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Department of the Environment and Heritage

National Pollutant Inventory

Emission Estimation Technique Manual

for

Inorganic Chemicals Manufacturing

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20 February 2004

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The Manual was prepared in conjunction with Australian States and Territories according to the National Environment Protection (National Pollutant Inventory) Measure.

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Erratum – version 2.0 – 20 February 2004

Inorganic Chemicals Manufacturing

Update (from first version published July 1999) – 20 February 2004 Erratum

Page	Outline of alteration
50	Table 5 pressure relief valve typographical error corrected. The value should be 0.104
10, 24	Changed fluosilicic acid to hexafluorosilicic acid

EMISSION ESTIMATION TECHNIQUES
FOR
INORGANIC CHEMICALS MANUFACTURING

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1. Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial, and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in inorganic chemical manufacturing.

The inorganic chemical manufacturing activities covered by this Manual include facilities primarily engaged in the manufacture of chlorine, caustic soda, sodium carbonate, mineral acids, industrial gases, and sulfur recovery operations.

EET MANUAL:	Inorganic Chemicals Manufacturing
HANDBOOK:	Inorganic Industrial Chemical Manufacturing
ANZSIC CODE:	2535

This Manual was drafted by the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. The Manual has been developed through a process of national consultation involving State and Territory environmental authorities and key stakeholders, and has been considered by independent reviewers.

2. Process Description

This section describes the major industrial processes within the inorganic chemical industry, including the materials and equipment used, the processes employed, and the likely emissions generated. The section is designed to provide a general understanding of the inter-relationship between the industrial processes and the topics discussed in subsequent sections of the Manual - emission outputs, available emission estimation techniques, emissions estimations for the NPI, and control technologies and emission abatement opportunities available. This section does not attempt to replicate published engineering information that is available for this industry.

This section specifically contains a description of commonly used production processes, associated raw materials, the by-products produced and NPI-listed substances emitted, as well as the materials either recycled or transferred off-site. This discussion, schematic drawings of the identified processes, provides a concise description of where emissions may be produced in the process. This section also describes the potential fate - to air, water, or land - of these emissions.

The inorganic chemical industry manufactures chemicals which are often of a mineral origin, but not of a basic carbon molecular nature. Inorganic chemicals are used at some stage in the manufacture of a great variety of other products. The industry's products are used as basic chemicals for industrial processes (acids, alkalies, salts, oxidising agents, industrial gases, and halogens) and chemical products to be used in manufacturing products (pigments, dry colours, and alkali metals). The largest use of inorganic chemicals is as processing aids in the manufacture of chemical and non-chemical products. Consequently, inorganic chemicals often do not appear in the final products.

2.1 Characterisation and Scope of the Industry

The Australian inorganic chemical industry manufactures over 100 different chemicals and accounts for around 15 percent of the total value of chemical production in Australia.

This Manual covers facilities manufacturing hydrochloric acid, hydrofluoric acid, nitric acid, phosphoric acid, sulfuric acid, sodium carbonate, sulfur recovery, hydrogen cyanide, alkalies and chlorine, industrial gases (eg. hydrogen, helium, oxygen, nitrogen), and inorganic pigments. The Manual does not include the manufacture of inorganic fertilisers, such as phosphate and ammonium fertilisers. The manufacture of these materials is covered in separate Manuals in this series.

This Manual also includes integrated facilities engaged in the manufacture of other types of chemicals or products at the same site, such as organic chemicals facilities, fertiliser plants, pulp and paper mills, and iron and steel mills who produce and use inorganic chemicals in their processes at the same facility. For example, a significant number of inorganic chemical manufacturing processes are part of very large organic chemical manufacturing facilities, making the scope of this Manual for the NPI complex.

Wherever possible, this Manual describes the entire inorganic chemical industry. In many cases, however, specific details relating to some of the topics covered in this Manual (emissions of inventory substances, emission factors covering all potential emission points, and applicable control and abatement technologies) vary depending on the type of inorganic chemical process and the design of the manufacturing facility itself. The large number of different industrial processes and potential emission points in the inorganics industry could not all be covered in this Manual. As a result, most sections of this Manual describe the entire inorganic chemical industry as a whole. These sections are usually augmented with information specific to the largest industrial processes within the industry, such as chlorine, caustic soda as well as mineral acid production.

2.2 Chlor-Alkali Sector

2.2.1 Chlorine and Caustic Soda

This sector produces mainly chlorine, caustic soda (sodium hydroxide), soda ash (sodium carbonate), sodium bicarbonate, potassium hydroxide, and potassium carbonate. Chlorine and caustic soda production is the largest segment in terms of production and both chemicals are co-products produced in about equal amounts primarily though the electrolysis of salt (brine).

Chlorine and caustic soda are co-products of electrolysis of saturated aqueous solutions of sodium chloride, NaCl (salt water or brine). In addition, relatively small amounts (by weight) of hydrogen gas are produced in the process. The overall chemical reaction is as follows:

Equation 1

$$2\ NaCl + 2\ H_2O \Uparrow 2\ NaOH + Cl_2 + H_2$$

Energy, in the form of direct current electricity, is supplied to drive the reaction. The amount of electrical energy required depends on the design of the electrolytic cell, the voltage used, and the concentration of brine used. For each tonne of chlorine produced, 1.1 tonnes of sodium hydroxide and 29 kg of hydrogen are produced. Three types of electrolysis processes are used for the manufacture of chlorine, caustic soda, and hydrogen from brine:

- Mercury Cell Process, shown in Figure 1;
- Diaphragm Cell Process, shown in Figure 2; and
- Membrane Cell Process.

Virtually all chlorine produced in Australia is manufactured by one of these three electrolysis processes. Each electrolytic cell consists of an anode and cathode in contact with the brine solution. The distinguishing feature of each cell type is the method employed to separate and prevent the mixing of the chlorine gas and sodium hydroxide. Consequently, each process produces a different purity of chlorine gas and a different concentration of caustic soda. Table 1 is a summary of the major differences between each cell type.

Table 1 - Main Characteristics of the Different Electrolysis Processes

Component	Mercury Cell	Diaphragm Cell	Membrane Cell
Cathode	Mercury flowing over steel	Steel or steel coated with activated nickel	Steel or nickel with a nickel based catalytic coating
Diaphragm / Membrane	None	Asbestos or polymer modified asbestos	Ion-exchange membrane
Anode	Titanium with RuO_2 or TiO_2 coating	Titanium with RuO_2 or TiO_2 coating	Titanium with RuO_2 or TiO_2 coating
Cathode Product	Sodium amalgam	10-12% NaOH with 15-17% NaCl and H_2	30-33% NaOH and H_2
Decomposer / Evaporator Product	50% NaOH and H_2 from decomposer	50% NaOH with 1% NaCl and solid salt from evaporator	50% NaOH with very little salt

Source: Queensland Department of Environment and Heritage, 1998.

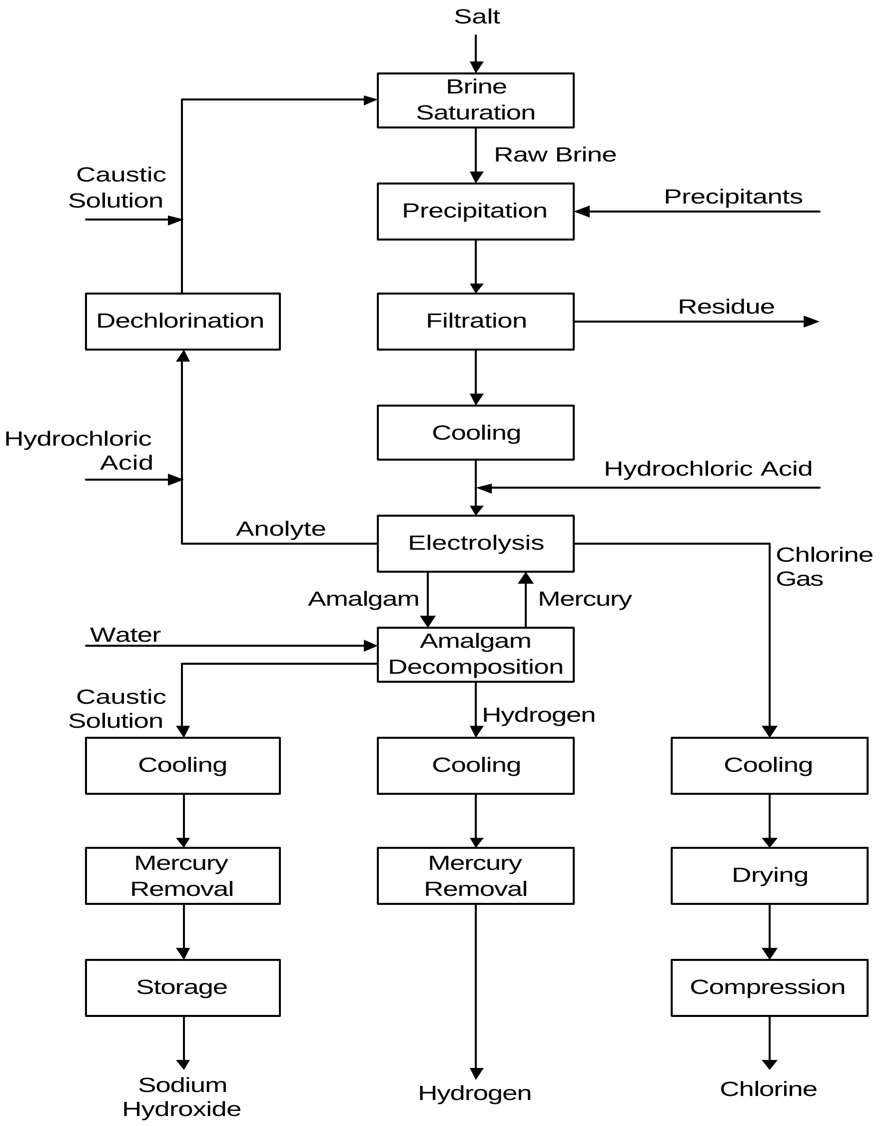


Figure 1 - Simplified Diagram of the Mercury Cell Process

Source: USEPA *AP-42* Section 8.0, 1996.

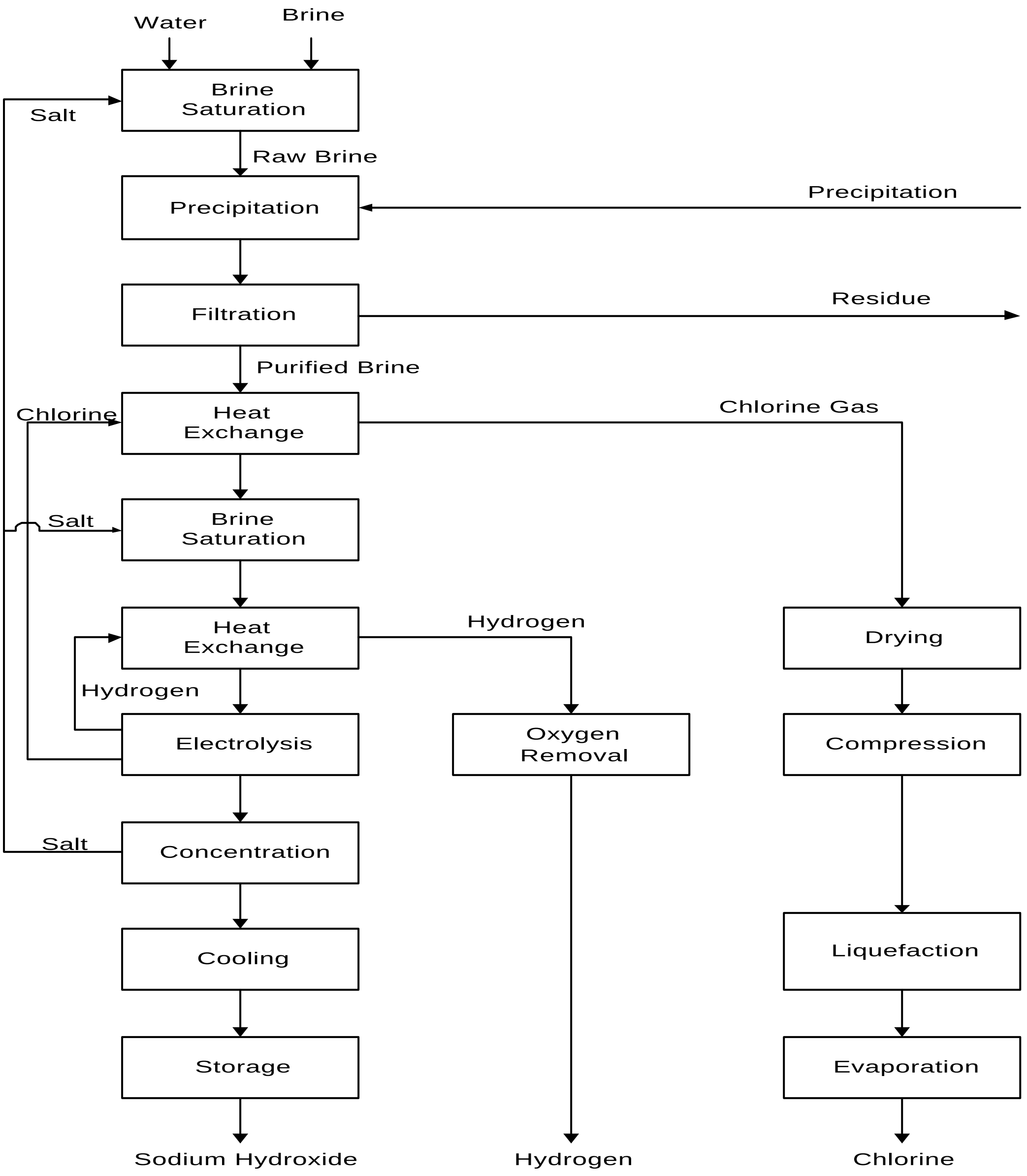


Figure 2 - Simplified Process Diagram of the Diaphragm Cell Process

Source: USEPA *AP-42* Section 8.0, 1996.

2.2.2 Sodium Carbonate

Sodium carbonate (Na_2CO_3), commonly referred to as soda ash, is one of the largest volume products produced by the Australian inorganic chemical industry. Soda ash is used mostly in the production of glass, chemicals, soaps and detergents, and in the treatment of water. Demand depends to a great extent on the market prices of, and environmental issues surrounding, caustic soda, which is interchangeable with soda ash in many uses and is predominantly co-produced with chlorine.

Sodium carbonate, or soda ash, may be manufactured synthetically or from naturally occurring raw materials. The synthetic process used in Australia is the Solvay process, which involves saturation of brine with ammonia (NH_3) and carbon dioxide (CO_2) gas. This process generates ammonia emissions. Natural processes include the calcination of sodium bicarbonate ($NaHCO_3$).

Benefaction of soda ash is accomplished through either of two methods, called the sesquicarbonate and the monohydrate processes. In the sesquicarbonate process, shown schematically in Figure 3, mined ore is first dissolved in water (H_2O) and then treated as brine. This liquid is filtered to remove insoluble impurities before the sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) is precipitated out.

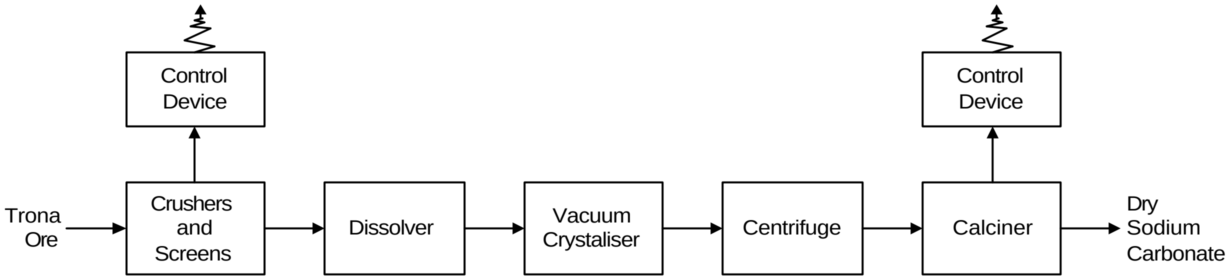


Figure 3 - Flow Diagram for Sesquicarbonate Na_2CO_3 Processing
Source: USEPA *AP-42* Section 8.0, 1996.

The result is centrifuged to remove remaining water, and can either be sold as a finished product or further calcined to yield soda ash of light to intermediate density. In the monohydrate process, shown schematically in Figure 4, crushed ore is calcined in a rotary kiln. The calcined material is combined with water to allow the settling out of impurities and is then concentrated to precipitate sodium carbonate monohydrate ($Na_2CO_3.H_2O$).

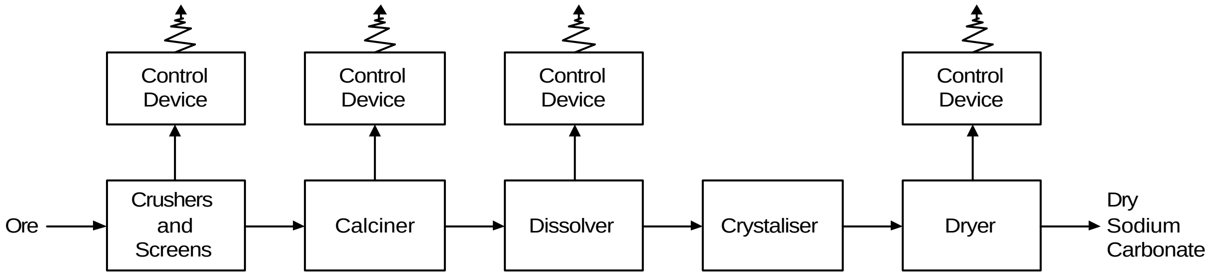


Figure 4 - Flow Diagram for Monohydrate Na_2CO_3 Processing
Source: USEPA *AP-42* Section 8.0, 1996.

2.3 Mineral Acids Sector

2.3.1 Hydrochloric Acid

Hydrochloric acid (HCl) is a versatile chemical used in a variety of chemical processes, including hydrometallurgical processing such as the production of alumina and titanium dioxide, chlorine dioxide syntheses, hydrogen production, activation of petroleum wells, and miscellaneous cleaning and etching operations including metal cleaning (eg. steel pickling). HCl is used by bricklayers to clean finished brick work. It is also a common ingredient in many chemical reactions, and is the preferred acid for catalysing organic processes.

HCl can be manufactured by following several different processes, although in Australia it has been traditionally produced by reacting sodium chloride with sulfuric acid (Equation 2 to Equation 4) or more recently as a by-product of the chlorination reaction (Equation 5 and Equation 6).

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

Equation 2

$NaCl + H_2SO_4 \wedge NaHSO_4 + HCl$

Equation 3

$NaCl + NaHSO_4 \wedge Na_2SO_4 + HCl$

Equation 4

$2NaCl + H_2SO_4 \wedge Na_2SO_4 + 2HCl$

2. As a by-product of chlorination, for example in the production of dichloromethane, trichloroethylene, perchlorethylene, or vinyl chloride:

Equation 5

$C_2H_4 + Cl_2 \wedge C_2H_4Cl_2$

Equation 6

$C_2H_4Cl_2 \wedge C_2H_3Cl + HCl$

Figure 5 is a simplified diagram of the steps used for the production of by-product HCl from the chlorination process and shows likely pollutant emission points.

