National Pollutant Inventory

Emission Estimation Technique Manual

for

Synthetic Ammonia Manufacturing

First published in June 1999

EMISSION ESTIMATION TECHNIQUES
FOR
SYNTHETIC AMMONIA MANUFACTURING

TABLE OF CONTENTS

SYNTHETIC AMMONIA MANUFACTURING

LIST OF FIGURES AND TABLES

1.0 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 synthetic ammonia manufacturing.

EET MANUAL:	Synthetic Ammonia Manufacturing
HANDBOOK:	Fertiliser Manufacturing
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This Manual was drafted by the NPI Unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

2.0 Processes and Emissions

The following section presents a brief description of the synthetic ammonia manufacturing industry and identifies likely sources of emissions of NPI-listed substances.

2.1 Process Description

Synthetic ammonia (NH_3) refers to ammonia that has been synthesised from natural gas. Natural gas molecules are reduced to carbon and hydrogen. The hydrogen is then purified and reacted with nitrogen to produce ammonia. The great majority of the ammonia produced in Australia is used as agricultural fertiliser, either directly as ammonia or indirectly after synthesis as urea, ammonium nitrate, and mono-ammonium or di-ammonium phosphates. The remainder is used as raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products.

Synthetic ammonia plants are located in Brisbane, Newcastle, Geelong, and Kwinana with plans for a further plant at Yarwun near Gladstone. Total production in Australia is approaching 750 000 tonnes per annum.

Anhydrous ammonia is synthesised by reacting hydrogen with nitrogen at a molar ratio approximately of 3 to 1, then compressing the gas and cooling it to -33^{o}C. Nitrogen is obtained from the air, while hydrogen is obtained from either the catalytic steam reforming of natural gas (methane [CH_4] or naphtha), or the electrolysis of brine at chlorine plants. Almost all synthetic ammonia manufacturing uses the catalytic steam method. Figure 1 shows a general process flow diagram of a typical ammonia plant. As each synthetic ammonia facility in Australia is different from any other facility, you are urged to develop a flow diagram for your particular operations that details the input of materials and listed substances and the waste sources and emissions resulting from the operation of each process.

There are six process steps that are required to produce synthetic ammonia using the catalytic steam reforming method:

(1) natural gas desulfurisation;
(2) catalytic steam reforming;
(3) carbon monoxide (CO) shift;
(4) carbon dioxide (CO_2) removal;
(5) methanation; and
(6) ammonia synthesis.

The first, third, fourth, and fifth steps, remove impurities such as sulfur, CO, CO_2 and water (H_2O) from the feedstock, hydrogen, and from the synthesis gas streams. In the second step, hydrogen (H_2) is manufactured and nitrogen (air) is introduced. The sixth step produces anhydrous ammonia from the synthetic gas. While most ammonia plants use this basic process detail such as operating pressures, temperature, and quantities of feedstock vary from plant to plant, some plants add nitrogen (N_2) in the final stages and H_2 in the initial stages.

