 2,000 pounds of acid and 500 pounds is added during the year then the total amount applied towards acid aerosol thresholds would be 2,500 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 “manufacture” 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 computer software program, is useful for estimating emissions from fixed- and floating-roof storage tanks. The last version of TANKS was 4.09D but it is outdated and may not work on newer computers. For more information see: <https://www3.epa.gov/ttn/chief/software/tanks/>.

The TANKS 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 A to assist in such calculations.

WATER9 (Wastewater Treatment Compound Property Processor and Air Emissions Estimator program) is another computer software program that is useful for estimating chemical-specific emissions from wastewater collection and treatment systems. WATER9 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 and is available at: <https://www3.epa.gov/ttn/chief/software/water/index.html>.

waste or fuels may result in emissions of hydrochloric acid aerosols. This may occur at Electric Utilities burning coal or at a Commercial Hazardous Waste Treatment facility (burning chlorine-containing waste). Similarly, not all activities involving HCl at a given industry are addressed.

3.1.1 Pulp and Paper Mills

The kraft pulping process involves the digesting of wood chips at elevated temperature in “white 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 “black 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 emissions 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 emissions factors for kraft pulp mills appear in Table 3-1

Table 3-1.

Table 3-1: Emissions and Emissions Factors from Kraft Pulp Mills

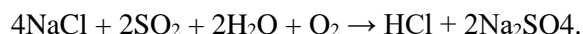
Process Unit	Example Kraft Mill Emission Estimates (Mg/yr) (based on 1000 TODP per day)		Typical HCl Emissions Factors (lb/TODP)
	Range	Typical Emissions	
Causticizing area	0.81-6.6	2.5	0.0159
DCE Recovery furnaces	9.2-85	58	0.362
NDCE Recovery furnaces	NA	(59)	0.365
Bleach plant air vents	NA	0.63	0.0396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

Equation 2



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 3-2. 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 3-2. Results are reported in lb of HCl per ton of black liquor solids (BLS) or lb of HCl per ton of air-dried pulp (ADTP).

Table 3-2: Kraft Mill Emissions 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 HCl concentration could be best expressed as a Langmuir-type absorption isotherm, shown in Equation 3.

Equation 3

$$[HCl] = \frac{1.28 \times [SO_2]}{1 + 0.017 \times [SO_2]}$$

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, emissions 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 emissions factor for their furnaces is 0.18 lb/ton BLS. Therefore, the pounds of HCl, H, emitted during the year will be:

Equation 4

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

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

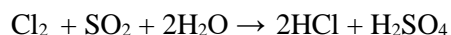
The pounds of hydrochloric acid aerosols produced in recovery furnaces on site should be combined with that produced from the bleach plant and from waste wood combustion and coal combustion in boilers which are used for steam and power generation. Generally, bark is the major type of waste burned in 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 emissions factor for 'chlorine' from wood waste combustion is 7.8×10^{-3} lb/ton (7). Assuming the emissions to be HCl, this emissions 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 under "Coal Combustion".

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 SO₂ is used to treat vent gas for controlling Cl₂ and ClO₂ emissions (6). The following reactions indicate that HCl is released in the process.

Equation 5



Equation 6



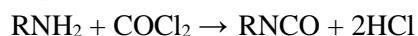
3.1.2 Acid Aerosols from Hydrochloric Acid Manufacture

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):

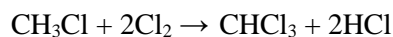
Equation 7: Vinyl chloride from dehydrochlorination of 1,2-dichloroethane



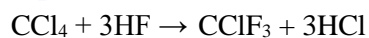
Equation 8: Isocyanates from amine phosgenation



Equation 9: Chlorination of aliphatic hydrocarbons



Equation 10: Fluorocarbons from alkyl chlorides

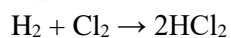


Much of the vinyl chloride monomer and chlorinated solvents byproduct acid is recycled into the production process. If HCl is recycled in a closed system no HCl aerosol emissions are likely to occur. After the chlorination process, the HCl-containing gas stream goes to an absorption tower where concentrated 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).