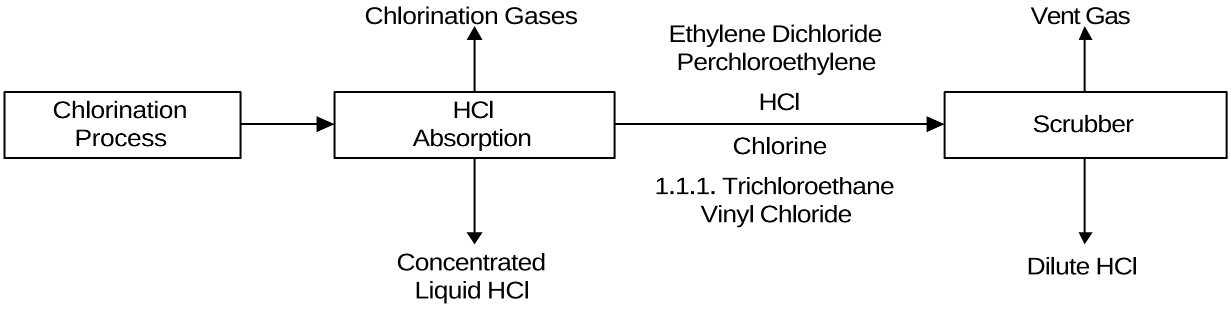


Figure 5 - Hydrochloric Acid Production from the Chlorination Process
Source: USEPA *AP-42* Section 8.0, 1996.

After leaving the chlorination process, the HCl-containing gas stream proceeds to the absorption column, where concentrated liquid HCl is produced by absorption of HCl vapours into a weak solution of hydrochloric acid. The HCl-free chlorination gases are removed for further processing. The liquid acid is then either sold or used elsewhere in the plant. The final gas stream is sent to a scrubber to remove the remaining HCl prior to venting.

2.3.2 Hydrofluoric Acid

Hydrogen fluoride (HF) is produced in two forms, as anhydrous hydrogen fluoride and as aqueous hydrofluoric acid. The predominant form manufactured is hydrogen fluoride, a colourless liquid or gas that fumes when in contact with air and is water-soluble.

In Australia, hydrogen fluoride is only produced as a fortuitous by-product in the manufacture of superphosphate fertilisers. HF, as hydrofluoric acid, is used in glass etching and polishing, uranium processing, petroleum alkylation, and stainless steel pickling. Hydrofluoric acid is also used to produce fluorocarbons for the manufacture of resins, solvents, stain removers, surfactants, and pharmaceuticals.

Hydrofluoric acid manufactured by the reaction of acid-grade fluorspar (CaF_2) with sulfuric acid (H_2SO_4) is shown by Equation 7:

Equation 7

$$CaF_2 + H_2SO_4 \wedge CaSO_4 + 2HF$$

A typical HF plant, along with likely pollutant emission points, is shown schematically in Figure 6. The endothermic reaction requires 30 to 60 minutes in horizontal rotary kilns externally heated to 200 to 250°C. Dry fluorspar and a slight excess of sulfuric acid are fed continuously to the front end of a stationary prereactor or directly to the kiln by a screw conveyor. The prereactor mixes the components prior to charging to the rotary kiln. Calcium sulfate ($CaSO_4$) is removed through an air lock at the opposite end of the kiln.

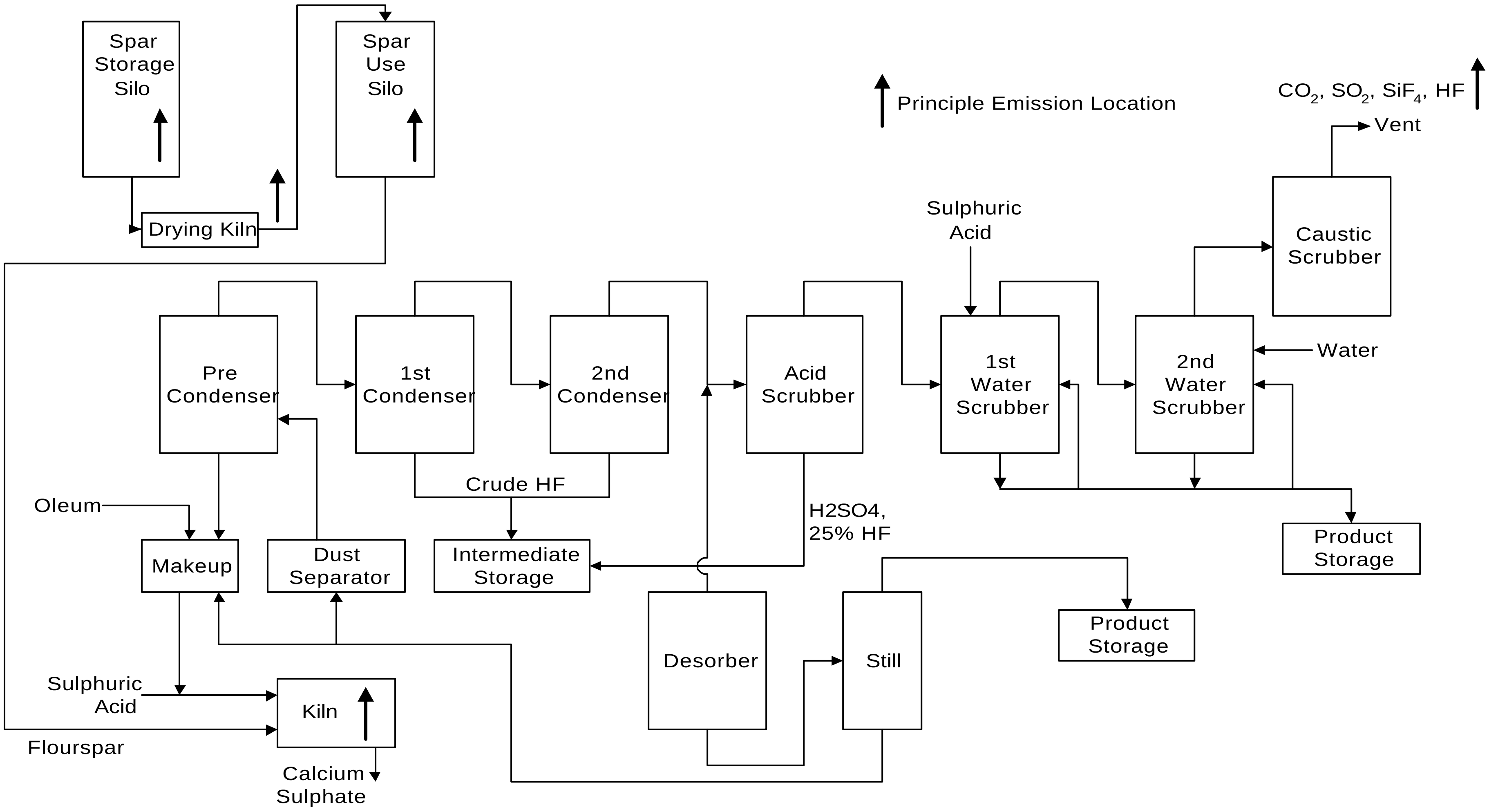


Figure 6 - Hydrofluoric Acid Process Flow Diagram

Source: USEPA *AP-42* Section 8.0, 1996.

The gaseous reaction products - hydrogen fluoride and excess H_2SO_4 from the primary reaction and silicon tetrafluoride (SiF_4), sulfur dioxide (SO_2), carbon dioxide (CO_2), and water produced in secondary reactions - are removed from the front end of the kiln along with entrained particulate. The particulate matter is then removed from the gas stream by a dust separator and returned to the kiln. Sulfuric acid, and water, are removed by a precondenser.

Hydrogen fluoride vapours are subsequently condensed in refrigerant condensers forming *crude HF*, which is removed to intermediate storage tanks. The remaining gas stream passes through a sulfuric acid absorption tower or acid scrubber, removing most of the remaining hydrogen fluoride and some residual sulfuric acid, which are also placed in intermediate storage. The gases exiting the scrubber then pass through water scrubbers, where the SiF_4 and remaining HF are recovered as hexafluorosilicic acid (H_2SiF_6).

The water scrubber tail-gases are passed through a caustic scrubber before being emitted to the atmosphere. The hydrogen fluoride and sulfuric acid are delivered from intermediate storage tanks to distillation columns, where the hydrofluoric acid is extracted at 99.98 percent purity. Weaker concentrations (typically 70 to 80 percent) are prepared by dilution with water.

2.3.3 Nitric Acid

Most nitric acid (HNO_3) manufactured in Australia is consumed as an intermediate in the manufacture of ammonium nitrate (NH_4NO_3), which in turn is used in explosives and fertilisers. Other uses of HNO_3 include organic oxidation in adipic and terephthalic acids and other organic compound manufacturing. Explosive manufacturing utilises HNO_3 for organic nitrations. Nitric acid nitrations are used in producing dinitrotoluenes and other chemical intermediates. Other end uses of HNO_3 are in gold and silver separation, military munitions, steel and brass pickling, photoengraving, and acidulation of phosphate rock.

Nitric acid is produced by two methods. The first method utilises oxidation, condensation, and absorption to produce a weak HNO_3. Weak HNO_3 can have concentrations ranging from 30 to 70 percent HNO_3. The second method combines dehydrating, bleaching, condensing, and absorption to produce a high-strength nitric acid from weak nitric acid. This is shown schematically in Figure 7. High-strength HNO_3 generally contains more than 90 percent HNO_3.

Nearly all HNO_3 is produced by the high-temperature catalytic oxidation of ammonia as shown schematically in Figure 8. This process typically consists of three steps:

(1) ammonia oxidation;
(2) nitric oxide oxidation; and
(3) absorption.

Each step corresponds to a distinct chemical reaction. Figure 8 also highlights emission points across a nitric acid manufacturing facility.

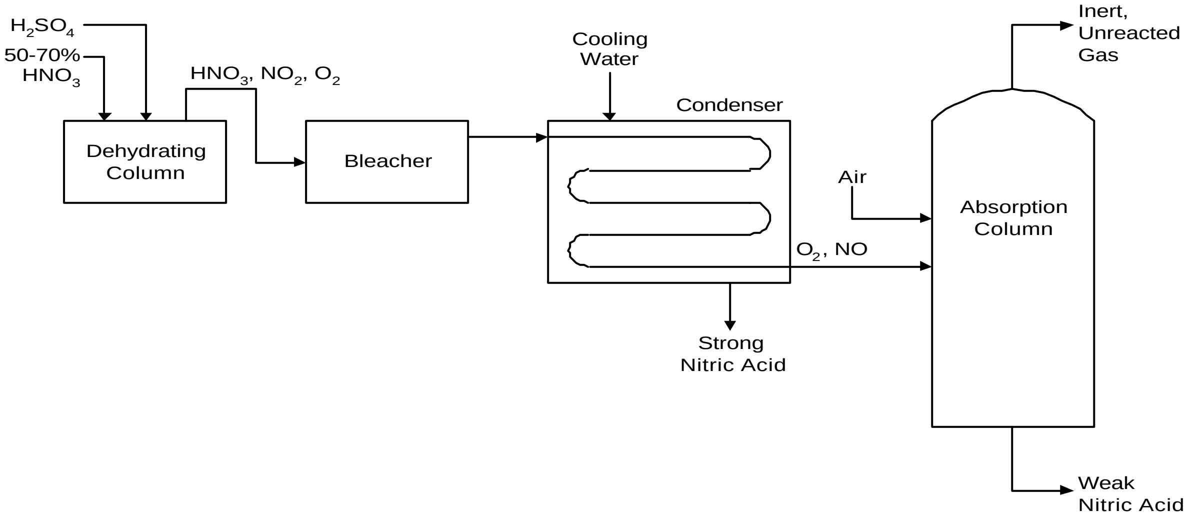


Figure 7 - Flow Diagram of High-Strength Nitric Acid Production
Source: USEPA *AP-42* Section 8.0, 1996.

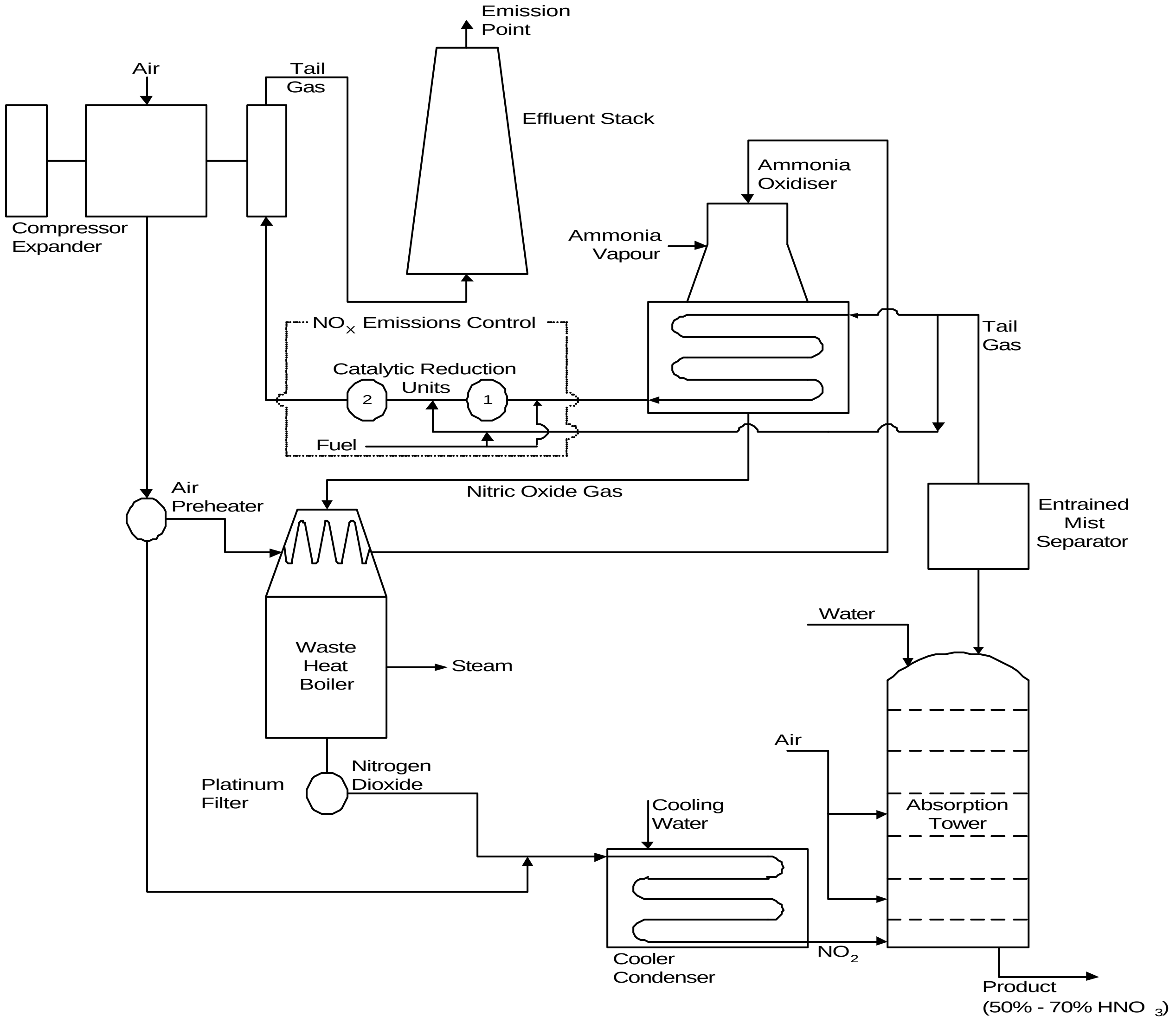


Figure 8 - Flow Diagram of a Typical Nitric Acid Plant Using Single Pressure Process
Source: USEPA *AP-42* Section 8.0, 1996.

A high-strength nitric acid (98-to-99 percent concentration) can be obtained by concentrating the weak nitric acid (30-to-70 percent concentration) using extractive distillation. Figure 7 shows a schematic of a high-strength nitric acid plant and the likely pollutant emission points. The weak nitric acid cannot be concentrated by simple fractional distillation. The distillation must be carried out in the presence of a dehydrating agent. Concentrated sulfuric acid (typically 60 percent sulfuric acid) is most commonly used for this process.

2.3.4 Phosphoric Acid

Phosphoric acid (H_3PO_4) is produced by two commercial methods: wet process and thermal process. Wet process phosphoric acid is used in fertiliser production. Thermal process phosphoric acid is of a much higher purity and is used in the manufacture of high-grade chemicals, pharmaceuticals, detergents, food and beverage products, and other non-fertiliser products. In Australia, phosphoric acid production is confined to the manufacture of phosphate fertilisers and polyphosphates by the thermal process using imported elemental phosphorus although plans to produce phosphoric acid by the wet process are well advanced in Queensland and Western Australia.

In a wet process facility, see Figure 9 and Figure 10, phosphoric acid is produced by reacting sulfuric acid with naturally occurring phosphate rock. The phosphate rock is dried, crushed, and then continuously fed into the reactor along with sulfuric acid. The reaction combines calcium from the phosphate rock with sulfate, forming calcium sulfate ($CaSO_4$), commonly referred to as gypsum. Gypsum is separated from the reaction solution by filtration.