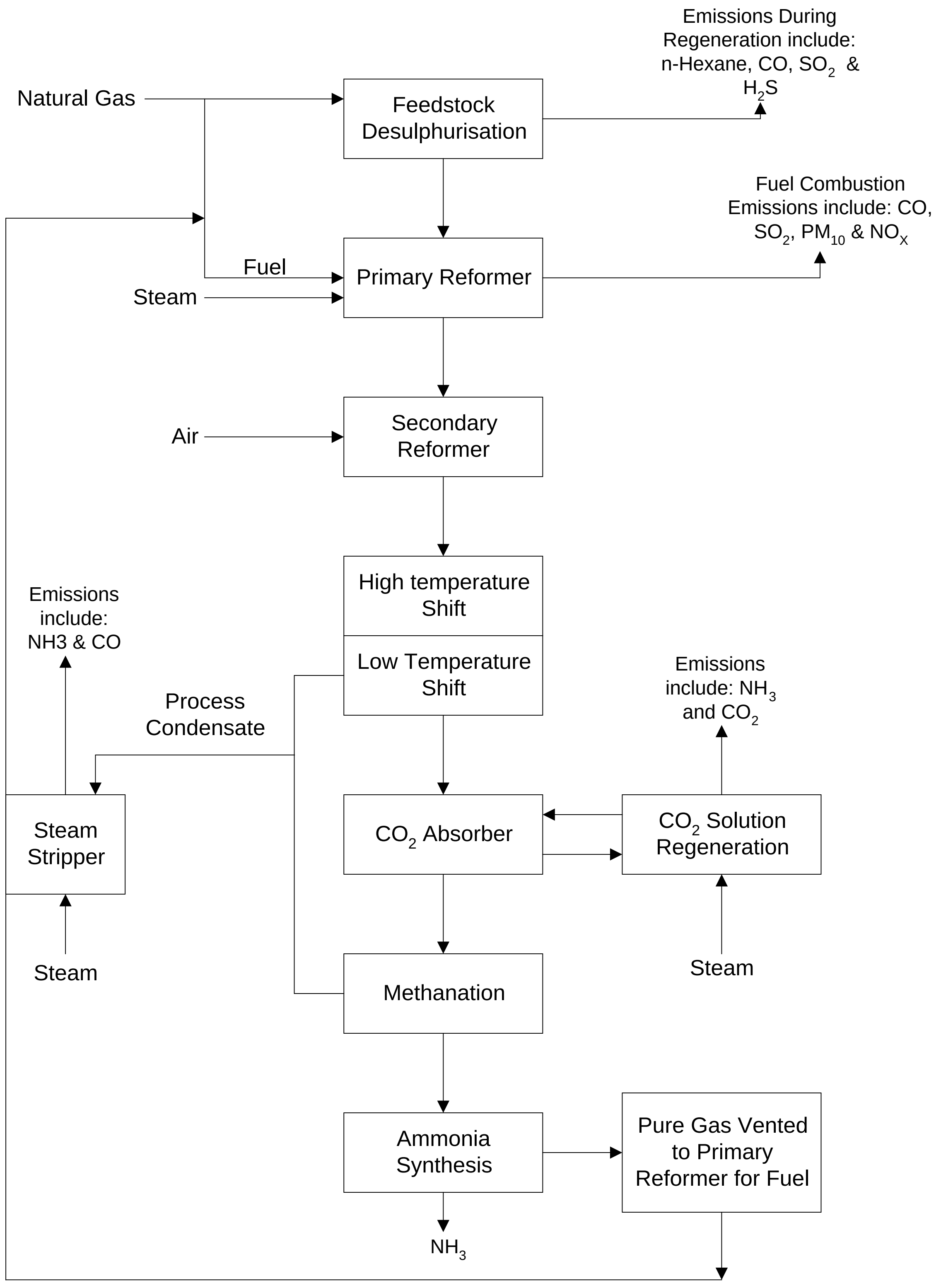

Figure 1 - General Flow Diagram of a Typical Ammonia Plant
Source: USEPA, AP 42, Section 8.1, 1993

2.1.1 Natural Gas Desulfurisation

In this step, the sulfur content (as hydrogen sulfide [H_2S]) in natural gas is reduced to below 280 micrograms per cubic metre ($\mu g/m^3$) to prevent poisoning of the nickel catalyst in the primary reformer. Desulfurisation can be accomplished by using either activated carbon or zinc oxide. Heavy hydrocarbons can decrease the effectiveness of an activated carbon bed. This carbon bed also has another disadvantage in that it cannot remove carbonyl sulfide. Regeneration of carbon is accomplished by passing superheated steam through the carbon bed.

A zinc oxide bed offers several advantages over the activated carbon bed. Steam regeneration to use as energy is not required when using a zinc oxide bed. No air emissions are created by the zinc oxide bed, and the higher molecular weight hydrocarbons are not removed. Therefore, the heating value of the natural gas is not reduced.