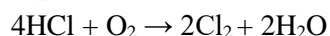
Equation 11



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,

Equation 12



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°C 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°C.

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 emissions 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.

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 has been 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 (26). By 1994, less than 0.1% of batteries contained PVC. Therefore, secondary lead production is no longer a major source of HCl emissions (26).

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 emissions factors, reported in the FIRE database (9), are listed for reference in Table 3-3.

Table 3-3: Emissions Factors for Secondary Metal Production

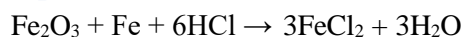
Source	Feed	Emissions Factor	Pollution Control Device	Reference Date
Secondary lead production	spent lead batteries	2.5×10^{-3} lb/ton lead produced	Afterburner, baghouse, ammonia scrubber	1994
Secondary lead production	spent lead batteries	2.7 lb/ton lead produced	Afterburner, baghouse	1994
Secondary aluminum production	aluminum cans, de-lacquering plant	1.6×10^{-3} lb/lb cans	Multiple cyclones	1991

3.1.4 Steel Pickling

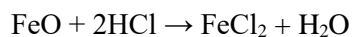
During the hot forming or heat treating of steel, oxygen from the air reacts with the iron to form iron oxides or scale on the surface of the steel. This scale must be removed before the iron is subsequently shaped or coated. One method of removing this scale is pickling with hydrochloric acid. Pickling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

Equation 13

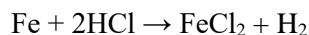


Equation 14



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:

Equation 15



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, as shown in Equation 16.

Equation 16



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 FeCl₂ 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 Table 3-4.

Table 3-4: 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, emissions factors were calculated. These appear in Table 3-5.

Table 3-5: Emissions and Emissions Factors for Model Pickling Plants

Type of Facility	Production (tpy)*	Hours of Operation (hr)	Uncontrolled HCl Emissions (lb/hr)	Control Efficiency %	Emissions Factor lb HCl/tons processed**	
					(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	-	13.8	-
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

Type of Facility	Production (tpy)*	Hours of Operation (hr)	Uncontrolled HCl Emissions (lb/hr)	Control Efficiency %	Emissions Factor lb HCl/tons processed**	
					(U)	(C)
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; S = large; U = uncontrolled; C = controlled.

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

**Emissions factor units for acid regeneration facilities are in lb 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.

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 emissions factors for brick manufacture, cement kilns, and glass manufacture.

An emissions 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 emissions factor developed is D-rated (below average).

Emissions 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. Emissions 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 emissions factors for stone, clay and glass products are summarized in Table 3-6.

Table 3-6: Emissions Factors for Stone, Clay and Glass Products

Industry	Pollution Control	Emissions Factors	
		lb/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	

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.

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 emissions factors presented in Table 3-7. These factors are more appropriate than those AP- 42 factors, which are averages of factors for each type of coal (10). Use the emissions 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 emissions factors in Table 3-7. 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 3-7: Emissions Factors for HCl Manufactured during the Combustion of Coal

Source	Emissions Factor (lb/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 as follows:

Equation 17

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

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 4.0 MEASUREMENT METHODS

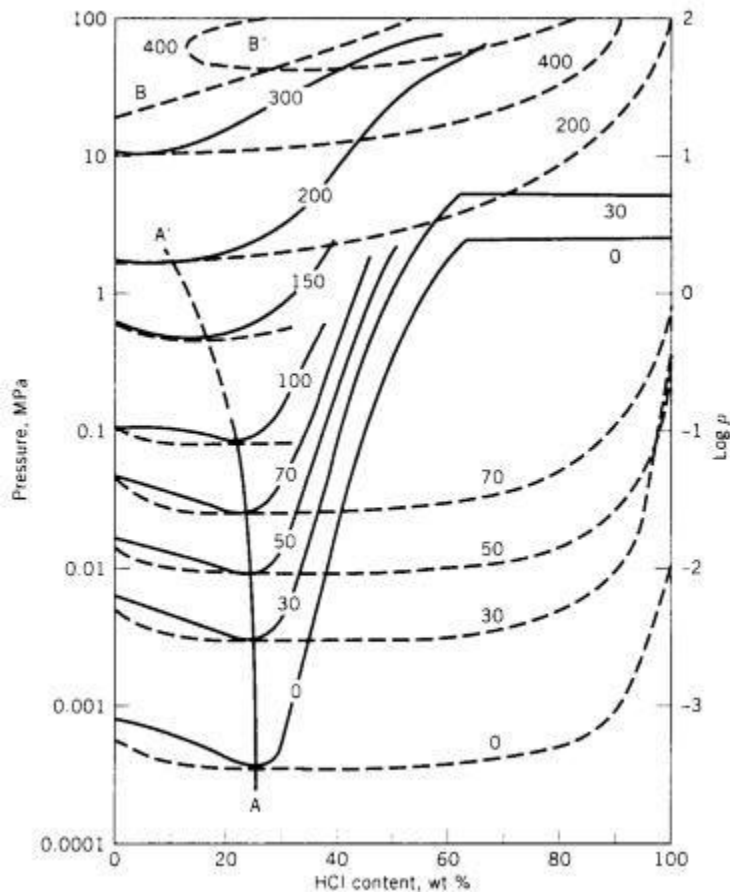
For source sampling, EPA has specified extractive sampling trains and analytical procedures for the determination of hydrogen chloride emissions from stationary sources (3).

SECTION 5.0 REFERENCES

1. Austin S, Glowacki, A. 1989. Hydrochloric Acid. *Ullmann's Encyclopedia of Industrial Chemistry*, Vol A13, pp. 283-296.
2. Hisham MWM, Bommaraju TV. 1995. Hydrogen Chloride. *Kirk Othmer Encyclopedia of Chemical Technology*, 4th ed. Vol 13, pp. 894-925.
3. 81 FR 59800-59826, August 30, 2016. Revisions to Test Methods, Performance Specifications, and Testing Regulations for Air Emission Sources.
4. 59 FR 19306-19323, April 22, 1994. Standards of Performance for New Stationary Sources; Appendix A - Test Methods; Revisions to Methods 18 and 26 and Additions of Methods 25D and 26A to Appendix A.
5. National Council for Air and Stream Improvement (NCASI). 1994. A study of kraft recovery furnace hydrochloric acid emissions. Technical Bulletin No. 674, National Council for Air and Stream Improvement, New York, NY. August 1994.
6. National Council for Air and Stream Improvement (NCASI). 1991. Bleach plant Cl and ClO₂ emissions and their control. Technical Bulletin No. 616, National Council for Air and Stream Improvement, New York, NY. September 1991. p. 7.
7. EPA. 1995. Compilation of Air Pollutant Emission Factors (AP-42). Wood Waste Combustion in Boilers. pp. 1.6-1 to 1.6-18. October 1996. Research Triangle Park, NC: U.S. EPA, OAQPS.
8. EPA. 1986. Compilation of Air Pollutant Emission Factors (AP-42). Glass Manufacturing. pp. 1.15-1 to 1.15-10. October 1986. Research Triangle Park, NC: U.S. EPA, OAQPS.
9. EPA. Factor Information Retrieval Data System (FIRE). Version 5.1B (December 1996). Research Triangle Park, NC: U.S. EPA, OAQPS. (for current web version see <https://cfpub.epa.gov/webfire/>)
10. EPA. 1996. Compilation of Air Pollutant Emission Factors (AP-42). Bituminous and Subbituminous Coal. pp. 1.1-1 to 1.1-46. October 1996. Research Triangle Park, NC: U.S. EPA, OAQPS.
11. EPA. 1997. Compilation of Air Pollutant Emission Factors (AP-42). Brick and Structural Clay Product Manufacture. pp. 11.3-1 to 11.3-68. August 1997. Research Triangle Park, NC: U.S. EPA, OAQPS.
12. EPA. 1997. Background Report. AP-42 Section 8.6. Hydrochloric Acid Manufacture. pp. 8.6- 1 to 11.3-68. October 1997. Research Triangle Park, NC: U.S. EPA, OAQPS.
13. SRI International. 1996. 1996 Directory of Chemical Producers. United States of America. pp. 660-662. Menlo Park. CA: SRI International.
14. Chemical Manufacturing Reporter. Chemical Profile. Hydrochloric Acid. September 25, 1995.
15. Buice JE, Bowlin RL, Mall KW, Wilkinson JA. 1987. Hydrochloric Acid. *Encyclopedia of Chemical Processing and Design*, Vol 26, pp. 396-417.
16. Wilson CB, Claus KG, Earlam MR, and Hillis JE. 1995. Magnesium and Magnesium Alloys.
17. *Kirk Othmer Encyclopedia of Chemical Technology*, 4th ed. Vol 15, pp. 622-674.