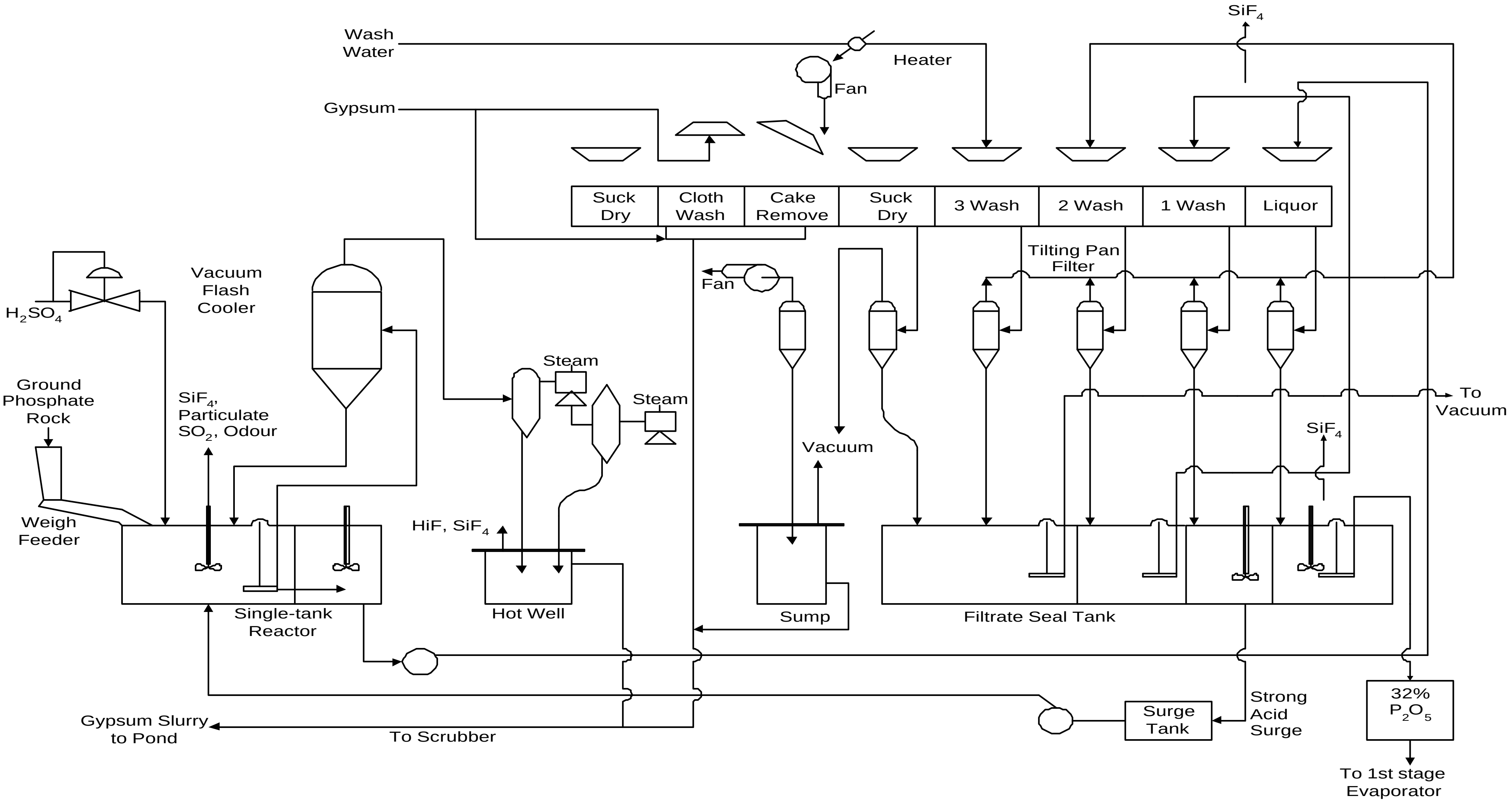


Figure 9 - Flow Diagram of a Wet Process Phosphoric Acid Plant

Source: USEPA *AP-42* Section 8.0, 1996.

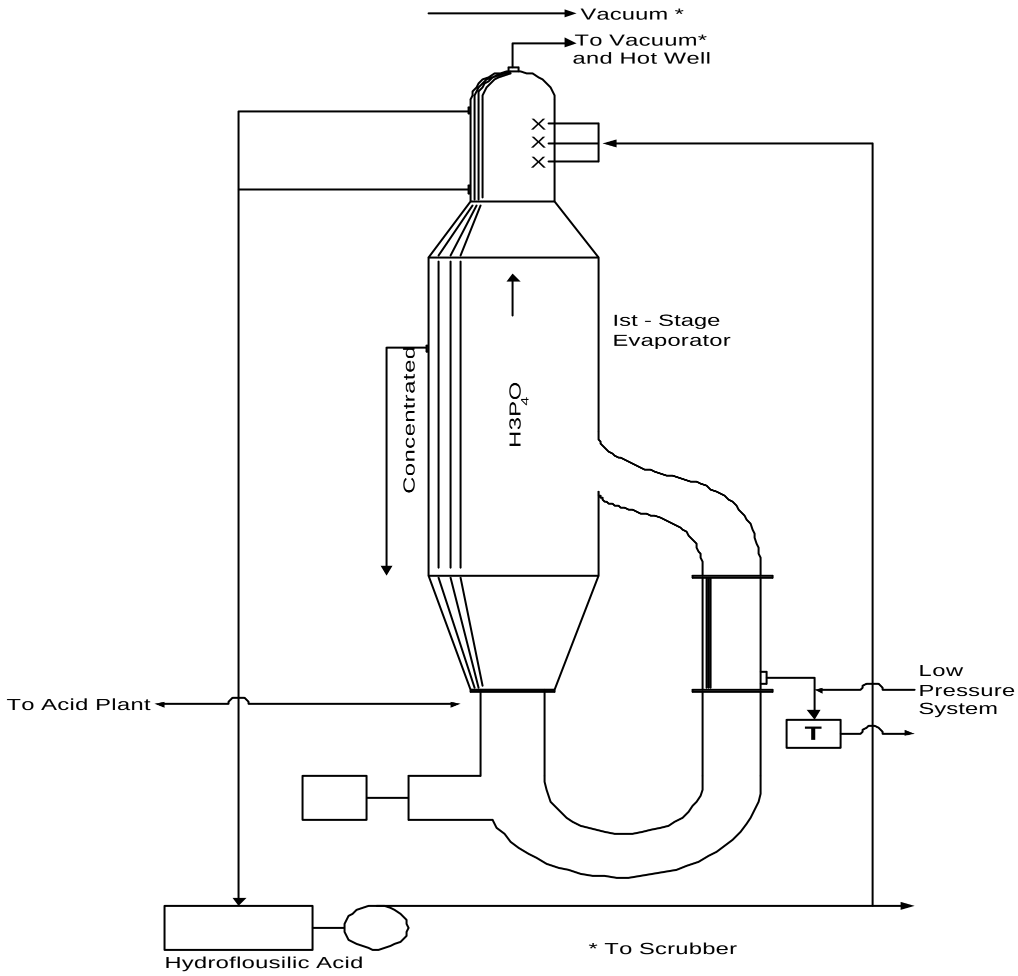


Figure 10 - Flow Diagram of a Wet Process Phosphoric Acid Plant

Source: USEPA *AP-42* Section 8.0, 1996.

The production of wet process phosphoric acid generates a considerable quantity of acidic cooling water with high concentrations of phosphorus and fluoride. This excess water is collected in cooling ponds that are used to temporarily store excess precipitation for subsequent evaporation and to allow recirculation of the process water to the plant for reuse. Leachate seeping is therefore a potential source of groundwater contamination and emission of inventory substances. Excess rainfall also results in water overflows from settling ponds.

Raw materials for the production of phosphoric acid by the thermal process are elemental (yellow) phosphorus, air, and water. Thermal process phosphoric acid manufacture, as shown schematically in Figure 11, involves three major steps:
(1) combustion;
(2) hydration; and
(3) demisting.

Concentration of H_3PO_4 produced from thermal process normally ranges from 75 to 85 percent. This high concentration is required for high-grade chemical production and other non-fertiliser product manufacturing. Efficient plants recover about 99.9 percent of the elemental phosphorus burned as phosphoric acid.

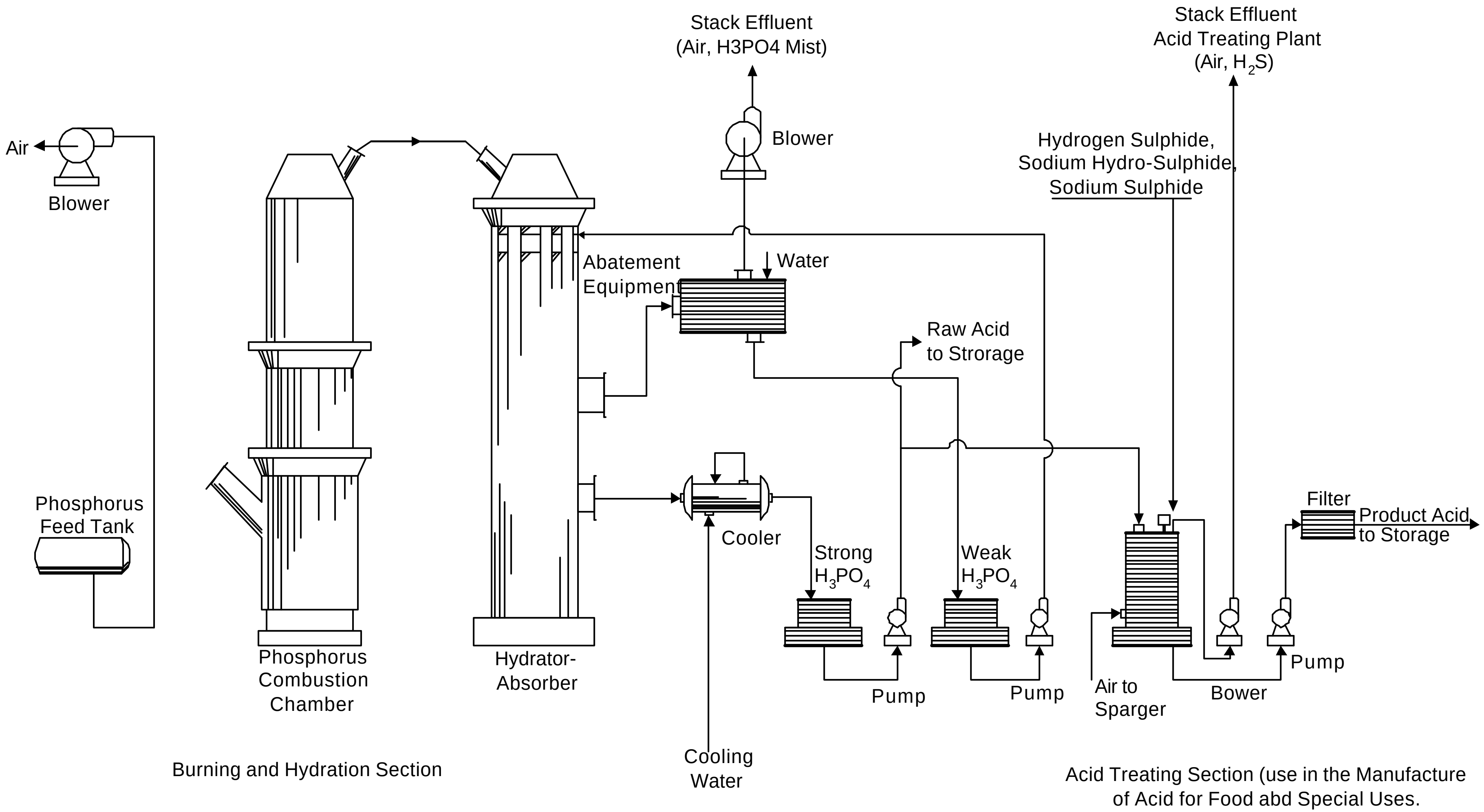


Figure 11 - Flow Diagram of a Thermal Process Phosphoric Acid Plant

Source: USEPA *AP-42* Section 8.0, 1996.

2.3.5 Sulfuric Acid

Sulfuric acid (H_2SO_4) is a basic raw material used in a wide range of industrial processes and manufacturing operations. Around 80 percent of sulfuric acid manufactured in Australia is used in the production of phosphate (superphosphate) fertilisers. It is also used to produce ammonium phosphates and for the extraction of nickel from laterite nickel ores. Other uses include copper leaching, inorganic pigment production, petroleum refining, paper production, and industrial organic chemical production. Currently there are ten sulfuric acid production units in Australia with production expected to rise to 3.8 million tonnes per year by 2 000 when Australia will become a major exporter of sulfuric acid.

In recent years in Australia there has been a move towards smelter-sourced acid that has been largely driven by environmental improvements promoting the clean-up and recovery of sulfur dioxide in smelter off-gases. The closure of all fertiliser phosphoric acid plants in Australia and the cutbacks in single superphosphate production capacity, has led to a total shutdown of the sulfur-burning sulfuric acid operations that were integrated with the phosphate fertiliser manufacturing industry. Major producers of smelter acid are located at Kalgoorlie, Roxby Downs, Risdon, Port Kembla, Townsville, and a major plant being developed in Mt Isa.

Figure 12 shows a process flow diagram of a smelter gas recovery process typical of the methods used in Australia today to produce sulfuric acid. The feed used in these plants is smelter gas, available from such equipment as copper converters, reverberatory furnaces, roasters, and flash smelters. The sulfur dioxide in the gas is contaminated with dust, acid mist, and gaseous impurities. To remove the impurities, the gases must be cooled and passed through purification equipment consisting of cyclone dust collectors, electrostatic dust and mist precipitators, as well as scrubbing and gas cooling towers. After the gases are cleaned and the excess water vapour is removed, they are scrubbed with 98 percent acid in a drying tower.

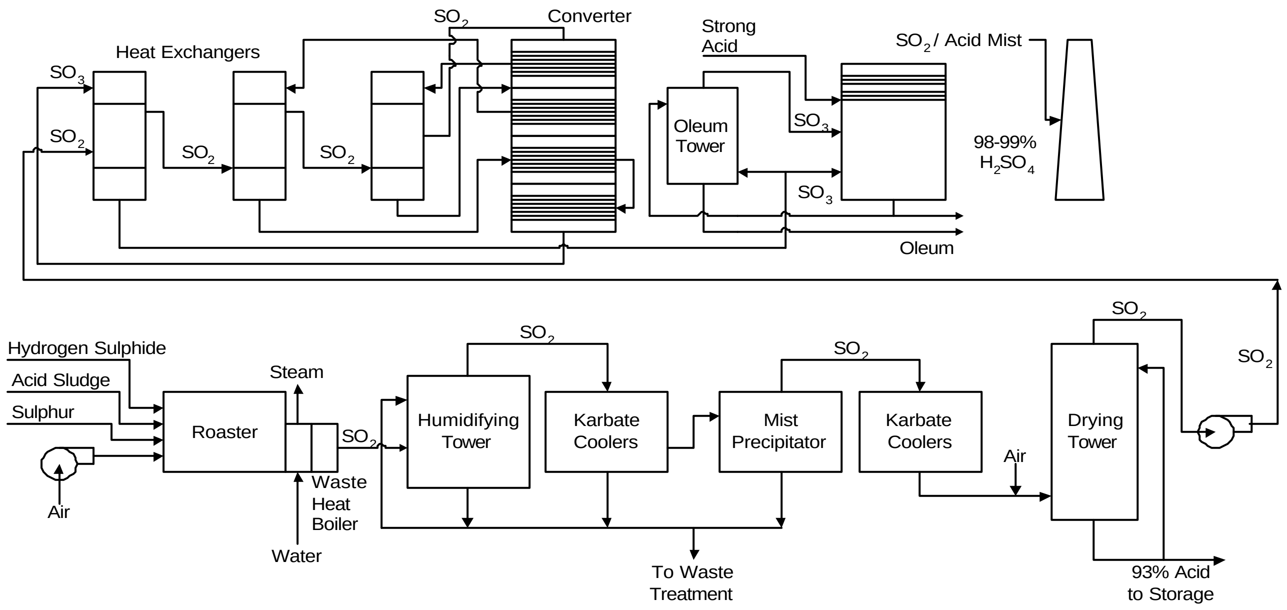
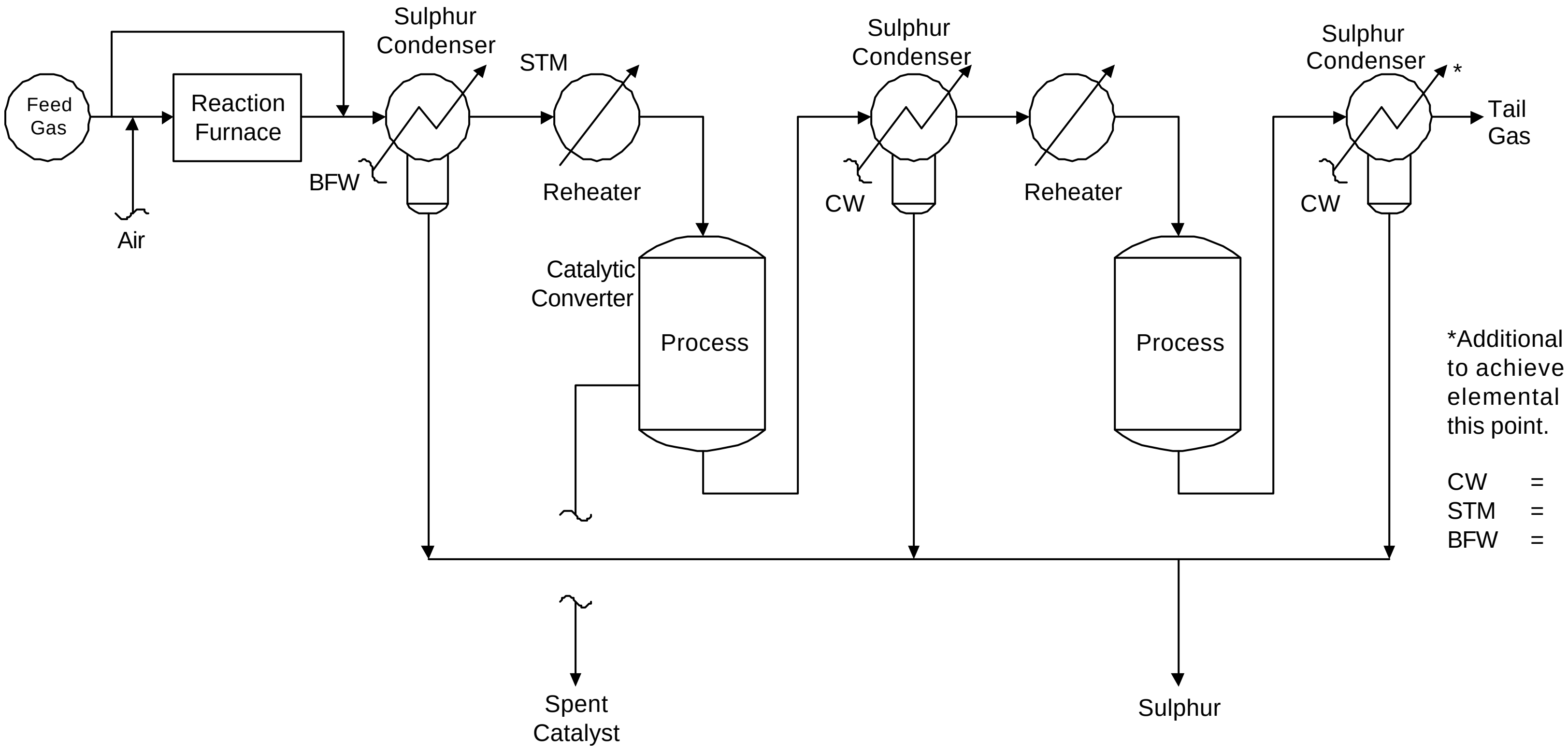


Figure 12 - Basic Flow Diagram of a Sulfide Ore and Smelter Gas Plant
Source: USEPA *AP-42* Section 8.0, 1996.

2.4 Sulfur Recovery

Sulfur recovery refers to the conversion of hydrogen sulfide (H_2S) to elemental sulfur. Hydrogen sulfide is a by-product of the processing of natural gas and the refining of high-sulfur crude oils. The most common conversion method is the Claus process. Approximately 90 to 95 percent of recovered sulfur is produced using the Claus process. The Claus process generally recovers 95 to 97 percent of the hydrogen sulfide feedstream. Figure 13 shows a typical Claus sulfur recovery unit.