2.1.2 Catalytic Steam Reforming

Natural gas leaving the desulfurisation tank is mixed with process steam and preheated to approximately 540 ^{o}C. The mixture of steam and gas enters the primary reformer (natural gas fired or oil fired) tubes, which are filled with a nickel-based reforming catalyst. Approximately 70 percent of the CH_4 is converted to hydrogen and CO_2. An additional amount of CH_4 is converted to CO. This process gas is then sent to the secondary reformer, where it is mixed with compressed air that has been preheated to about 540 ^{o}C. Sufficient air is added to produce a final synthesis gas having a hydrogen-to-nitrogen mole ratio of approximately 3 to 1. The gas leaving the secondary reformer is then cooled to 360 ^{o}C in a waste heat boiler.

2.1.3 Carbon Monoxide Shift

After cooling, the secondary reformer effluent gas enters a high temperature CO shift converter that is filled with chromium oxide initiator and iron oxide catalyst. The following reaction takes place in the carbon monoxide converter:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The exit gas is then cooled in a heat exchanger. In some plants, the gas is passed through a bed of zinc oxide to remove any residual sulfur contaminants that would poison the lower temperature shift catalyst. In other plants, excess low-temperature shift catalyst is added to ensure that the unit will operate as expected. The low-temperature shift converter is filled with a copper oxide/zinc oxide catalyst. Final shift gas from this converter is cooled from approximately 210 to 110^{o}C and enters the bottom of the carbon dioxide absorption system. Unreacted steam is condensed and separated from the gas in a knockout drum. This condensed steam (process condensate) contains ammonium carbonate ($[(NH_4)_2CO_3.H_2O]$) from the high temperature shift converter, methanol (CH_3OH) from the low-temperature shift converter, and small amounts of sodium, iron, copper, zinc, aluminium, and calcium.

Process condensate is sent to the stripper to remove volatile gases such as ammonia, methanol, and carbon dioxide. Trace metals remaining in the process condensate can be removed by the ion exchange unit.

2.1.4 Carbon Dioxide Removal

In this step, CO_2 in the final shift gas is removed. CO_2 removal can be done by using two methods: amine scrubbing and hot potassium scrubbing. Most ammonia plants use amine to aid in removing CO_2. The CO_2 gas is passed upward through an adsorption tower countercurrent to a 15 to 30 percent solution of amine in water fortified with effective corrosion inhibitors. After absorbing the CO_2, the amine solution is preheated and regenerated (carbon dioxide regenerator) in a reactivating tower. This reactivating tower removes CO_2 by steam stripping and then by heating. The CO_2 is either vented to the atmosphere or used for chemical feedstock in other parts of the complex. The regenerated amine is pumped back to the absorber tower after being cooled in a heat exchanger and solution cooler.

2.1.5 Methanation

Residual CO and CO_2 in the synthesis gas is removed by catalytic methanation, which is conducted over a nickel catalyst at temperatures of 400 to 600 °C and pressures up to 3 000 kilopascals (kPa) according to the following reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Exit gas from the methanator, which has approximately a 3:1 mole ratio of hydrogen and nitrogen, is then cooled to 38 °C or lower.

2.1.6 Ammonia Synthesis

In the synthesis step, the synthesis gas from the methanator is compressed at pressures ranging from 13 800 to 34 500 kPa, mixed with recycled synthesis gas, and cooled to 0 °C, or lower. Condensed ammonia is separated from the unconverted synthesis gas in a liquid-vapour separator and sent to a letdown separator. The unconverted synthesis is compressed and preheated to 180 °C before entering the synthesis converter that contains iron oxide catalyst. Ammonia from the exit gas is condensed and separated, then sent down to the letdown separator. A small portion of the overhead gas is purged to prevent the buildup of inert gases, such as argon, in the circulating gas system.

Ammonia in the letdown separator is flashed to 100 kPa at -33 °C to remove impurities from the liquid. The flash vapour is condensed in the letdown chiller where anhydrous ammonia is drawn off and stored at low temperature.