18. EPA. 1995. Hydrochloric acid: Toxic chemical release reporting: Community right-to-know. Final rule. 61 FR 38600. July 25, 1996.
19. EPA. 1995. Toxic Release Inventory.
20. Othmer DF, Naphtali LM. 1956. Correlating pressures and vapor compositions of aqueous hydrochloric acid. *Industrial and Engineering Chemistry* 1: 6-10.
21. Kindler W, Wüster G. 1978. Equation of state for the vapour of concentrated and diluted hydrochloric acid. *Ber. Bunsenges. Phys. Chem.* 82: 543-545.
22. EPA. 1997. National Emission Standard for Hazardous Air Pollutants (NESHAP) for Steel Pickling - HCl Process - Background Information for Proposed Standards. EPA-453/R-97-012. June 1997. Research Triangle Park, NC: U.S. EPA, OAQPS.
23. Rosenberg, DS. 1980. Hydrogen Chloride. *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd ed. Vol 12, pp. 983-1014.
24. Fritz JJ, Fuget CR. 1956. Vapor pressure of aqueous hydrogen chloride solutions, 0 to 50 °C. *Industrial and Engineering Chemistry* 1: 10-12.
25. EPA. 1997. Chemical Pulping Emission Factor Development Document (Revised Draft). 1997. July 8, 1997. Research Triangle Park, NC: U.S. EPA, OAQPS.
26. EPA. 1995. National Emission Standards for Hazardous Air Pollutants from Secondary Lead Smelting. 60 FR 32587, June 23, 1995.
27. EPA. 1997. Compilation of Air Pollutant Emission Factors (AP-42). Organic Liquid Storage Tanks. pp. 7.1-1 to 7.1-101. February 1996. Research Triangle Park, NC: U.S. EPA, OAQPS.
28. EPA. 1997. Emergency Planning and Community Right-to-Know Act Section 313. Guidance for Electricity Generating Facilities. EPA-745-B-97-016. September 26, 1997. Washington, DC: Office of Pollution Prevention and Toxics.

APPENDIX A.



**Figure A-1: 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 A-1, 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 A-A' connects the azeotropic points and B-B' represents the critical segregation curve above the critical point of water. Figure A-2 illustrates the use of this diagram.