*Additional converters/condensers to achieve additional recovery of elemental sulphur are optional at this point.

CW = Cooling water
STM = Steam
BFW = Boiler Feed Water

Figure 13 - Typical Claus Sulfur Recovery Unit

Source: USEPA *AP-42* Section 8.0, 1996.

3. Material Inputs, Emissions, and Control Technologies

Emissions from the manufacture and use of inorganic chemicals and chemical products are generally large in volume but, because of economic necessity and environmental responsibility, these emissions are usually recovered. In many modern Australian facilities, the manufacturing operation is run as a closed system, allowing little or no emissions to escape to the environment. Emission sources from chemical processes include heaters and boilers; valves, flanges, pumps, and compressors; storage and transfer of products and intermediates; wastewater handling; and emergency vents.

The emissions that do reach the environment from the inorganic chemical industry are generally gaseous and can be controlled by adsorption or absorption. Particulate emissions also could be of concern, since the particulate emitted is usually extremely small and well within the inventory criteria of less than 10 microns in aerodynamic diameter, requiring efficient treatment for complete removal.

Existing emissions data from many inorganic chemical processes is sparse. It will be necessary, therefore, for many Australian facilities reporting to the NPI to estimate emissions on the basis of material balances, yields, process similarities, or predictive emissions monitoring. Nevertheless, suggested emission estimation techniques are described in Section 4.0 and a range of emission factors are presented in Section 5.0 covering a limited range of inorganic chemical industrial processes.

3.1 Chlor-Alkali Sector

Inputs and pollutant emissions of the chlor-alkali industry are relatively small, both in number and volume, compared to the chemical manufacturing industry as a whole. The inputs are primarily salt and water as feedstocks; acids and chemical precipitants used to remove impurities in the input brine or output chlorine and caustic soda; and freon used for liquefying and purifying the chlorine gas produced. The major NPI-listed pollutant outputs from all three electrolytic processes are both fugitive and point source chlorine gas emissions. Fugitive and point source emissions of freon, impurities removed from the input salt or brine, and pollutants originating from electrolytic cell materials and other system parts are also produced.

Emissions of gaseous pollutants have decreased in recent years as the industry moves away from the mercury and diaphragm cell processes to the more efficient (in terms of material and energy inputs and emissions) membrane cell process. In addition, improved cell part materials have been developed, such as DSA anodes and Modified Diaphragms, which are more stable and create less undesirable by-products.

Inputs and likely emissions from the auxiliary processes, such as brine purification, chlorine, caustic soda and hydrogen processes, are described in Section 3.1.4.

3.1.1 Mercury Cell

Wastewater streams from mercury cell facilities arise from the chlorine drying process, brine purge, and miscellaneous sources. Small amounts of mercury are found in the brine purge and miscellaneous sources, which include floor sumps and cell wash water. Before treatment, mercury concentrations (principally in the form of the mercuric chloride complex ion, $HgCl_4^{2-}$) typically range from 0 to 20 ppmv. Prior to treatment, sodium hydrosulfide is used to precipitate mercuric sulfide. The mercuric sulfide is removed through filtration before the water is discharged.

Air emissions consist of mercury vapour and chlorine gas (both NPI-listed substances) emitted in relatively small amounts as fugitive emissions from the cells; and in the tail gases of the chlorine processing, caustic soda processing, and hydrogen processing. Process tail gases are wet scrubbed with caustic soda or soda ash solutions to remove chlorine and mercury vapour. Residual chlorine emissions in tail gases after treatment are less than one kilogram per 1 000 kilograms of chlorine produced and mercury emissions are negligible. The tail gas scrubber water is typically reused as brine make-up water.

Solid wastes containing mercury include: solids generated during brine purification; spent graphite from decomposer cells; spent caustic filtration cartridges from the filtration of caustic soda solution; spilled mercury from facility sumps; and mercury cell butters. These are semi-solid amalgams of mercury with barium or iron, formed when an excess of barium is used during salt purification. Most mercury bearing solid wastes are transferred off-site to reclaimers who recover the mercury. In these instances, this transfer off-site of mercury emissions does not require NPI reporting. The remaining wastes are disposed of in secure landfills using either chemical or physical methods to recover maximum feasible amounts of mercury. Again, these are off-site transfers and emissions do not require reporting, although if emissions are being estimated using a mass balance, the solid waste will still require characterising.

3.1.2 Diaphragm Cell

Wastewater streams from the diaphragm cell process originate from the barometric condenser during caustic soda evaporation, chlorine drying, and from purification of salt recovered from the evaporators. These wastewaters and their treatment are described below in Section 3.1.4. The use of lead and graphite anodes, as well as asbestos diaphragms generates lead, asbestos, and chlorinated hydrocarbons in the caustic soda and chlorine processing emission streams. Lead salts and chlorinated hydrocarbons are generated from corrosion of the anodes, and asbestos particles are formed by the degradation of the diaphragm over time. Over the past twenty years, all but a few diaphragm cell facilities have switched from the use of lead and graphite anodes with asbestos diaphragms to DSA anodes and Modified Diaphragms that resist corrosion and degradation. The lead, asbestos, and chlorinated hydrocarbon contaminants are, therefore, no longer emitted in significant amounts from most diaphragm cell chlorine-alkali facilities. Those facilities that emitted caustic processing wastewater streams to on-site pondages may, however, still have significant levels of contaminants on-site and may be required to estimate emissions of listed substances from on-site pondages to groundwater, land, and surface waters.

Chlorine is emitted in relatively small amounts as fugitive emissions from the cells and in the process tail gases. Process tail gases are wet scrubbed with soda ash or caustic soda solutions to remove chlorine. Residual chlorine emissions in tail gases after treatment are negligible. The spent caustic solution is neutralised prior to discharge.

Solid wastes generated in the diaphragm process consist primarily of solids generated during brine purification and scrapped cell parts including, cell covers, piping and used diaphragms. Discarded cell parts are either landfilled on-site, as is typically the case for spent diaphragms, or transferred off-site for the recovery of their titanium content.

3.1.3 Membrane Cell

Wastewater from the membrane cell process originates from the barometric condenser during caustic soda evaporation, chlorine drying, and wash water from the ion exchange resin used to purify the brine solution. The ion exchange wash water consists of dilute hydrochloric acid with small amounts of dissolved calcium, magnesium, and aluminium chloride. The wastewater is combined with the other process wastewaters and treated by neutralisation.

Chlorine is emitted in relatively small amounts as fugitive emissions from the cells and in the process tail gases. Process tail gases are wet scrubbed with soda ash or caustic soda solutions to remove chlorine. Residual chlorine emissions in tail gases after treatment are negligible. The spent caustic solution is neutralised prior to discharge.

Solid wastes generated in the membrane process consist primarily of solids generated during brine purification and used cell parts that include membranes, cathodes, and DSA anodes. The used membranes are generally returned to the supplier and the used cathodes and DSA anodes are shipped off-site for recovery of their titanium content. In all cases, where solid wastes containing listed substances are transferred off-site for disposal, recovery, or recycling, the emission does not require reporting to the NPI.

3.1.4 Auxillary Processes

Brine Purification

Brine solutions are typically treated with a number of chemicals to remove impurities prior to contact with the electrolytic cells. In the case of mercury and membrane cell systems, the brine is first acidified with HCl to remove dissolved chlorine. Next, sodium hydroxide and sodium carbonate are added to precipitate calcium and magnesium ions as calcium carbonate and magnesium hydroxide. Barium carbonate may be added to remove sulfates that precipitate out as barium sulfate. The precipitants are removed from the brine solution by settling and filtration. Pollutant outputs from this process include fugitive chlorine emissions and brine muds.

Brine muds are one of the largest waste streams of the chlor-alkali industry. On average, about 30 kg of brine mud are generated for every tonne of chlorine produced. The volume of mud will vary, however, depending on the purity of the salt used. Some facilities use pre-purified (chemical grade) evaporated salts that will produce only 0.7 to 6 kilograms of brine mud per tonne of chlorine produced. Brine mud typically contains magnesium hydroxide, calcium carbonate, and, in most cases, barium sulfate. Mercury cell brine muds usually contain mercury either in the elemental form or as the mercuric chloride complex ion ($HgCl_4^{2-}$). Brine muds containing mercury are typically transferred to landfill, after treatment with sodium sulfide, which converts the mercury to an insoluble sulfide or transferred without treatment to a hazardous waste receiver. The method used for final disposal is often a condition of a State or Territory licence requirement or local government environment regulation.

Brine muds are usually segregated from other process wastes and stored in pondages on-site. When the pondages become filled, the brine mud is dredged, landfilled off-site, and/or drained and covered over.

Chlorine Processing

The chlorine gas recovered from electrolytic cells is cooled to remove water vapour. The condensed water is usually recycled as brine make-up, although some facilities combine this emission stream with other waterborne emission streams prior to treatment. The remaining water vapour is removed by scrubbing the chlorine gas with concentrated sulfuric acid. The chlorine gas is then compressed and cooled to form liquid chlorine. Between six and 35 kilograms of 79 percent sulfuric acid wastewater is generated per tonne of chlorine produced. The majority of the spent sulfuric acid waste is transferred off-site for refortification to concentrated sulfuric acid or for use in other processes. The remainder is used to control effluent pH, and/or is emitted to water or landfilled. Only the amounts of sulfuric acid emitted in wastewater to water or land at pH below 6.0 requires reporting. Emission reporting to the NPI should be done in 100 percent concentration equivalents.

The process of purifying and liquefying impure chlorine gas involves the absorption of the chlorine in a stream of an organic reagent. The chlorine is subsequently removed in a stripping process in which the reagent is recovered, and reused, and/or is vented to the atmosphere.

Caustic Soda Processing

Caustic soda solution generated from chlor-alkali processes is generally processed to remove impurities and, in the case of the diaphragm and membrane processes, is concentrated to either a 50 percent or 73 percent water-based solution or to anhydrous caustic soda. About five tonnes of water must be evaporated per tonne of 50 percent caustic soda solution produced.

The water vapour from the evaporators is condensed in barometric condensers and, in the case of the diaphragm process, will primarily contain about 15 percent caustic soda solution and high concentrations of salt. If sodium sulfate is not removed during the brine purification process, salt recovered from the evaporators is often recrystallised to avoid sulfate build-up in the brine. If the salt is recrystallised, the wastewater from sodium hydroxide processing will also contain sodium sulfates. Significant levels of copper may also be present in the wastewater due to corrosion of pipes and other equipment. Wastewater from the membrane process contains caustic soda solution and virtually no salt or sodium sulfates.

Caustic soda processing wastewater is typically neutralised with hydrochloric acid, ponded, and then emitted directly to a receiving water or landfill. The caustic soda generated from the mercury process only requires filtration to remove mercury droplets that are recovered for reuse.

Hydrogen Processing

The hydrogen produced in all of the electrolytic processes contains small amounts of water vapour, sodium hydroxide, and salt that are removed through cooling. Condensed salt water and sodium hydroxide solution are either recycled as brine make-up or treated with other waterborne waste streams. The hydrogen produced during the mercury cell process, however, also contains small amounts of mercury that must be removed prior to liquefaction. Most of the entrained mercury is extracted by cooling the gas. The condensed mercury is then returned to the electrolytic cells. Some facilities further purify the hydrogen gas of mercury using activated carbon treatment. Spent activated carbon is typically transferred off-site as a hazardous waste.

3.2 Sodium Carbonate

The principal air emissions from sodium carbonate production methods are particulate emissions from ore calciners; soda ash coolers and dryers; ore crushing, screening, and transportation operations; product handling and shipping operations. Emissions of products of combustion, such as carbon monoxide, nitrogen oxides, and sulfur dioxide occur from direct-fired process heating units such as ore calcining kilns and soda ash dryers. Emissions of ammonia may also arise. There are no emission factors available to quantify these emissions from Australian facilities with any reasonable level of confidence and, therefore, other emission estimation techniques must be used to determine emissions from sodium carbonate manufacturing.

However, controlled and uncontrolled emissions of filterable and total particulate matter from individual processes and process components are given in Section 6.0. No data quantifying emissions of organic condensable particulate matter from sodium carbonate manufacturing processes is available, but this emission portion of particulate matter can be assumed to be negligible. Emissions from combustion sources such as boilers, and from the evaporation of hydrocarbon fuels used to fire these combustion sources, are covered in the *Combustion in Boilers* and *Fuel and Organic Liquid Storage EET Manuals* respectively.

Particulate matter (particles with an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10μm), emissions from calciners and dryers are typically controlled by venturi scrubbers, electrostatic precipitators, and/or cyclones. Baghouse filters are not very well suited to applications such as these, because of the high moisture content of the effluent gas. Particulate emissions from ore and product handling operations are typically controlled by either venturi scrubbers, or baghouse filters. These control devices are an integral part of the manufacturing process, capturing raw materials and product for both economic and environmental reasons. Because of a lack of suitable emissions data for uncontrolled processes, both controlled and uncontrolled emission factors are presented for this industry in Section 5.4.2. The uncontrolled emission factors have been calculated from US facilities by applying nominal control efficiencies to the controlled emission factors.

3.3 Mineral Acids Sector

3.3.1 Hydrochloric Acid

Emissions from HCl production result primarily from gases exiting the HCl purification system. The contaminants are HCl gas, chlorine, and chlorinated organic compounds. Emission factors in this Manual shown in Section 5.4.3 are only available for HCl gas emissions. Other emission estimation techniques outlined in Section 5.0 should be used to estimate emissions of HCl to other media.

3.3.2 Hydrofluoric Acid

Emission factors for HF process operations are shown in Section 5.4.4. Emissions of HF are suppressed to a great extent by the condensing, scrubbing, and absorption equipment used in the recovery and purification of the hydrofluoric and hexafluorosilicic acid products. Particulate matter in the gas stream is controlled by a dust separator near the outlet of the kiln and is recycled to the kiln for further processing. The precondenser removes water vapour and sulfuric acid mist, and the condensers, acid scrubber, and water scrubbers remove all but small amounts of HF, SiF_4, SO_2, and CO_2 from the tail-gas. A caustic scrubber is employed to further reduce the levels of these pollutants in the tail-gas.

Particulate matter (PM_{10}) is emitted during handling and drying of the fluorspar. Emissions are controlled by bag filters at the spar silos and drying kilns. PM_{10} emissions from spar handling and storage are controlled with flexible coverings and chemical additives.

Hydrogen fluoride emissions are minimised by maintaining a slight negative pressure in the kiln during normal operations. A stand-by caustic scrubber, or a bypass to the tail caustic scrubber, are used to control HF emissions from the kiln.

3.3.3 Nitric Acid

Emissions from nitric acid manufacture consist primarily of NO, NO_2 (which accounts for visible emissions), trace amounts of HNO_3 mist, and ammonia (NH_3). By far, the major source of nitrogen oxides (NO_x) is the tail-gas from the acid absorption tower. In general, the quantity of NO_x emissions is directly related to the kinetics of the nitric acid formation reaction and absorption tower design. NO_x emissions can increase when there is

- insufficient air supply to the oxidiser and absorber,
- low pressure, especially in the absorber,
- high temperatures in the cooler-condenser and absorber,
- production of an excessively high-strength product acid,
- operation at high throughput rates, and
- faulty equipment such as compressors or pumps that lead to lower pressures and leaks, and decrease plant efficiency.

The two most common techniques used to control absorption tower tail-gas emissions are extended absorption and catalytic reduction. Extended absorption reduces NO_x emissions by increasing the efficiency of the existing process absorption tower or incorporating an additional absorption tower. Efficiency is improved by increasing the number of absorber trays, operating the absorber at higher pressures, or cooling the weak acid liquid in the absorber. The existing tower can also be replaced with a single tower of a larger diameter and/or additional trays.

In the catalytic reduction process (often termed catalytic oxidation or incineration), tail gases from the absorption tower are heated to ignition temperature, mixed with fuel (natural gas, hydrogen, propane, butane, naphtha, carbon monoxide, or ammonia) and passed over a catalyst bed. In the presence of the catalyst the fuels are oxidised, and the NO_x are reduced to N_2. The extent of reduction of NO_2 and NO to N_2 is a function of plant design, fuel type, operating temperature and pressure, space velocity through the reduction catalytic reactor, type of catalyst, and reactant concentration. Catalytic reduction can be used in conjunction with other NO_x emission controls. Other advantages include the capability to operate at any pressure and the option of heat recovery to provide energy for process compression as well as extra steam. Catalytic reduction can achieve greater NO_x reduction than extended absorption.

Two (seldom-used) alternative control devices for absorber tail-gas are molecular sieves and wet scrubbers. In the molecular sieve adsorption technique, tail-gas is contacted with an active molecular sieve that catalytically oxidises NO to NO_2 and selectively adsorbs the NO_2. The NO_2 is then thermally stripped from the molecular sieve and returned to the absorber. Molecular sieve adsorption has successfully controlled NO_x emissions in existing plants. However, many new plants do not install this method of control. Its implementation incurs high capital and energy costs. Molecular sieve adsorption is a cyclic system, whereas most new nitric acid plants are continuous systems. Sieve bed fouling can also cause problems.

Wet scrubbers use an aqueous solution of alkali hydroxides or carbonates, ammonia, urea, potassium permanganate, or caustic chemicals to *scrub* NO_x from the absorber tail-gas. The NO and NO_2 are absorbed and recovered as nitrate or nitrate salts. When caustic chemicals are used, the wet scrubber is referred to as a caustic scrubber. Some of the caustic chemicals used are solutions of sodium hydroxide, sodium carbonate, or other strong bases that will absorb NO_x in the form of nitrate or nitrate salts. Although caustic scrubbing can be an effective control device, it is often not used due to its associated high costs and the necessity to treat its spent scrubbing solution.

Comparatively small amounts of nitrogen oxides are also lost from acid concentrating plants. These losses, mostly NO_2, are from the condenser system, but the emissions are small enough to be controlled easily by inexpensive absorbers.

Acid mist emissions do not occur from the tail-gas of a properly operated plant. The small amounts, which may be present in the absorber exit gas streams are removed by a separator, or collector prior to entering the catalytic reduction unit or expander.

The acid production system and storage tanks are the only significant sources of visible emissions at most nitric acid plants. Emissions from acid storage tanks may occur during tank filling.

Nitrogen oxide emission factors shown in Section 5.4.5 vary considerably with the type of control employed and the process conditions. For comparison purposes the US New Source Performance Standard on nitrogen emissions expressed as NO_2 for both new and modified plants is 1.5 kg of NO_2 emitted per tonne of 100 percent nitric acid produced.

3.3.4 Phosphoric Acid

Emission factors for controlled and uncontrolled wet phosphoric acid and controlled thermal phosphoric acid production are shown in Section 5.4.6 of this Manual.

Thermal Process

Major emissions from wet process acid production include; gaseous fluorides, mostly silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF). Phosphate rock contains 3.5-to-4 percent fluorine. In general, part of the fluorine from the rock is precipitated out with gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporised in the reactor or evaporator. The relative quantities of fluorides in the filter acid and gypsum depend on the type of rock and the operating conditions. Final disposition of the volatilised fluorine compounds depends on the design and operation of the plant.