2.2 Emissions to Air

Air emissions may be categorised as either fugitive or point source emissions.

Fugitive Emissions

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include dust from stockpiles, volatilisation of vapour from vats, open vessels, or spills and materials handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions.

Point Source Emissions

These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere.

Table 1 summarises potential NPI-listed substances emitted from synthetic ammonia manufacturing and highlights the environmental media to which these emissions are likely to occur.

Table 1 - Common Emissions of NPI-Listed Substances from Synthetic Ammonia Manufacturing Processes

Substance	Emission Media		
	To Atmosphere	**To Water**	**Via Solid Waste**
Ammonia	X	X	X
Methanol	X	X	X
Particulate matter (PM_{10})	X		
Total VOCs	X		
n-Hexane	X		
Zinc		X	X
Manganese		X	X
Cyclohexane	X		
Benzene	X		
Acetone	X		
Toluene	X		
Carbon monoxide	X		
Sulfur dioxide	X		

Source: Queensland Department of Environment and Heritage, 1998

2.3 Emissions to Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

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 sampling data can be used to calculate annual emissions.

If no wastewater monitoring data exists, emissions to process water can be calculated based on a mass balance calculation or by using emission factors. The discharge of listed substances to a sewer or tailings dam does not require reporting to the NPI. However, leakage and other emissions (including dust) from a tailings storage facility are reportable. (See also Section Three of *The NPI Guide.*) Table 1 outlines listed substances that may be emitted to water from ammonia production.

2.4 Emissions to Land

Emissions of substances to land on-site include solid wastes, slurries, and sediments. Emissions arising from spills, leaks, and storage and distribution of materials containing listed substances may also occur to land. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries; and
- unintentional leaks and spills.

3.0 Emission Estimation Techniques

This section presents equations and examples of calculations for estimating emissions of particulate matter (PM_{10}), speciated organics (formaldehyde and methanol), and inorganic substances (ammonia, total nitrogen) from synthetic ammonia manufacturing processes.

Estimates of emissions of NPI listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility. The four types described in the *NPI Guide* are:

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; 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 emission estimation techniques 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 Manual does not necessarily imply that an emission should not 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.

In general, direct measurement is the most accurate method for characterising emissions and, where available, such data should be used in preference to other EETs presented in this Manual. However, additional direct measurement is not required under the NPI Measure. Direct monitoring may be undertaken as an element of other EETs.

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 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.

Table 2 lists the variables and symbols used throughout this Manual and indicates the level of information that may be required in estimating emissions of NPI-listed substances from synthetic ammonia manufacturing 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 or kg/hr/source
Substance entering the process	Q_{in}	kg/yr
Substance leaving the process (as an emission, transfer, or in product)	Q_{out}	kg/yr
Filter catch	C_f	grams
Moisture content	R	%
Overall control efficiency	CE	%
Average weight fraction of pollutant i	WF_i	%
Number of pieces of applicable equipment type	N	unitless
Volume of sample at standard temperature and pressure	$V_{m,STP}$	m^3
Volume of mixture containing substance i	M_i	kg/yr
Hourly volume of wastewater	V_w	L/hr
Stack gas flow rate (actual)	Q_a	m^3/s
Concentration of pollutant i	C_i	ppmv or g/m^3 or mg/L or mg/kg
Molecular weight of pollutant i	MW_i	kg/kg-mole
Stack gas volumetric flow rate (dry)	Q_d	m^3/sec
Operating hours	OpHrs	h/yr
Emission factor for pollutant i	EF_i	kg/tonne or kg/units
Activity factor	A	tonnes/hr or units/hr
Temperature	T	°C

Source: Queensland Department of Environment and Heritage, 1998.