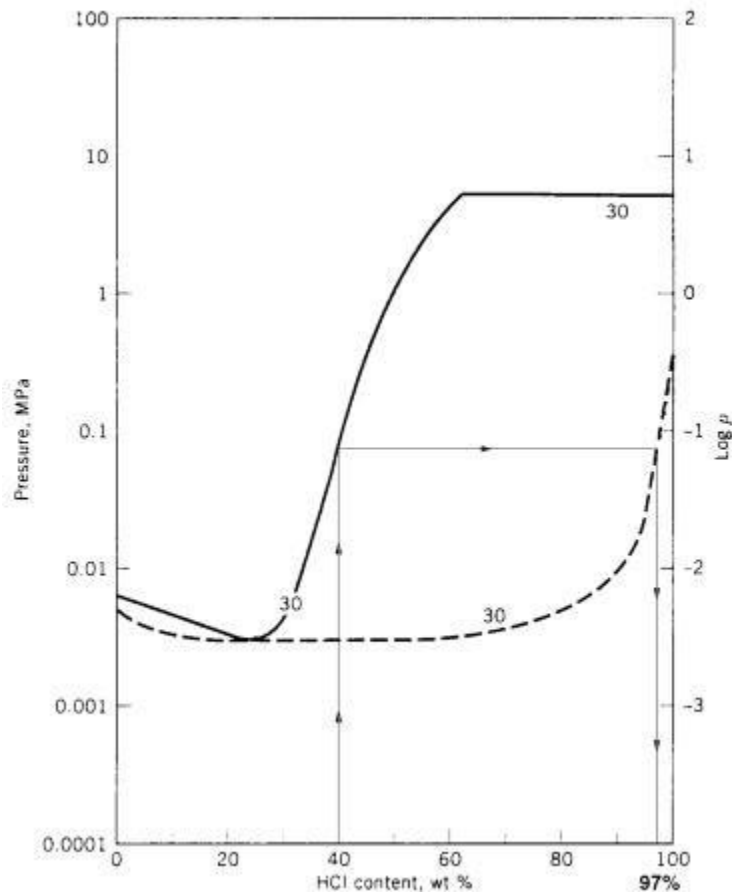


Figure A-2: Vapor—liquid phase diagram for HCl–H₂O system at 30 °C

Figure A-2 contains the vapor–liquid phase diagram for 30 °C and has been drawn to illustrate the use of Figure A-1. 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 A- and Figure A-3. 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 A- 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 A-1: Vapor Composition of HCl-H₂O Systems

Liquid			Vapor, Mole % HCl					
Molality	Weight %	Mole %	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
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	0.0616

Liquid			Vapor, Mole % HCl					
Molality	Weight %	Mole %	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
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

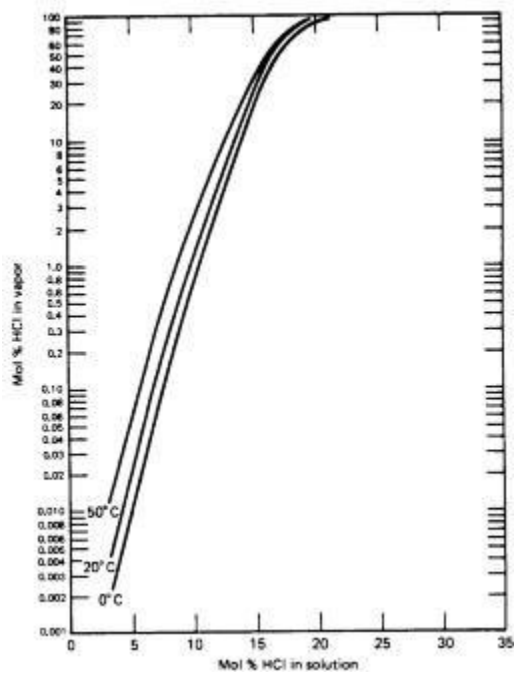


Figure A-3: Vapor composition of hydrogen chloride–water systems (Reference 22, p. 988)

Table A-2: Partial Pressure of HCl And Total Vapor Pressure of HCl-H₂O Systems

Liquid			HCl Partial Pressure (Total Vapor Pressure) (torr)					
Molality	Wt %	Mole %	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
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 A-3: 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

Example: To convert atm to kPa, use the entry in the atm row and the kPa column to obtain 1 atm = 101.33 kPa.

Table A-4: 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

Example: To convert $x = 0.1$ to molality: $m = 55.5 (0.1) / (1-0.1) = 6.17$.