Scrubbers may be used to control fluorine emissions. Scrubbing systems used in phosphoric acid plants include venturi, wet cyclonic, and semi-cross-flow scrubbers. The leachate portion of the fluoride may be deposited in settling ponds as insoluble fluorides (eg. calcium fluoride).

The reactor in which phosphate rock is reacted with sulfuric acid is the main source of emissions. Fluoride emissions accompany the air used to cool the reactor slurry. Vacuum flash cooling has replaced the air cooling method to a large extent, because its closed system minimises emissions.

Acid concentration by evaporation is another source of fluoride emissions. Approximately 20 to 40 percent of the fluorine originally present in the rock vaporises in this operation.

Particulate emissions occurring from phosphate rock handling are discussed in the EET Manual for *Mining of Non-Metallic Minerals.*

Wet Process

The major source of emissions from the thermal process is H_3PO_4 mist contained in the gas stream from the hydrator. The particle size of the acid mist ranges from 1.4 to 2.6 µm. It is not uncommon for as much as half of the total P_2O_5 to be present as liquid phosphoric acid particles suspended in the gas stream. Efficient plants are economically motivated to control this potential loss with control equipment. Control equipment commonly used in thermal process phosphoric acid plants includes venturi scrubbers, cyclonic separators with wire mesh mist eliminators, fibre mist eliminators, high-energy wire mesh contactors, and electrostatic precipitators.

3.3.5 Sulfuric Acid

Sulfur Dioxide

Nearly all sulfur dioxide emissions from sulfuric acid plants are found in the exit stack gases. Extensive testing has shown that the mass of these SO_2 emissions is an inverse function of the sulfur conversion efficiency (SO_2 oxidised to SO_3). This conversion is always incomplete, and is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentrations of the reactants - sulfur and oxygen. For example, if the inlet SO_2 concentration to the converter was 9 percent by volume (a representative value), and the conversion temperature was 430°C, the conversion efficiency would be 98 percent. The uncontrolled emission factor for SO_2 would then be 13 kg per tonne of 100 percent sulfuric acid produced. Of course, the ongoing improvements in catalyst technology would also need to be factored into the control efficiency calculation.

Dual absorption, as described above, has generally been accepted as the best available technology. There are no by-products or waste scrubbing materials created, only additional sulfuric acid. Conversion efficiencies of 99.7 percent and higher are achievable, whereas most single absorption plants have SO_2 conversion efficiencies ranging only from 95 to 98 percent. Furthermore, dual absorption permits higher converter inlet sulfur dioxide concentrations than are used in single absorption plants, because the final conversion stages effectively remove any residual sulfur dioxide from the interpass absorber.

In addition to exit gases, small quantities of sulfur oxides are emitted from storage tank vents and vehicle tankers vents during the loading operations, from sulfuric acid concentrators, and through leaks in the process equipment. Section 5.1 provides detail on the emission estimation techniques available for calculating these fugitive losses.

Acid Mist

Nearly all the acid mist emitted from sulfuric acid manufacturing can be traced to the absorber exit gases. Acid mist is created when sulfur trioxide combines with water vapour at a temperature below the dew point of sulfur trioxide. Once formed within the process system, this mist is so stable that only a small quantity can be removed in the absorber.

In general, the quantity and particle size distribution of acid mist is dependent on the type of sulfur feedstock used, the strength of acid produced, and the conditions within the absorber. Because it contains virtually no water vapour, bright elemental sulfur produces little acid mist when burned. However, the hydrocarbon impurities in other feedstocks (dark sulfur, spent acid, and hydrogen sulfide) oxidise to water vapour during combustion. The water vapour, in turn, combines with sulfur trioxide as the gas cools in the system.

The strength of acid produced, whether oleum or 99 percent sulfuric acid, also affects mist emissions. Oleum plants produce greater quantities of finer, more stable mist. For example, uncontrolled mist emissions from oleum plants burning spent acid range from 0.5 to 5 kg/tonne, while those from 98 percent acid plants burning elemental sulfur range from 0.2 to 2 kg/tonne. Furthermore, 85 to 95 weight percent of the mist particles from oleum plants are less than 2µm in diameter, compared with only 30 weight percent that are less than 2µm in diameter from 98 percent acid plants.

The operating temperature of the absorption column directly affects sulfur trioxide absorption and, accordingly, the quality of acid mist formed after exit gases leave the stack. The optimum absorber operating temperature depends on the strength of the acid produced, throughput rates, inlet sulfur trioxide concentrations, and other variables particular to each individual plant. Finally, it should be emphasised that the percentage conversion of sulfur trioxide has no direct effect on acid mist emissions. For NPI reporting, sulfur trioxide emissions should be reported as sulfur dioxide equivalents using the molecular weight ratio to achieve the conversion.

3.4 Sulfur Recovery

Section 5.4.8 presents emission factors and recovery efficiencies for modified Claus sulfur recovery plants. Factors are expressed in units of kilograms of pollutant emitted per tonne of sulfur produced. Emissions from the Claus process are directly related to the recovery efficiency. Higher recovery efficiencies mean less sulfur emitted in the tail-gas. Older plants, or very small Claus plants producing less than 20 tonnes per day of sulfur without tail-gas cleanup, have varying sulfur efficiencies. The efficiency depends upon several factors, including the number of catalytic stages, the concentrations of H_2S and contaminants in the feedstream, stoichiometric balance of gaseous components of the inlet stream, operating temperature, and catalyst maintenance.

A two-bed catalytic Claus plant can achieve 94-to-96 percent efficiency. Recoveries range from 96 to 97.5 percent for a three-bed catalytic plant and range from 97 to 98.5 percent for a four-bed catalytic plant. At normal operating temperatures and pressures, the Claus reaction is thermodynamically limited to 97-to-98 percent recovery. Tail-gas from the Claus plant still contains 0.8-to-1.5 percent sulfur compounds.

Emissions from the Claus process may be reduced by extending the Claus reaction into a lower temperature liquid phase, including the BSR/selectox, Sulfreen, Cold Bed Absorption, Maxisulf, and IFP-1 processes. These processes take advantage of the enhanced Claus conversion at cooler temperatures in the catalytic stages. All of these processes give higher overall sulfur recoveries of 98 to 99 percent when following downstream of a typical 2 or 3-stage Claus sulfur recovery unit, and therefore reduce sulfur emissions.

Sulfur emissions can also be reduced by adding a scrubber at the tail-end of the plant. There are essentially two generic types of tail-gas scrubbing processes: oxidation tail-gas scrubbers and reduction tail-gas scrubbers. The first scrubbing process is used to scrub SO_2 from incinerated tail-gas and recycle the concentrated SO_2 stream back to the Claus process for conversion to elemental sulfur. There are at least three oxidation-scrubbing processes: the Wellman-Lord, Stauffer Aquaclaus, and IFP-2.

The Wellman-Lord process uses a wet generative process to reduce stack gas sulfur dioxide concentration to less than 250 ppmv and can achieve approximately 99.9 percent sulfur recovery. Claus plant tail-gas is incinerated and all sulfur species are oxidised to form SO_2 in the Wellman-Lord process. Gases are then cooled and quenched to remove excess water and to reduce gas temperature to absorber conditions. The rich SO_2 gas is then reacted with a solution of sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$) to form the bisulfite:

Equation 8

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$$

The offgas is reheated and vented to the atmosphere. The resulting bisulfite solution is boiled in an evaporator-crystalliser, where it decomposes to SO_2 and water vapour with sodium sulfite precipitated as a result. Equation 9 shows this reaction:

Equation 9

$$2NaHSO_3 \rightarrow Na_2SO_3\downarrow + H_2O + SO_2\uparrow$$

Sulfite crystals are separated and redissolved for reuse as lean solution in the absorber. The wet SO_2 gas is directed to a partial condenser where most of the water is condensed and reused to dissolve sulfite crystals. The enriched SO_2 stream is then recycled back to the Claus plant for conversion to elemental sulfur.

In the second type of scrubbing process, sulfur in the tail-gas is converted to H_2S by hydrogenation in a reduction step. After hydrogenation, the tail-gas is cooled and water is removed. The cooled tail-gas is then sent to the scrubber for H_2S removal prior to venting. There are at least four reduction scrubbing processes developed for tail-gas sulfur removal: Beavon, Beavon MDEA, SCOT, and ARCO. In the Beavon process, H_2S is converted to sulfur outside the Claus unit using a H_2S-to-sulfur process (the Strefford process). The other three processes utilise conventional amine scrubbing and regeneration to remove H_2S and recycle back as Claus feed.

Emissions from the Claus process may also be reduced by incinerating sulfur-containing tail-gases to form sulfur dioxide. To properly remove the sulfur, incinerators must operate at a temperature of 650°C or higher if all the H_2S is to be combusted. Proper air-to-fuel ratios are needed to eliminate pluming from the incinerator stack. The stack should be equipped with analysers to monitor the SO_2 level and in these instances, reporting emissions of SO_2 and H_2S should be a straightforward process.

4. Emission Estimation Techniques: Acceptable Reliability and Uncertainty

There are several emission estimation techniques (EETs) available for calculating emissions from inorganic chemical manufacturing activities. The techniques ultimately chosen are dependent on available data, available resources, the degree of accuracy sought by the facility in undertaking the estimate, and the source of emissions being quantified.

Although the NPI does not favour the use of one EET over other techniques, this section attempts to evaluate the available EETs with regards to accuracy. In general, site-specific data that is representative of normal operating conditions at a particular facility is preferred over data obtained from other similar sites, or industry-averaged data such as the emission factors presented in Section 5.4 of this Manual.

This section discusses the methods available for calculating emissions from inorganic chemical manufacturing facilities and identifies the different methods of calculation available on a pollutant basis. These EETs are listed in no particular order and the reader should not infer a preference based on the order they are listed in this section.

In general, there are five types of EETs for calculating emissions of NPI-listed substances in the inorganic chemistry industry:

- Continuous Emission Monitoring System (CEMS);
- Engineering or Source-Specific Equations;
- Sampling or Direct Measurement;
- Mass Balance; and
- Emission Factors.

Select the EET, (or mix of EETs), that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EETs, your data will be displayed on the NPI database as being of ‘acceptable reliability’. Similarly, if your relevant environmental authority has approved the use of EETs that are not outlined in this handbook, your data will also be displayed as being of ‘acceptable reliability’.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this handbook does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site-specific emission factors, you may use these if approved by your relevant environmental authority.

You should note that the EETs presented in this manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie. the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

The **usage*** of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for Total Volatile Organic Compounds**,** VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

[a]Usage is defined as meaning the handling, manufacture, import, processing, coincidental production or other uses of the substances.

4.1 Continuous Emission Monitoring System (CEMS)

A CEMS provides a continuous record of emissions over an extended and uninterrupted period of time. Various principles are employed to measure the concentration of pollutants in the gas stream; they are usually based on photometric measurements. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric stack gas flow rate. The accuracy of this technique may be problematic at low pollutant concentrations.

Instrument calibration drift can be problematic for CEMS and uncaptured data can create long-term incomplete data sets. However, it is misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment and the corresponding emissions data.

4.2 Engineering or Source-Specific Equations

Theoretical and complex equations or *models* can be used for estimating emissions from inorganic chemical manufacturing processes. Emission estimation equations are available for the following types of emissions found at inorganic chemical manufacturing facilities:

- surface evaporation during chemical mixing and blending operations;
- tank and container filling;
- fugitive emissions;
- material storage;
- spills; and
- wastewater storage.

Inputs for theoretical equations generally fall into the following categories:

- chemical/physical properties of the material involved, such as vapour pressure and vapour molecular weight;
- operating data, such as the amount of material processed and operating hours; and
- physical characteristics and properties of the source, such as tank colour and diameter.

Use of engineering equations to estimate emissions from inorganic chemical manufacturing activities is a more complex and time-consuming process than the use of emission factors. Engineering equations require more detailed inputs than the use of emission factors but they do provide an emission estimate that is based on facility-specific conditions.

Engineering equations are suitable for estimating emissions from several inorganic chemical manufacturing processes. For example, for any process involving a transfer of a chemical species from the liquid phase to the vapour phase, the saturation or equilibrium vapour pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that particular process. This is a conservative approach because of the assumption that the total airflow is saturated. An alternative method based on mass transfer kinetics does not assume airflow saturation and results in a lower emission rate estimate than would be obtained assuming saturation.

However, because both these approaches are based on theoretical equations and not measured values, they are potentially the least accurate of the emission estimation techniques discussed in this Manual.

4.3 Sampling or Direct Measurement

Sampling can be performed to quantify point source or fugitive emissions. In point source sampling, effluent gas samples are usually collected from the stack using probes inserted through a port or stack wall. Pollutants in the gas are collected in or on various media that are subsequently sent to a laboratory for analysis. Pollutant concentrations are obtained by dividing the amount of pollutant collected during the test by the volume of gas sampled. Emission rates are then determined by multiplying the pollutant concentration by the volumetric stack gas flow rate. Because there are many steps in the stack sampling procedures where errors can occur, only experienced stack testers should perform the tasks.

Workplace health and safety data (concentrations) can be used in conjunction with exhaust system flow rates to estimate fugitive emissions from a room, floor, or building at a chemical manufacturing plant. Direct-reading instruments that may be used to obtain an instantaneous reading of vapour concentrations include photoionisation detectors, portable infrared spectrophotometers, and portable gas chromatographs. Emissions of volatile organic compounds (VOCs) and inorganic compounds, such as acid mists, can also be measured by performing a gravimetric analysis.

Use of stack and/or workplace health and safety sampling data can be a relatively accurate method of estimating air emissions from inorganic manufacturing facilities. However, collection and analysis of air samples from facilities can be very expensive and especially complicated where a variety of NPI-listed substances are emitted and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation and may provide only one example of the facility's emissions.

To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover production of all or representative formulations.

4.4 Mass Balance

The mass balance approach to emissions estimation considers the facility as a *black box* where the total quantity of NPI-listed substances in the raw materials consumed versus amounts of listed substances leaving the facility as product, emissions, and waste is compared and analysed.

Calculating emissions from an inorganic chemical manufacturer using a mass balance appears to be a straightforward approach to emission estimations. However, for the calculations to be relatively accurate, facilities need to consistently track material usage and emissions and waste generation, as inaccuracies associated with individual material tracking or other activities inherent in each material handling stage can often result in large deviations of total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only ± 5 percent in any one step of the operation can significantly skew emission estimations.

When selecting a mass balance for emission estimations from inorganic chemical manufacturing activities, the uncertainty in the extent of the chemical reactions occurring should be recognised. For example, while hydrochloric acid is a widely used chemical in this industry, it is also readily formed from the use and presence of other substances such as hexafluoroethane, sulfur hexafluoride, and nitrogen trifluoride.

Other potential sources of error in the mass balance estimation technique include:

- The delivery of bulk raw materials to a chemical manufacturer is often tracked by volume and not by weight. Since density varies with temperature, the actual mass per unit volume of materials delivered in the summer may be less than that received in the winter months.

- Raw materials received by manufacturers may potentially be used in hundreds of finished products. In order to complete the mass balance, it is crucial that the exact quantity and characterisation of each material shipped off-site that contains NPI-listed substances is known. This involves precise analysis of the concentration of the listed pollutant of interest in each product, waste, or recycling stream.

- Many inorganic chemical manufacturing processes require the manual addition of raw materials. Sometimes these additions are conducted by contractors and are not accurately measured or recorded or the data is unavailable to the person completing the NPI reporting.

4.5 Emission Factors

Emission factors are available for a number of inorganic chemical manufacturing sources and processes and are based on the results of source tests performed at an individual facility or at one or more facilities within the industry. Basically, an emission factor is the pollutant emission rate relative to the level of source activity. The user should recognise that, in most cases, emission factors adopted for the NPI are averages of available industry-wide data, usually US or European and seldom Australian, with varying degrees of quality. Emission factors are, however, an acceptable method for estimating emissions from all industry sectors and source categories for the NPI where estimations of emissions are required to quantify medium to long-term emission trends.

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to emission factors for all industries and sectors and therefore, to all industry Manuals and Handbooks. EFRs are based on rating systems developed by the United States Environmental Protection Agency (USEPA) and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in Section 6.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

When using emission factors, the reader should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment or process selected in applying the factor, and the target equipment or process from which the factor was derived.

The EFR system is as follows:

A - Excellent
B - Above Average
C - Average
D - Below Average
E - Poor
U - Unrated

Australian inorganic chemical manufacturing facilities may develop their own in-house emission factors. Development of an accurate emission factor would require detailed knowledge of the process conditions and chemical usage rates during the time period for which emissions are known. Such emission factors developed from measurements for a specific unit or process may then be used to estimate emissions at other similar units or processes or even at different but similar facilities. You are required to have the emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

5. Estimating Emissions

This section presents equations and examples of calculations for estimating emissions of total VOCs, speciated organics, and speciated inorganic substances from inorganic chemical manufacturing processes.

Table 2 lists the variables and symbols used throughout Section 5.0 and indicates the level of information required in estimating emissions of NPI-listed substances from inorganic chemical manufacture using the emission estimation techniques illustrated.

Table 2 - List of Variables and Symbols

Variable	Symbol	Units
Annual emissions of pollutant i	$E_{kpy,i}$	kg/yr
Hourly emissions of pollutant i	E_i	kg/hr
Material entering the process	Q_{in}	L/hr
Material leaving the process (as an emission, transfer, or in product)	Q_{out}	L/hr
Concentration of pollutant i	C_i	ppmv, kg/L, mg/L, %
Average concentration of pollutant i	$C_{a,i}$	ppmv
Molecular weight	MW	kg/kg-mole
Molecular weight of pollutant i	MW_i	kg/kg-mole
Partial pressure of species i	P_i	kPa
Liquid mole fraction of species i	m_i	mole/mole
True vapour pressure of species i	VP_i	kPa
Henry's Law constant for species i	H_i	kPa
Liquid mass fraction of species i	z_i	kg/kg
Vapour mole fraction of species i	y_i	mole/mole
Vapour mass fraction of species i	x_i	kg/kg
Wet volumetric flow rate of stack gas	Q_w	wet cubic metres per second (m^3/s)
Dry volumetric flow rate of stack gas	Q_d	dry cubic metres per second (m^3/s)
Molar volume @ STP (standard temperature and pressure)	V	22.4 m^3/kg-mole @ 0°C and 101.3 kPa (1 atm)
Operating hours	OpHrs	hr/yr
Uncontrolled emission factor of pollutant i	EF_i	kg/t
Activity rate	A	t/hr
Evaporation rate of pollutant i	W_i	kg/yr
Gas-phase mass transfer coefficient for VOC species i	K_i	m/sec
Surface area	area	m^2
Vapour pressure of pollutant i	$P_{vap,i}$	kPa
Universal gas constant	R	kPa * m^3 /(kgmol) * K
Moisture content	$moist_R$	%
Temperature	T	K
VOC content of material	C_{VOC}	kg/L
Density of material	ρ_m	kg/L

Variable	Symbol	Units
Percentage weight of pollutant i	$wt\%_i$	%
Duration of spill	HR	hr/event
Event duration time	H	hr/event
Wind speed	U	km/hr
Hourly volume of wastewater	V_H	L/hr
Saturation factor	S	dimensionless
Vapour pressure	P	kPa
Volume of material loaded	V_m	100L/yr
Diffusion co-efficient for species i in air	D_i	ft^2/sec
Number of events per year	B	events/yr
Emission rate of pollutant i	ER_i	kg/yr/source
Applicable emission factor for equipment type	EF	kg/hr/source
Number of pieces of applicable equipment type in the *Stream*	N	dimensionless
Concentration of PM or gram loading	C_{PM}	g/m^3
Filter catch	C_f	grams
Metered volume of sample at STP	$V_{m,STP}$	m^3
Hourly emissions of PM	E_{PM}	kg/hr
Amount of pollutant i used	AU_i	kg/yr
Amount of pollutant i incorporated into product in the reporting year	AI_i	kg/yr
Amount of pollutant i treated on-site or transferred off-site	AT_i	kg/yr
Amount of pollutant i in sludge	$AS_{kpy,i}$	kg/yr
Process losses in pollutant i	PL_i	kg/yr
Losses from wastewater of pollutant i	WL_i	kg/yr
Overall control efficiency of pollutant i	CE_i	%

Source: Queensland Department of Environment and Heritage, 1998.