3.1 Using Sampling or Direct Measurement

3.1.1 For Emissions to Atmosphere

Particulate Matter (PM_{10}) Emissions

Stack sampling test reports often provide emissions data in terms of kilograms per hour or grams per cubic meter (dry standard). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative or normal operating conditions. Some tests undertaken for a State or Territory license condition may require that the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions. Data from these tests may need to be *scaled back* for NPI reporting purposes.

An example summary of a test method is shown in Table 3. 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 cubic meters. The filter weight gain is determined gravimetrically and divided by the volume of gas sampled (as shown in Equation 1) to determine the PM concentration in grams per cubic meter.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation 2. Example 1 illustrates the application of Equation 1 and Equation 2.

Equation 1

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

where:

C_{PM} = concentration of PM or gram loading, g/m^3
C_f = filter catch, g
V_{STP} = metered volume of sample at standard temperature and pressure, m^3

Equation 2

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

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 3 - 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 1 - Estimating Particulate Matter (PM_{10}) Emissions

PM emissions calculated using Equation 1 and Equation 2, the stack sampling data for Test 1 (presented in Table 3), and an exhaust gas temperature of 150°C (423K)). This is shown below:

C_{PM} = C_f / $V_{m, STP}$
= 0.0851 / 1.185
= 0.072 g/m^3

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

The information from some stack tests may be reported in grams of particulate per cubic metre of exhaust gas (wet). Use Equation 3 to calculate the dry particulate emissions in kg/hr.

Equation 3

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

where:

E_{PM} = hourly emissions of PM in kilograms per hour, kg/hr
Q_a = actual (ie. 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

Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM_{10} from total PM emissions, a size analysis may need to be undertaken. The weight PM_{10} fraction can then be multiplied by the total PM emission rate to produce PM_{10} emissions. Alternatively, assume that 100% of PM emissions are PM_{10}; ie assume that all particulate matter emitted to air has an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10μm.

To calculate moisture content use Equation 4

Equation 4

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

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

where

$moist_R$ = moisture content, %

g_{moist} = moisture collected, g

$V_{m,STP}$ = metered volume of sample at STP, m3

ρ_{STP} = dry density of stack gas sample, kg / m3 at STP {if the density is not known a default value of 1.62 kg / m3 may be used. This assumes a dry gas composition of 50% air, 50% CO_2}

Example 2 - Calculating Moisture Percentage

A 1.2m^3 sample (at STP) of gas contains 410g of water. To calculate the moisture percentage use Equation 4.

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

$g_{MOIST} / 1000 * V_{m,STP}$ = 410 / (1000 * 1.2)

= 0.342

$moist_R$ = 100 (0.342 / 0.342 + 1.62)

= 17.4%

Gaseous Emissions

Sampling test methods can be used to estimate inorganic pollutant emission rates from synthetic ammonia 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 5 can be used to calculate hourly emissions of a substance based on the concentration measurements in the units parts per million:

Equation 5

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

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
22.4 = volume occupied by one mole of gas at standard temperature and pressure (0 °C and 101.3 kPa), m^3/kg-mole
3 600 = conversion factor, s/hr
T = temperature of gas sample, °C

Emissions in kilograms per year can be calculated by multiplying the average hourly emission rate (kg/hr) from Equation 5 by the number of operating hours (shown in Equation 6 below) or by multiplying an average emission factor (kg/L) by the total annual amount of material used (L).

Equation 6

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

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 volume (ppmv), 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 3 illustrates the use of Equation 5 and Equation 6.

Example 3 - Estimating Ammonia Emissions to Atmosphere

This example shows how annual ammonia (NH_3) emissions can be calculated using the data obtained from a stack or other point-source emission point from a plant manufacturing synthetic ammonia. The hourly emissions of ammonia are calculated using Equation 5, and annual emissions are calculated using Equation 6.