5.1 Using Engineering or Source-Specific Equations

5.1.1 Emissions from Material Loading Operations

Emissions of VOCs resulting from the addition of organic solvents to vessels or storage tanks may be calculated using a loading loss equation. The equation, shown below as Equation 10, can be applied to any tank or vessel loading or unloading operation. This equation can only be used for organic materials and is not suitable for use in estimating emissions from adding ammonia, mineral acids, or other inorganic compounds to process or storage vessels.

Equation 10

$$E_{kpy,VOC} = 0.1203 * (S * P * M * V_m) / T$$

where:

$E_{kpy,VOC}$ = total VOC loading emissions, kg/yr
S = saturation factor (dimensionless); obtained from Table 3.
P = vapour pressure of material loaded at temperature T, kPa
M = vapour molecular weight, kg/kg-mole
V_m = volume of material loaded, 1 000 L/yr
T = temperature, K
0.1203 = constant, {(kg-mole * K) / (kPa * 1000L)}

Calculation of VOC emissions using Equation 10 is based on the following assumptions:

- the vapours displaced from the process vessel are identical to the vapours from the materials being loaded;
- the volume of the vapour being displaced is equal to the volume of material being loaded into the vessel;
- the vapour within the headspace of the vessel is saturated at room temperature and remains at room temperature during loading; and
- all solvent additions are coincident at a constant temperature (in reality, solvent are generally added in stages).

Table 3 - Saturation (S) Factors for Calculating Organic Liquid Loading Emissions

Transport Carrier	Mode of Operation	S Factor
Road and Rail Tankers	Submerged loading of a clean cargo tank	0.50
	Submerged loading: normal service	0.60
	Submerged loading: vapour balance service	1.00
	Splash loading of a clean cargo tanker	1.45
	Splash loading : normal service	1.45
	Splash loading: vapour balance service	1.0
Marine Vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

Source: USEPA *AP-42 Section 5.2 Transportation & Marketing of Petroleum,* 1995.

If a mixture of NPI-listed organics is used in a solution, the vapour pressure (P) will need to be calculated using Equation 11.

Equation 11

$$P = \Sigma P_i$$

where:

P = vapour pressure of material loaded, kPa
P_i = partial pressure of VOC species i, kPa

P_i may be calculated using Raoult's Law (for ideal solutions) or Henry's Law constants (when gases are dissolved at low concentrations in water). Raoult's Law is given in Equation 12.

Equation 12

$$P_i = m_i * VP_i$$

where:

P_i = partial vapour pressure of VOC species i, kPa
m_i = liquid mole fraction of VOC species i, mole/mole
VP_i = true vapour pressure of VOC species i, kPa

P_i may be calculated using Henry's Law constants and Equation 13.

Equation 13

$$P_i = m_i * H_i$$

where:

P_i = partial vapour pressure of VOC species i, kPa
m_i = liquid mole fraction of VOC species i, mole/mole
H_i = Henry's Law constant for VOC species i, kPa

The liquid mole fraction of VOC species i (m_i) may be calculated if the liquid weight fractions of all species are known using Equation 14.

Equation 14

$$m_i = (z_i / MW_i) / \Sigma (z_i / MW_i)$$

where:

m_i = liquid mole fraction of VOC species i, mole/mole
z_i = liquid mass fraction of VOC species i, kg/kg
MW_i = molecular weight of VOC species i, kg/kg-mole

The vapour molecular weight (M) will also need to be calculated if multiple solvents are used for a single cleaning event and this is shown by Equation (15).

Equation 15

$$M = \Sigma (y_i * MW_i)$$

where:

M = vapour molecular weight, kg/kg-mole
y_i = vapour mole fraction of VOC species i, mole/mole
MW_i = molecular weight of VOC species i, kg/kg-mole

The vapour mole fraction is calculated using Equation 16.

Equation 16

$$y_i = P_i \,/\, P$$

where:

y_i = vapour mole fraction of VOC species i, mole/mole
P_i = partial pressure of VOC species i (calculated using Equation 12 or Equation 13 kPa
P = vapour pressure of the material loaded (calculated using Equation 11)

Speciated VOC emissions are calculated using Equation 17.

Equation 17

$$E_{kpy,i} = E_{kpy,VOC} * x_i$$

where:

$E_{kpy,i}$ = loading emissions of VOC species i, kg/yr
$E_{kpy,VOC}$ = total VOC loading emissions (calculated using Equation 10.) kg/yr
x_i = vapour mass fraction of VOC species i, kg/kg

The vapour mass fraction of VOC species i (x_i) is calculated using Equation 18.

Equation 18

$$x_i = y_i * MW_i \,/\, M$$

where:

x_i = vapour mass fraction of VOC species i, kg/kg
y_i = vapour mole fraction of VOC species i (calculated using Equation 16), mole/mole
MW_i = molecular weight of VOC species i, kg/kg-mole
M = vapour molecular weight (from Equation 15), kg/kg-mole

Example 1 illustrates the use of Equation 10 through to Equation 18.

Example 1 - Calculating Material Loading Emissions

A chemical manufacturer regularly uses an organic process formulation during a manufacturing process. The following data is given:

- the yearly consumption of the formulation (Q) is 600 000 litres;
- the formulation is a 50/50 mixture (by weight) of toluene and *n*-heptane;
- the solvent mixture is splash loaded into the vessel (S = 1.45 from Table 3); and
- the temperature of the solvent is 298 K (25°C).

The following Steps 1 through 8 below calculate emissions.

Step 1: Apply Equation 14 - Calculation of Liquid Mole Fraction (m_i)

Component i	Liquid Mass Fraction, z_i (kg of i/kg of liquid)	Molecular Weight, MW_i (kg of i/kg-mole of i	Liquid Mole Fraction, m_i (mole of i/mole of liquid)
Toluene	0.50	92	$(z_i / MW_i) / \Sigma (z_i / MW_i)$............................. $(0.5/92)/[(0.5/92) + (0.5/100)]$ $= 0.52$
n-Heptane	0.50	100	$(z_i / MW_i) / \Sigma (z_i / MW_i)$............................. $(0.5/100)/[(0.5/92) + (0.5/100)]$ $= 0.48$

Step 2: Apply Equation 12 - Calculation of Partial Vapour Pressure (P_i)

Component i	Liquid Mole Fraction, m_i (mole of i/mole of liquid)	True Vapour Pressure, VP_i (kPa)	Partial Vapour Pressure, P_i (kPa)
Toluene	0.52	4.0	$m_i * VP_i = 0.52 * 4.0$ $= 2.08$
n-Heptane	0.48	6.2	$m_i * VP_i = 0.48 * 6.2$ $= 2.98$

Step 3: Apply Equation 11 - Calculation of Vapour Pressure (P)

$$\begin{aligned} P &= \Sigma P_i \\ &= 2.08 + 2.98 \\ &= 5.06 \text{ kPa} \end{aligned}$$

Step 4: Apply Equation 16 - Calculation of Vapour Mole Fraction (y_i)

Component i	Partial Vapour Pressure, P_i (kPa)	Total Vapour Pressure, P (kPa)	Vapour Mole Fraction, y_i (mole of i/mole of vapour)
Toluene	2.08	5.06	P_i / P = 2.08 / 5.06 = 0.41
n-Heptane	2.98	5.06	P_i / P = 2.98 / 5.06 = 0.59

Step 5: Apply Equation 15 - Calculation of Vapour Molecular Weight (M)

$$\begin{aligned} M &= \Sigma (y_i * MW_i) \\ &= (0.41 * 92) + (0.59 * 100) \\ &= 97 \text{ kg / kg-mole} \end{aligned}$$

Step 6: Apply Equation 18 - Calculation of Vapour Mass Fraction (x_i)

Component i	Vapour Mole Fraction, y_i (mole of i/mole of vapour)	Molecular Weight, MW_i (kg of i/kg-mole of i)	Vapour Molecular Weight, M (kg of vapour /kg mole of vapour	Vapour Mass Fraction, x_i (kg of i/kg of vapour)
Toluene	0.41	92	97	y_i *MW_i / M = 0.41 * 92 / 97 = 0.39
n-Heptane	0.59	100	97	y_i *MW_i / M = 0.59 *100 / 97 = 0.61

Step 7: Apply Equation 10 - Calculate Total VOC Emissions ($E_{kpy,VOC}$)

$$\begin{aligned} E_{kpy,VOC} &= 0.1203 * (S * P * M * V) / T \\ &= 0.1203 * (1.45 * 5.06 * 97 * 600) / 298 \\ &= 172.4 \text{ kg / yr} \end{aligned}$$

Step 8: Apply Equation 17 - Calculate Speciated VOC Emissions ($E_{kpy,i}$)

Component i	VOC Emissions, $E_{kpy,VOC}$ (kg VOCs)	Vapour Mass Fraction, x_i (kg of i/kg of VOCs)	Speciated VOC Emissions, $E_{kpy,i}$ (kg of i/yr)
Toluene	172.4	0.39	$E_{kpy,VOC} * x_i = 172.4 * 0.39$ = 67.2 kg Toluene/yr
n-Heptane	172.4	0.61	$E_{kpy,VOC} * x_i = 172.4 * 0.61$ = 105.2 kg *n*-Heptane/yr

Annual VOC emissions of Toluene and *n*-Heptane are:

$E_{kpy,Toluene}$ = 67.2 kg/yr
$E_{kpy,n\text{-}Heptane}$ = 105.2 kg/yr

5.1.2 Emissions using Mass Transfer Kinetics

An EET based on mass transfer kinetics is shown by Equation 19:

Equation 19

$$W_i = (MW_i * K_i * area * P_{vap,i} * 3600 * OpHrs) / (R * T)$$

where:

W_i = evaporation rate of pollutant i, kg/yr
MW_i = molecular weight of pollutant i, kg/kg-mole
K_i = gas-phase mass transfer coefficient for VOC species i, m/sec $[0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}]/3.2808$
U = wind speed, km/hr
area = surface area, m^2
$P_{vap,i}$ = vapour pressure of pollutant i, kPa
3600 = conversion of 3600 sec/hr
OpHrs= hours of operation each year hr/yr
R = universal gas constant (8.314 kPa * m^3 /(kgmol * K))
T = temperature, K

Example 2 - Using Mass Transfer Kinetics

This example shows how methanol emissions may be estimated using mass transfer kinetics and Equation 19 given the following data:

MW_i = 32 kg/kg-mole
U = 7.24 km/hr
area = 0.6 m^2
$P_{vap,i}$ = 13.16 kPa
3600 = 3600 sec/hr
OpHrs= 1000 hr/yr
T = 296 K
R = 8.314 kPa * m^3 /(kgmol * K)

First, calculate the mass transfer coefficient, K_i:

$K_i = [0.00438 * (0.62138 * U)^{0.78} * (18 / MW_i)^{1/3}] / 3.2808$
$= [0.00438 * (0.62138 * 7.24)^{0.78} * (18 / 32\ \text{kg/kg-mole})^{1/3} / 3.2808$
$= 0.0035\ \text{m/s}$

Then, calculate W_i:

$W_i = (MW_i * K_i * \text{area} * P_{vap,i} * 3600 * OpHrs) / (R * T)$
$= (32\ \text{kg/kg-mole} * 0.0035\ \text{m/sec} * 0.6\ \text{m}^2 * 13.16\ \text{kPa} * 3600\ \text{sec/hr} * 1000\ \text{hr/yr}) / (8.314\ \text{kPa} * \text{m}^3 / (\text{kgmol} * 296\ \text{K})$
$= 1310\ \text{kg/yr}$

5.1.3 Emissions from Spills

A vaporisation equation can be used to estimate the evaporation rate of a liquid chemical spill if the size area of the spill is known or can be estimated. Equation 20 illustrates this.

Equation 20

$$E_i = (MW_i * K_i * \text{area} * P_i * 3\,600 * HR) / R * T$$

where:

E_i = emissions of VOC species i from the spill, kg/event
MW_i = molecular weight of VOC species i, kg/kg-mole
K_i = gas-phase mass transfer coefficient for VOC species i, m/sec
area = surface area of spill, m^2
P_i = partial pressure of VOC species i (if a pure chemical is spilled) or the partial pressure of chemical i (if a mixture of VOCs is spilled) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 12 or Equation 13
3 600 = conversion factor, sec/hr

HR = duration of spill, hr / event
R = universal gas constant at 101.3 kPa of pressure,
T = temperature of the liquid spilled, K

The gas-phase mass transfer coefficient (K_i) may be calculated using Equation 21.

Equation 21

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (D_i / 3.1 * 10^{-4})^{2/3}) / 3.2808$$

where:

K_i = gas-phase mass transfer coefficient for VOC species i, m / sec
U = wind speed, km / hr
D_i = diffusion coefficient for VOC species i in air, ft^2 / sec

Diffusion coefficients (D_i) can be found in chemical handbooks and are usually expressed in units of square centimetres per second (cm^2 / sec). If a diffusion coefficient is not available for a particular NPI-listed chemical, the gas-phase mass transfer coefficient (K_i) may be estimated using Equation 22.

Equation 22

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (18 / MW_i)^{1/3}) / 3.2808$$

where:

K_i = gas-phase mass transfer coefficient for VOC species i, m / sec
U = wind speed, km / hr
MW_i = molecular weight of VOC species i, kg / kg-mole

Example 3 illustrates the use of Equation 20 through to Equation 22. Emissions are calculated by following Steps 1 and 2.

Example 3 - Calculating Spill Emissions

Methyl ethyl ketone (MEK) is spilled onto the ground outside a building. The following data is given:

- the spill is not detected for 1 hour; it takes an additional 2 hours to recover the remaining MEK; the duration of the spill (hr), therefore, is 3 hours;
- the average wind speed (U) is 33.6 km / hr (21 miles / hr);
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the spill (area) is 11 m^2;
- the molecular weight of MEK (MW_i) is 72 kg / kg-mole;
- the partial pressure of MEK (P_i) at 298 K (25°C) is approximately 13.31 kPa;

Step 1: Using Equation 22, Calculate the Gas-Phase Mass Transfer .... Coefficient (K_i)

K_i = $(0.00438 * (0.62138 * U)^{0.78} * (18 / MW_i)^{1/3}) / 3.2808$
= $(0.00438 * (0.62138 * 33.6)^{0.78} * (18 / 72)^{1/3}) / 3.2808$
= 0.0093 m / sec

Step 2: Using Equation 20, Calculate Emissions (E_i)

E_i = $(MW_i * K_i * area * P_i * 3\,600 * HR) / R * T$
= $(72 * 0.0093 * 11 * 13.31 * 3\,600 * 3) / (8.314 * 298)$
= 427.35 kg MEK / spill

5.1.4 Emissions from Surface Evaporation

Emissions from surface evaporation during organic chemical mixing operations can be estimated using Equation 23.

Equation 23

$E_{kpy,i}$ = $[(MW_i * K_i * area * P_i * 3\,600 * H) / R * T] * B$

where:

$E_{kpy,i}$ = emissions of VOC species i, kg / yr
MW_i = molecular weight of VOC species i, kg / kg-mole
K_i = gas-phase mass transfer coefficient for VOC species i, m / sec
area = surface area of VOC species i, m^2
P_i = vapour pressure of VOC i (if a pure chemical is used) or the partial pressure of chemical i (if a mixture of VOCs is used) at temperature T, kPa; the partial pressure of VOC species i (P_i) is be calculated using Equation 12 or Equation 13
3 600 = conversion factor, sec / hr
H = event duration time, hr / event
R = universal gas constant at 101.3 kPa of pressure,
T = temperature of the liquid, K
B = number of events per year, event / yr

Equation 21 or Equation 22 can be used to estimate K_i. Total VOC emissions would equal the sum of all VOC species emissions.

Example 4 shows how to use Equation 23. Emissions are calculated by following Steps 1 and 2.

Example 4 - Calculating Surface Evaporation Emissions

This example estimates emissions from an open vessel due to surface evaporation. The following data is given:

- event time (H) is 4 hours;
- the number of events per year (B) is 550;
- the average wind speed (U) is 1.28 km / hr (0.8 miles / hr);
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the vessel (area) is 8.75 m^2;
- the molecular weight of toluene (MW_i) is 92 kg / kg-mole; and
- the partial vapour pressure of toluene (P_i) at 298 K (25°C) is approximately 4 kPa

Step 1: Using Equation 22, Calculate the Gas-Phase Mass Transfer .... Coefficient (K_i)

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (18 \ / MW_i \ )^{1/3}) / 3.2808$$
$$= (0.00438 * (0.62138 * 1.28)^{0.78} * (18 \ / 92)^{1/3}) / 3.2808$$
$$= 6.66 * 10^{-4} \text{ m / sec}$$

Step 2: Using Equation 23, Calculate Emissions ($E_{kpy,i}$)

$$E_{kpy,i} = [(MW_i * K_i * \text{area} * P_i * 3\,600 * H) \ / \ R * T] * B$$
$$= [(92 * 6.66 * 10^{-4} * 8.75 * 4 * 3\,600 * 4) \ / \ 8.314 * 298] * 550$$
$$= 6\,855 \text{ kg toluene / yr}$$

5.1.5 Estimating Fugitive Emissions

Many of the engineering equations presented in this section are to be applied to estimate emissions of organic compounds. Other than using emission factors or applying the mass balance technique for estimating emissions, there is little information currently available for estimating fugitive emissions of inorganic compounds. However, in inorganic chemical manufacturing, it may be necessary to estimate emissions of inorganic compounds for NPI-reporting purposes. This is particularly the case for hydrochloric, sulfuric, and other mineral acids, ammonia, and chlorine in the gas / vapour phase.

Emission estimates of inorganic compounds can be obtained for inorganic chemical manufacturing processes by the following methods (in no specific order of preference):

- Develop correlations specific to particular chemical manufacturing processes;
- Use a portable monitoring instrument to obtain actual concentrations of the inorganic compounds and then apply the screening values obtained (see paragraph below) into the applicable correlation equation shown in Table 4 and Equation 26; or

- Use the emission factors from Table 5.

Screening data is collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value (SV) is a measure of the concentration of leaking compounds in the ambient air that provides an indication of the leak rate from an equipment piece, and is measured in units of parts per million by volume (ppmv).

Also, surrogate measurements can be used to estimate emissions of inorganic compounds. For example, potassium iodide (KI), or a similar salt solution, is an indicator for equipment leaks from acid (hydrochloric acid [HCl], hydrofluoric acid [HF]) process lines at chemical plants. Equation 24 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 4. An example of this estimation technique is given at Example 5.

Equation 24

$$E_{kpy,i} = ER_i * C_i / 100 * OpHrs$$

where:

$E_{kpy,i}$ = mass emissions of pollutant i calculated from either the screening values, correlation equation, or emission factors, kg/source

ER_i = emission rate, kg/hr/source

C_i = concentration of inorganic pollutant i in the equipment, %

OpHrs = operating hours, hr/yr

Table 4 - Correlation Equations, Default Zero Emission Rates, and Pegged[c] Emission Rates for Estimating Fugitive Emissions

Equipment Type	Default Zero Emission Rate (kg/hr/source)	Pegged Emission Rates (kg/hr per source)		Correlation Equation (kg/hr per source) [a]
		10 000 ppmv	100 000 ppmv	
Gas valves	$6.6 * 10^{-7}$	0.024	0.11	$LR = 1.87 * 10^{-6} * (SV)^{0.873}$
Light liquid valves	$4.9 * 10^{-7}$	0.036	0.15	$LR = 6.41 * 10^{-6} * (SV)^{0.797}$
Light liquid pumps[b]	$7.5 * 10^{-6}$	0.14	0.62	$LR = 1.90 * 10^{-5} * (SV)^{0.824}$
Connectors	$6.1 * 10^{-7}$	0.044	0.22	$LR = 3.05 * 10^{-6} * (SV)^{0.885}$

Source: Eastern Research Group, 1996.

LR = leak rate.

[a] SV is the screening value (ppmv) measured by the monitoring device. To estimate emissions, use the default zero emission rates only when the screening value (adjusted for background) equals 0.0 ppmv; otherwise use the correlation equations. If the monitoring device registers a pegged value, use the appropriate pegged emission rate.

[b] The emission estimates for light liquid pump seals can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

[c] When the monitoring device reads a pegged value; for example 10 ppmv for a gas valve, the pegged emission rate of 0.024 kg/hr per source would be used rather than determining the emission rate using a correlation equation, or a default zero emission rate.

Example 5 - Calculating Fugitive Chemical Leaks

A chemical plant operates a light-liquid pump on a 80 percent hydrochloric acid solution storage tank. The pump is run for 8760 hours during the year.

For a Screening Value of Zero ppmv

OpHrs = 8760 hr/yr
SV (screening value) = 0 ppmv
Default-zero emission rate = $7.5 * 10^{-6}$ kg/hr/source

$$\begin{aligned} \text{HCl emissions} &= ER_i * C_i / 100 * \text{OpHrs} \\ &= 7.5 * 10^{-6} \text{ kg/hr/source} * (80/100) * 8760 \text{ hr/yr} \\ &= 5.26 * 10^{-2} \text{ kg/yr/source} \end{aligned}$$

For a Screening Value of 20 ppmv

OpHrs = 8760 hr/yr
SV (screening value) = 20 ppmv

$$\begin{aligned} \text{HCl emissions (kg/hr)} &= 1.90 * 10^{-5} (SV)^{0.824} \\ &= 1.90 * 10^{-5} (20)^{0.824} \\ &= 2.24 * 10^{-4} \text{ kg/hr} \end{aligned}$$

$$\begin{aligned} \text{HCl emissions (kg/yr)} &= 2.24 * 10^{-4} \text{ kg/hr} * 8760 \text{ hr/yr} * (80/100) \\ &= 1.57 \text{ kg/source} \end{aligned}$$

The average emission factor approach is commonly used to calculate emissions when site-specific screening data is unavailable. To estimate emissions using the emission factors in Table 5, the concentration in weight percent of the pollutant of interest within the equipment is needed. This is important because equipment with higher pollutant concentrations tend to have higher emission leak rates. The equipment should be grouped into *streams*, such that all equipment within a *stream* has approximately the same pollutant weight percent.

This approach for estimating emissions allows use of average emission factors in combination with unit-specific data that is relatively simple to obtain. This data includes:

- The number of each type of component in a unit (valve, connector, etc.);

- the service each component is in (gas, light liquid, or heavy liquid);
- the pollutant concentration of the stream; and
- the time period each component was in that service during the NPI reporting year.

Equation 25 can be used to estimate emissions from all of the equipment of a given equipment type in a *stream* using the emission factors from Table 5.

Equation 25

$$E_{kpy,i} = EF * WF_i * OpHrs * N$$

where:

$E_{kpy,i}$ = emission rate of pollutant i from all equipment in the *stream* of a given equipment type, kg/yr/source
EF = applicable average emission factor for the equipment type, kg/hr/source
WF_i = average weight fraction of pollutant i in the *stream*,
OpHrs = annual operation hours of equipment in the *stream*, hr/yr
N = number of pieces of the applicable equipment type in the *stream*

Example 6 illustrates the emission factor approach for Streams A and B. Note that Stream A contains water, which is not an NPI-listed substance, and that this is accounted for when total emissions are estimated from Stream A.

Example 6 - Average Emission Factor Technique

This example shows how annual ammonia (NH_3) emissions can be calculated from pump seals using the emission factors from Table 5 and Equation 25. The following data is given:

Stream ID	Equipment Count (N)	Emission Factor (kg/hr/source)	Weight Fraction	OpHrs (hr/yr)
A	15	0.0199	0.80	8 760
B	12	0.0199	1.00	4 380

$$E_{kpy,NH3} = EF * WF_{NH3} * OpHrs * N$$

Stream A

$$E_{kpy,NH3} = 0.0199 * 0.80 * 8\,760 * 15$$
$$= 2\,092 \text{ kg/yr}$$

Stream B

$$E_{kpy,NH3} = 0.0199 * 1.00 * 4\,380 * 12$$
$$= 1\,046 \text{ kg/yr}$$

Table 5 - Emission Factors for Equipment Leaks

Equipment Type	Service	Emission Factor (kg/hr/source)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals [a]	Light liquid Heavy liquid	0.0199 0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connections	All	0.0150

Source: Eastern Research Group, 1996.

[a] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

5.2 Using Sampling or Direct Measurement

For Particulate Emissions

This section shows how to calculate emissions in kg/hr based on stack sampling data and then how to convert this to an annual emissions figure. Calculations involved in determining PM_{10} emissions are used as an example, although the same calculations are applicable for most NPI-listed substances.

An example of test results is summarised in Table 6. The table shows the results of three different sampling runs conducted during one test event. The source parameters measured as part of the test run include gas velocity and moisture content, which are used to determine exhaust gas flow rates in m^3/s. The filter weight gain is determined gravimetrically and divided by the volume of gas sampled, as shown in Equation 26 to determine the PM concentration in grams per m^3. Note that this example does not present the condensable PM emissions.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation 27 and Example 7.

Equation 26

$$C_{PM} = C_f \; / \; V_{m, STP}$$

where:

C_{PM} = concentration of PM or gram loading, g/m^3

C_f = filter catch, g

$V_{m,STP}$ = metered volume of sample at STP, m^3

Equation 27

$$E_{PM} = C_{PM} * Q_d * 3.6 * [273 \; / \; (273 + T)]$$

where:

E_{PM} = hourly emissions of PM, kg/hr
C_{PM} = concentration of PM or gram loading, g/m^3
Q_d = stack gas volumetric flow rate, m^3/s, dry
3.6 = 3600 seconds per hour multiplied by 0.001 kilograms per gram
T = temperature of the gas sample, °C

Table 6 - Stack Sample Test Results

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (sec)		7 200	7 200	7 200
Moisture collected (g)	g_{MOIST}	395.6	372.6	341.4
Filter catch (g)	C_f	0.0851	0.0449	0.0625
Average sampling rate (m^3/s)		$1.67 * 10^{-4}$	$1.67 * 10^{-4}$	$1.67 * 10^{-4}$
Standard metered volume (m^3)	$V_{m, STP}$	1.185	1.160	1.163
Volumetric flow rate (m^3/s), dry	Q_d	8.48	8.43	8.45
Concentration of particulate (g/m^3)	C_{PM}	0.0718	0.0387	0.0537

Source: Queensland Department of Environment and Heritage, 1998

Example 7 - Using Stack Sampling Data

PM emissions calculated using Equation 26 and Equation 27 and the stack sampling data for Test 1 (presented in Table 6, and an exhaust gas temperature of 150°C (423 K)). This is shown below:

$$\begin{aligned} C_{PM} &= C_f \,/\, V_{m, STP} \\ &= 0.0851 \,/\, 1.185 \\ &= 0.072\ g/m^3 \end{aligned}$$

$$\begin{aligned} E_{PM} &= C_{PM} * Q_d * 3.6 * [273/(273+T)] \\ &= 0.072 * 8.48 * 3.6 * (273/423K) \\ &= 1.42\ kg/hr \end{aligned}$$

The information from some stack tests may be reported in grams of particulate per cubic metre of exhaust gas (wet). Use Equation 28 to calculate the dry particulate emissions in kg/hr.

Equation 28

$$E_{PM} = Q_w * C_{PM} * 3.6 * \left(1 - {moist_R}/{100}\right) * \left[{273}/{(273+T)}\right]$$

where:

E_{PM} = hourly emissions of PM in kilograms per hour, kg/hr
Q_w = wet cubic metres of exhaust gas per second, m^3/s
C_{PM} = concentration of PM or gram loading, g/m^3
3.6 = 3600 seconds per hour multiplied by 0.001 kilograms per gram
$moist_R$ = moisture content, %

273 = 273 K (0°C)
T = stack gas temperature, °C

To determine PM_{10} emissions from PM, it may be necessary for facility operators to first undertake a size analysis of the stack filter catch. The weight PM_{10} fraction can then be multiplied by the total PM emission rate to produce PM_{10} emissions.

To calculate moisture content use Equation 29

Equation 29

Moisture percentage = 100 % * weight of water vapour per specific volume of stack gas / total weight of the stack gas in that volume.

$$moist_R = \frac{100\% * \frac{g_{moist}}{(1000 * V_{m,STP})}}{\frac{g_{moist}}{(1000 * V_{m,STP})} + r_{STP}}$$

where

$moist_R$ = moisture content, %
g_{moist} = moisture collected, g
$V_{m,STP}$ = metered volume of sample at STP, m^3
ρ_{STP} = dry density of stack gas sample, kg / m^3 at STP
{if the density is not known a default value of 1.62 kg / m^3 may be used. This assumes a dry gas composition of 50% air, 50% CO2}.

Example 8 - Calculating Moisture Percentage

A 1.2m^3 sample (at STP) of gas contains 410g of water. To calculate the moisture percentage use Equation 29.

$$moist_R = \frac{100\% * \frac{g_{moist}}{(1000 * V_{m,STP})}}{\frac{g_{moist}}{(1000 * V_{m,STP})} + r_{STP}}$$

$(g_{MOIST} / 1000 * V_{m,STP})$ = 410 / (1000 * 1.2)
= 0.342
$moist_R$ = 100 (0.342 / 0.342 + 1.62)
= 17.4%

For Gaseous Emissions

Sampling test methods can be used to estimate inorganic pollutant emission rates from various inorganic chemical manufacturing processes. Airflow rates can be determined from flow rate metres or from pressure drops across a critical orifice.

Sampling test reports often provide chemical concentration data in parts per million by volume (ppmv).

Equation 30 can be used to calculate hourly emissions of a substance based on the concentration measurements in the units parts per million.

Equation 30

$$E_i = (C_i * MW_i * Q_d * 3600) / (22.4 * [(T + 273)/273] * 10^6)$$

where:

E_i = total emissions of pollutant i, kg/hr
C_i = concentration of pollutant i, $ppm_{v,d}$
MW_i = molecular weight of pollutant i, kg/kg-mole
Q_d = stack gas volumetric flow rate, m^3 /s
3 600 = conversion factor, s/hr
22.4 = volume occupied by one mole of gas at standard temperature and pressure (0°C and 101.3kPa), m^3/kg-mole
T = temperature of gas sample, °C
273 = 273 K (0°C)

Emissions in kilograms per year can be calculated by multiplying the average hourly emission rate (kg/hr) from Equation 30 by the number of operating hours (as shown in Equation 31 below) or by multiplying an average emission factor (kg/L) by the total annual amount of material used (L).

Equation 31

$$E_{kpy,i} = E_i * OpHrs$$

where:

$E_{kpy,i}$ = annual emissions of pollutant i, kg/yr
E_i = total hourly emissions of pollutant i, kg/hr
OpHrs= annual operating hours, hr/yr

Concentration data obtained from source testing may come in a variety of units, including parts per million (ppm), or grams per cubic metre (g/m^3), and in a variety of conditions, such as wet, dry, or excess O_2. This may require conversion of concentration data to consistent units for compatibility with the equations given above.

Example 9 illustrates the use of Equation 30 and Equation 31.

Example 9 - Estimating Gaseous Emissions

This example shows how annual hydrogen fluoride (HF) emissions can be calculated using the data obtained from a stack or other point-source emission point from a plant manufacturing inorganic chemicals. Hourly emissions are calculated using Equation 30, and annual emissions are calculated using Equation 31.

Given:
C_{HF} = 15.4 ppmv MW_{HF} = 17 kg/kg-mole of hydrogen fluoride
Q_d = 8.48 m^3/sec   OpHrs= 1760 hr/yr
T = 25°C

Hourly emissions are calculated using Equation 30:

$$E_{HF} = (C_{HF} * MW_{HF} * Q_d * 3600) / [22.4 * ((T + 273)/273) * 10^6]$$
$$= (15.4 * 17 * 8.48 * 3600) / [22.4 * ((25 + 273)/273) * 10^6]$$
$$= 3.269 * 10^{-1} \text{ kg/hr}$$

Annual emissions of HF are calculated using Equation 31:

$$E_{kpy,HF} = E_{HF} * OpHrs$$
$$= 3.269 * 10^{-1} * 1760$$
$$= 575.34 \text{ kg/yr}$$

For Emissions to Water

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing monitoring data can be used to calculate annual emissions for NPI-reporting purposes by the use of Equation 32.

Equation 32

$$E_{kgpy,i} = C_i * V_H * OpHrs / 1\,000\,000$$

where:

$E_{kgpy,i}$ = emissions of pollutant i, kg/yr
C_i = concentration of pollutant i in wastewater, mg/L
V_H = hourly volume of wastewater, L/hr
OpHrs = operating hours for which data apply, hr/yr
1 000 000 = conversion factor, mg/kg

In applying Equation 32 to water emission calculations, sampling data should be averaged and only representative concentrations used in emission calculations. The total emissions of an NPI-listed substance should equal the amount used during the year minus the amount incorporated into products minus the amounts processed in on-site treatment and transferred off-site for disposal by another facility. In estimating emissions, it is particularly helpful to first estimate the amount incorporated into inorganic chemicals for sale or distribution, or other end-products, before proceeding to individual emission estimates, as this will provide a reference point.

5.3 Using Mass Balance Calculations

Mass balance calculations for estimating emissions of VOCs and speciated organics and inorganics can be made by applying Equation 33 where the pollutant concentration is constant throughout the process.

Equation 33

$$E_i = (Q_{in} - Q_{out}) * C_i$$

where:

E_i = total emissions of pollutant i, in kg/hr
Q_{in} = material entering the process, in L/hr
Q_{out} = material leaving the process as waste, recycled or in product, L/hr
C_i = concentration of pollutant i, kg/L

The term Q_{out}.could include the amount recovered or recycled, the amount leaving the process in the manufactured product, the amount leaving the process in wastewater, or the amount of material transferred off-site as hazardous waste or to landfill. A thorough knowledge of the different destinations for the pollutant of interest is necessary for an accurate emission estimate to be made using the mass balance approach. Example 10 illustrates the application of Equation 33.

Example 10 - Using a Mass Balance for VOC Emissions

This example shows how VOC emissions may be calculated using Equation 33 for non-reactant materials (solvents and absorbents) added during a process operation given the following data:

Q_{in} = 6 L/hr
Q_{out} = 4 L/hr
C_{VOC} = 0.85 kg VOC/L

$$\begin{aligned} E_{VOC} &= (Q_{in} - Q_{out}) * C_{VOC} \\ &= (6\ L/hr - 4\ L/hr) * 0.85\ kg\ VOC/L \\ &= 1.7\ kg/hr \end{aligned}$$

Where the pollutant concentrations are different in the process and waste materials to the stream entering the process Equation 34 can be used.

Equation 34

$$E_i = Q_{in} * C_{in} - Q_{pr} * C_{pr} - * Q_{rec} * C_{rec}$$

where:

E_i = total emissions of pollutant i, kg/hr
Q_{in} = material entering the process, L/hr
Q_{pr} = amount of material leaving the process as a product (or amount of product), L/hr
Q_{rec} = material leaving the process as waste or recycled off-site, L/hr
C_{in} = concentration of pollutant i in Q_{in}, kg/L
C_{pr} = concentration of pollutant i in Q_{pr}, kg/L
C_{rec} = concentration of pollutant i in Q_{rec}, kg/L

Speciated VOC emissions may be estimated by a mass balance approach using Equation 35.

Equation 35

$$E_i = (Q_{in} - Q_{out}) * \rho_m * (wt\%_i)/100$$

where:

E_i = total emissions of pollutant i, kg/hr
Q_{in} = material entering the process, L/hr
Q_{out} = material leaving the process as an emission, transfer, or as an article or product, L/hr
ρ_m = density of material, kg/L
$wt\%_i$ = percentage by weight of pollutant i in material, %

Example 11 shows the application of Equation 35.

Example 11 - Using a Mass Balance to Speciate VOC Emissions

This example shows how toluene emissions may be calculated using Equation 35 for a material containing 25% toluene (by weight) added during a process operation given the following data:

$$\begin{aligned}
Q_{in} &= 6\ L/hr \\
Q_{out} &= 4\ L/hr \\
\rho_m &= 0.87\ kg\ (material)/L \\
wt\%_{toluene} &= 25\%
\end{aligned}$$

$$\begin{aligned}
E_{toluene} &= (Q_{in} - Q_{out}) * \rho_m * (wt\%_i)/100 \\
&= (6\ L/hr - 4\ L/hr) * 0.87\ kg\ /L * 25/100 \\
&= 0.435\ kg/hr
\end{aligned}$$

For Emissions to Wastewater

If no wastewater monitoring data exists, emissions to process water can be calculated based on a mass balance of the process, shown by Equation 36.

Equation 36

$$E_{kpy,i} = (Q_{in} - Q_{out})$$

where:

$E_{kpy,i}$ = emissions of pollutant i, kg/yr
Q_{in} = amount of pollutant i used, kg/yr
Q_{out} = amount of pollutant i incorporated into product + treated on-site + transferred off-site in the reporting year, kg/yr

Where a facility uses an NPI-listed mineral acid or base, with this acid or base being effectively neutralised in use or during wastewater treatment (to a pH of 6 to 8, as required by most State and Territory effluent standards), no emission quantities should be reported. If the acid or base is itself transformed into another listed substance, however, the quantity of this substance coincidentally produced must be determined to assess if a threshold value has been reached. For example, sulfuric acid often yields hydrogen sulfide (an NPI-listed substance) in effluent streams.

For Emissions via Solid Waste

Wastewater treatment may transport the NPI-listed substance to a sludge. Facilities are often required to obtain data on the concentration of metals or and other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge times concentrations of the substance in the sludge.

Alternatively, the loss in the sludge can be estimated by Equation 37. Although listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with determining other process losses or may require reporting if the sludge is disposed of on-site.

Equation 37

$$AS_{kpy,i} = (PL_i - WL_i) * OpHrs$$

where:

$AS_{kpy,i}$ = amount of pollutant i in sludge, kg/yr
PL_i = process losses of pollutant i, kg/hr
WL_i = losses from wastewater of pollutant i, kg/hr
$OpHrs$ = operational hours, hr/yr

For many chemicals used and emitted during inorganic chemical manufacturing processes, some degradation in treatment may occur so all the chemical is not transferred to the sludge. Facilities can estimate the amount of reportable substances in the sludge by using measured data, or by subtracting the amount biodegraded from the total amount removed in treatment. The amount of removal can be determined from operating data, and the extent of biodegradation might be obtained from published studies. If the biodegradability of the chemical cannot be measured or is not known, reporting facilities should assume that all removal is due to absorption to sludge.

5.4 Using Emission Factors

In this Manual, emission factors are provided for emissions to atmosphere, water, and via solid waste. Emission factors relate the quantity in kilograms of pollutants emitted from an inorganic chemical manufacturing activity to the amount of product produced per year.

Emission factors are used to estimate a facility's emissions by Equation 38.

Equation 38

$$E_{kpy,i} = [A * OpHrs] * EF_i * [1 - (CE_i / 100)]$$

where :

$E_{kpy,i}$ = emission rate of pollutant i, kg/yr
A = activity rate, t/hr
$OpHrs$ = operating hours, hr/yr
EF_i = uncontrolled emission factor of pollutant i, kg/t
CE_i = overall control efficiency for pollutant i, %.

Example 12 illustrates the application of Equation 38.

Example 12 - Estimating Mercury Emissions to Water

Table 9 shows that 0.157 kg of mercury are emitted to wastewater from uncontrolled sources for each tonne of chlorine gas produced in a chlor-alkali plant. During the reporting year the facility manufactured and shipped 1 685 tonnes of Cl_2. The facility also operates a wastewater treatment plant that effectively recovers 98 percent of mercury for recycling on-site. Emissions can be estimated using Equation 38.

EF_{Hg} = 0.15 kg / tonne
A Cl_2 production = 0.33 t / hr
CE_{Hg} = 98 %
OpHrs = 5400 hr / yr

$E_{kpy,Hg}$ = [A * OpHrs] * EF_i * [1 - (CE_i / 100)]
5.1.2.1.1.1.1.1 = [0.33 t / hr * 5400 hr / yr] * 0.15 kg / t * [1 - 98 / 100)]
= 5.3 kg / yr

The following tables contain emission factors to assist in estimating emissions from various processes throughout an inorganic chemical manufacturing facility. To aid in locating the relevant emission factors, the tables follow the same sequence of inorganic chemical product as shown in earlier sections of this Manual. Tables covering emission factors to atmosphere are given before the tables describing emission factors to water and solid waste.

5.4.1 Emission Factors for Chlor-Alkali Plants

Table 7 - Emission Factors for Chlorine from Chlor-Alkali Plants

Source	Chlorine Gas Emitted (kg/tonne of Cl_2 produced)[b]
Liquefaction blow gases	
Diaphragm cell	10 - 50
Mercury cell	20 - 80
Water absorber [a]	0.830
Caustic scrubber [a]	0.006
Chlorine loading	
Returned tanker vents	4.1
Shipping container vents	8.7
Mercury cell brine air blowing	2.7

Source: USEPA *AP-42*, 1995.
[a] Control devices.
[b] All emission factors have an uncertainty rating of E.

Table 8 - Emission Factors for Mercury from Mercury Cell Chlor-Alkali Plants

Type of Source	Mercury Gas (kg/tonne of Cl_2 Produced)[a]
Hydrogen vent	
Uncontrolled	0.0017
Controlled	0.0006
End box	0.005

Source: USEPA, 1995.

[a] All emission factors have an uncertainty rating of E.

Table 9 - Water and Solid Waste Emission Factors from Chlor-Alkali Plants[b]

Process Cell Description	Substance Emitted	Emission Factor[a]
Mercury Cell		
Uncontrolled emission	Mercury (Hg)	0.15
After activated sludge treatment	Mercury (Hg)	0.0001
Mercury-Cathode Cell		
Graphite, purification mud [c]	Mercury (Hg)	ND[d]
Diaphragm Cell (metal or graphic anodes)		
Uncontrolled emission	Lead (Pb)	0.046
After activated sludge treatment	Lead (Pb)	0.0025

Source: Economopoulos, 1993.

[a] Factor units are kg of substance emitted per tonne of chlorine produced.

[b] Emissions only require reporting if substances are emitted directly to a stream or water body or are emitted following activated sludge treatment on-site. Waters transferred off-site for treatment do not require characterisation and reporting.

[c] Graphite and purification mud are usually transferred off-site to landfill. Only waste streams disposed of on-site require characterisation and reporting.

[d] Graphite and purification mud typically contain $CaCO_3$, $Mg(OH)_2$, and Hg. Emission factor is 40 kg of mud produced per tonne of chlorine manufactured. Sample testing for mercury content is required.

ND = no data.

5.4.2 Sodium Carbonate

Table 10 - Controlled Emission Factors for Particulate Matter from Sodium Carbonate Production

Process	Filterable Emissions[a] (kg / tonne)	Factor Rating	Total Emissions [b] (kg / tonne)	Factor Rating
Ore mining	0.0016	C	ND	NA
Ore crushing and screening	0.0010	D	0.0018	C
Ore transfer	0.00008	E	0.0001	E
Monohydrate process: rotary ore calciner	0.091	A	0.12	B
Sesquicarbonate process: rotary calciner	0.36	B	0.36	C
Sesquicarbonate process: fluid-bed calciner	0.021	C	ND	NA
Rotary soda ash dryers	0.25	C	0.25	D
Fluid-bed soda ash dryers / coolers	0.015	C	0.019	D
Soda ash screening	0.0097	E	0.013	E
Soda ash storage loading and unloading	0.0021	E	0.0026	E

Source: USEPA, 1995.

[a] Filterable particulate matter is that material collected on or before the filter.

[b] Total particulate matter includes filterable particulate and inorganic condensable particulate. Factor units are kg of particulate emitted per tonne of sodium carbonate produced.

ND = no data.

NA = not applicable.

Table 11 - Uncontrolled Emission Factors for Particulate Matter from Sodium Carbonate Production

Process	Nominal Control Efficiency	Total Emissions[a] (kg/tonne)	Factor Rating
Ore mining	99.9	1.6	D
Ore crushing and screening	99.9	1.7	E
Ore transfer	99.9	0.1	E
Monohydrate process: rotary ore calciner	99.9	90	B
Sesquicarbonate process: rotary calciner	99	36	D
Sesquicarbonate process: fluid-bed calciner	99	2.1	D
Rotary soda ash dryers	99	25	E
Fluid-bed soda ash dryers / coolers	99	1.5	E
Soda ash screening	99.9	10	E
Soda ash storage loading and unloading	99.9	2.6	E

Source: USEPA, 1995.

[a] Values for uncontrolled total particulate matter can be assumed to include filterable particulate and both organic and inorganic condensable particulate. For processes operating at significantly greater than ambient temperatures, these factors have been calculated by applying the nominal control efficiency to the controlled (as-measured) filterable particulate emission factors above.

ND = no data.

NA = not applicable.

5.4.3 Hydrochloric Acid

Table 12 - Emission Factors for Hydrochloric Acid Manufacture

By-Product Hydrochloric Acid	HCl Emissions (kg/tonne) [a,b]
With final scrubber	0.08
Without final scrubber	0.90

Source: USEPA, 1995.

[a] Factor units are kg of HCl emitted per tonne of HCl produced.

[b] Emission factor rating E

5.4.4 Hydrofluoric Acid

Table 13 - Emission Factors for Hydrofluoric Acid Manufacture

Operations and Controls	Control Efficiency (%)	Gas Emissions[a] (kg/tonne of acid produced)	Particulate Emissions[b] (kg/tonne of fluorspar)
Spar drying [c]			
Uncontrolled	0	ND	37.5
Fabric filter	99	ND	0.4
Spar handling silos [d]	0	NA	30.0
Uncontrolled	99	NA	0.3
Fabric filter			
Transfer operations	0	NA	3.0
Uncontrolled	80	NA	0.6
Covers, additives			
Tail-gas			
Uncontrolled	0	12.5 (HF)	ND
		15.0 (SiF_4)	ND
		22.5 (SO_2)	ND
Caustic scrubber	99	0.1 (HF)	ND
		0.2 (SiF_4)	ND
		0.3 (SO_2)	ND

Source: USEPA, 1995.

[a] Factor units are kg of gas emitted per tonne of hydrofluoric acid produced.

[b] Factor units are kg of particulate matter emitted / tonne of fluorspar produced.

[c] Averaged from information from four US plants. Hourly fluorspar input calculated from reported year 1975 year capacity, assuming stoichiometric amount of calcium fluoride and 97.5% content in fluorspar. Hourly emission rates calculated from reported baghouse controlled rates. Values averaged are as follows:

Plant	1975 HF Capacity (tonnes)	Emissions Fluorspar (kg/tonne)
1	13 600	53
2	18 100	65
3	45 400	21
4	10 000	15

[d] Four plants averaged for silo emissions and two plants for transfer operations emissions.

All emission factors have an uncertainty code of E.

5.4.5 Nitric Acid

Table 14 - Nitrogen Oxide Emissions from Nitric Acid Plants

Source	Efficiency Control (%)	NO_x Emissions (kg/tonne) [a]
Weak acid plant tail-gas Uncontrolled [b,c]	0	28
Catalytic reduction [c] Natural gas [d] Hydrogen [e] Natural gas / hydrogen (25% / 75%) [f]	 99.1 97-98.5 98-98.5	 0.2 0.4 0.5
Extended absorption Single-stage process [g] Dual-stage process [h]	 95.8 	 0.95 1.1
Chilled absorption and caustic scrubber [j]	ND	1.1
High-strength acid plant [k]	ND	5

Source: USEPA, 1995

[a] Factor units are kg of acid emitted per tonne of nitric acid produced.

[b] Based on a study of 12 US plants, with average production rate of 207 tonnes (100% HNO_3) per day (range 50-680 tonnes) at average rated capacity of 97% (range 72-100%).

[c] Single-stage pressure process.

[d] Fuel is assumed to be natural gas. Based on data from 7 US plants, with average production rate of 309 tonnes (100% HNO_3) per day (range 50-977 tonnes).

[e] Based on data from 2 US plants, with average production rate of 208 tonnes (100% HNO_3) per day (range 109-190 tonnes) at average rated capacity of 98% (range 95-100%). Average absorber exit temperature is 29° C (range 25-30°C), and the average exit pressure is 586 kPa (range 552-648 kPa).

[f] Based on data from 2 US plants, with average production rate of 208 tonnes (100% HNO_3) per day (range 168-249 tonnes) at average rated capacity of 110% (range 100-119%). Average absorber exit temperature is 33°C (range 28-37°C), and average exit pressure is 586 kPa (range 552-648 kPa).

[g] Based on data from 5 US plants, with average production rate of 492 tonnes (100% HNO_3) per day (range 190-953 tonnes).

[h] Based on data from 3 US plants, with average production rate of 532 tonnes (100% HNO_3) / day (range 286 - 850 tonnes).

[j] Based on data from 1 US plant, with a production rate of 628 tonnes (100% HNO_3) per day.

[k] Based on data from 1 US plant, with a production rate of 1.4 tonnes (100% HNO_3) per hour at 100% rated capacity, of 98% nitric acid.

All emission factors have an uncertainty code of E.

ND = no data.

5.4.6 Phosphoric Acid

Table 15 - Controlled Emission Factors for Wet Phosphoric Acid Production

Source	Fluoride Emissions (kg/tonne P_2O_5 produced) [a]
Reactor [b]	$1.9 * 10^{-3}$
Evaporator	$0.022 * 10^{-3}$
Belt filter	$0.32 * 10^{-3}$
Belt filter vacuum pump	$0.073 * 10^{-3}$
Gypsum settling & cooling ponds [c]	site-specific

Source: USEPA, 1995.

[a] Factor units are kg of fluorine emitted per tonne of phosphoric acid produced.

[b] Emission factor uncertainty rating of A.

[c] Site specific. Hectares of cooling pond required: ranges from 0.04 hectare per daily tonne P_2O_5 in summer to closer to zero during the winter months although dependent on local climatic condition.

All emission factors have an uncertainty code of B except where noted.

Table 16 - Uncontrolled Emission Factors for Wet Phosphoric Acid Production

Source	Nominal Percent Control Efficiency	Fluoride Emissions (kg/tonne P_2O_5 produced) [a]
Reactor [b]	99	0.19
Evaporator	99	0.00217
Belt filter	99	0.032
Belt filter vacuum pump	99	0.0073
Gypsum settling & cooling ponds [c]	ND	site-specific

Source: USEPA, 1995.

[a] Factor units are kg of fluorides emitted per tonne of phosphoric acid produced.

[b] Emission factor uncertainty rating of B.

[c] Site specific. Hectares of cooling pond required: ranges from 0.04 hectare per daily tonne P_2O_5 in summer to closer to zero during the winter months although dependent on local climatic condition.

All emission factors have an uncertainty code of C except where noted.

ND = no data.

Table 17 - Controlled Emission Factors for Thermal Phosphoric Acid Production

Source	Nominal Percent Control Efficiency	Particulate Emissions (kg/tonne P_2O_5 produced) [a]
Packed tower	95.5	1.07
Venturi scrubber	97.5	1.27
Glass fibre mist eliminator	96 - 99.9	0.35
Wire mesh mist eliminator	95	2.73
High pressure drop mist	99.9	0.06
Electrostatic precipitator	98 - 99	0.83

Source: USEPA, 1995.

[a] Factor units are kg of fluorine emitted per tonne of phosphoric acid produced.

All emission factors have an uncertainty code of E.

5.4.7 Sulfuric Acid

Table 18 - Sulfur Dioxide Emission Factors for Sulfuric Acid Plants

SO_2 to SO_3 Conversion Efficiency (%)	SO_2 Emissions (kg/tonne of acid produced) [a,b]
93	48.0
94	41.0
95	35.0
96	27.5
97	20.0
98	13.0
99	7.0
99.5	3.5
99.7	2.0
100	0.0

Source: USEPA, 1995.

[a] Factor units are kg of SO_2 emitted per tonne of sulfuric acid produced.

[b] This linear interpolation formula can be used for calculating emission factors for conversion efficiencies between 93 and 100%: emission factor (kg / tonne of product) = 682 - 6.82 (% conversion efficiency).

All emission factors have an uncertainty code of E.

NA = not applicable.

Table 19 - Uncontrolled Acid Mist Emission Factors for Sulfuric Acid Plants

Raw Material	Oleum Produced, % Total Output	H_2SO_4 Emissions (kg/tonne H_2SO_4 produced) [a]
Recovered sulfur	0 - 43	0.174 - 0.4
Bright virgin sulfur	0	0.85
Dark virgin sulfur	0 - 100	0.16 - 3.14
Spent acid	0 - 77	1.1 - 1.2

Source: USEPA, 1995.

[a] Factor units are kg of sulfuric acid mist emitted per tonne of sulfuric acid produced. Emissions are proportional to the percentage of oleum in the total product. Use low end of ranges for low oleum percentage and high end of ranges for high oleum percentage.

All emission factors have an uncertainty code of E.

Table 20 - Controlled Acid Mist Emission Factors for Sulfuric Acid Plants

Raw Material	Oleum Produced, % Total Output	H_2SO_4 Emissions (kg/tonne H_2SO_4 produced) [a]
Elemental sulfur	-	0.064
Dark virgin sulfur	0 - 13	0.26 - 1.8
Spent acid	0 - 56	0.014 - 0.20

Source: USEPA, 1995.

[a] Factor units are kg of sulfuric acid mist emitted per tonne of sulfuric acid produced.

All emission factors have an uncertainty code of E except where noted.

5.4.8 Sulfur Recovery

Table 21 - Emission Factors for Modified Claus Sulfur Recovery Plants

Number of Catalytic Stages	Average % Sulfur Recovery [a]	SO_2 Emissions (kg/tonne of sulfur produced)
1, Uncontrolled	93.5 [b]	139 [b,c]
3, Uncontrolled	95.5 [d]	94 [e,d]
4, Uncontrolled	96.5 [e]	73 [c,e]
2, Controlled [f]	98.6	29
3, Controlled [g]	96.8	65

Source: USEPA, 1995.

[a] Efficiencies are for feedgas streams with high H_2S concentrations. Gases with lower H_2S concentrations would have lower efficiencies. For example, a 2- or 3-stage plant could have a recovery efficiency of 95% for a 90% H_2S stream, 93% for 50% H_2S, and 90% for 15% H_2S.

[b] Based on net weight of pure sulfur produced. The emission factors were determined using the average of the percentage recovery of sulfur. Sulfur dioxide emissions are calculated from percentage sulfur recovery by the following equation:

$$SO_2 \text{ emissions (kg / tonne)} = (100\% \text{ recovery}) \div \% \text{ recovery x } 2000$$

[c] Typical sulfur recovery ranges from 92 to 95%.

[d] Typical sulfur recovery ranges from 95 to 96%.

[e] Typical sulfur recovery ranges from 96 to 97%.

[f] Emission factor has uncertainty rating of B. US test data indicated sulfur recovery ranges from 98.3 to 98.8%.

[g] Emission factor has uncertainty rating of B. US test data indicated sulfur recovery ranges from 95 to 99.8% recovery efficiencies. The efficiency depends upon several factors, including the number of catalytic stages, the concentrations of H_2S and contaminants in the feedstream, stoichiometric balance of gaseous components of the inlet, operating temperature, and catalyst maintenance.

All emission factors have an uncertainty code of E except where noted.

6. References

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The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage (*http://www.npi.gov.au*) and from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Combustion in Boilers;
- Emission Estimation Technique Manual for Combustion Engines;
- Emission Estimation Technique Manual for Fuel & Organic Liquid Storage; and
- Emission Estimation Technique Manual for Sewage & Wastewater Treatment.