Given:

C_{NH3}	=	15.4 ppmv	MW_{NH3}	=	17 kg/kg-mole of ammonia
Q_d	=	8.48 m^3/sec	OpHrs	=	1 760 hr/yr
T	=	150°C (423K)			

Hourly emissions of NH_3 are calculated using Equation 5:

$$E_{NH3} = (C_{NH3} * MW_{NH3} * Q_d * 3600) / [(22.4 * (T+273/273) * 10^6]$$
$$= (15.4 * 17 * 8.48 * 3600) / [22.4 * (423/273) * 10^6]$$
$$= 7\,922\,330 / 34\,707\,692$$
$$= 2.303 * 10^{-1} \text{ kg/hr}$$

Annual emissions of NH_3 are calculated using Equation 6:

$$E_{kpy,NH3} = E_{NH3} * OpHrs$$
$$= 2.303 * 10^{-1} * 1\,760$$
$$= 405.33 \text{ kg of ammonia emitted per year}$$

3.1.2 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 by the use of Equation 7.

Equation 7

$$E_{kpy,i} = C_i * V_w * OpHrs / 1\,000\,000$$

where:

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

In applying Equation 7 to water emission calculations, monitoring data should be averaged and only representative concentrations used in emission calculations.

3.2 Using Mass Balance

A mass balance identifies the quantity of substance going in and out of an entire facility, process, or piece of equipment. Emissions can be calculated as the difference between input and output of each listed substance. Accumulation or depletion of the substance within the equipment should be accounted for in your calculation.

Mass balance calculations for estimating emissions to air of NPI-listed substances can be represented conceptually by Equation 8.

Equation 8

$$E_{kpy,i} = \text{Amount in}_i - \text{Amount out}_i$$

where:

$E_{kpy,i}$ = emissions of pollutant i, kg/yr
Amount in_i = amount of pollutant i entering the process, kg/yr
Amount out_i = amount of pollutant i leaving the process as a waste stream, article or product, kg/yr

The term "Amount out_i" may actually involve several different fates for an individual pollutant. This 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 fates for the pollutant of interest is necessary for an accurate emission estimate to be made using the mass balance approach.

The amount of a particular substance entering or leaving a facility is often mixed within a solution as a formulation component or as a trace element within the raw material. To determine the total weight of the substance entering or leaving the process, the concentration of the substance within the material is required. Using this concentration data, Equation 9 can be applied as a practical extension of Equation 8.

Equation 9

$$E_{kpy,i} = [Q_{in} * C_{in} - Q_{pr} * C_{pr} - Q_{rec} * C_{rec} - Q_{waste} * C_{waste}] / 10^6$$

where:

$E_{kpy,i}$ = emissions of pollutant i, kg/yr
Q_{in}, Q_{pr}, Q_{rec}, Q_{waste} = quantity of raw material, product, recycled material or waste respectively, that is processed annually (generally expressed in kg for solids, L for liquids)
C_{in}, C_{pr}, C_{rec}, C_{waste} = concentration of substance i in the raw material, product, recycled material or waste respectively, that is processed annually (generally expressed in mg/kg for solids, mg/L for liquids)
10^6 = conversion from milligrams to kilograms.

Example 4 illustrates the application of Equation 9.

Example 4 - Using a Mass Balance for NH_3 Emissions

This example shows how NH_3 emissions to air may be calculated using Equation 9 within a synthetic ammonia manufacturing process. The facility operates 7200 hours a year, and produces 235 150 tonnes of NH_3 per year determined from gas usage, however only 235 120 tonnes of NH3 a year is utilised as the final product. Assuming the only sources of loss are to wastewater and air, the following information is provided from water testing:

Volume of wastewater per year: 150 ML/y = $150 * 10^6$ L/y
Concentration of NH_3 in water: 80 mg/L

Utilising Equation 9:

$$E_{kpy,i} = [Q_{in} * C_{in} - Q_{pr} * C_{pr} - Q_{rec} * C_{rec} – Q_{waste} * C_{waste}] / 10^6$$
$$= [235\,150\,000 – 235\,120\,000 – ((150 * 10^6 * 80) / 10^6)]$$
$$= 30\,000 – 12\,000.$$
$$= 18\,000 \text{ kg } NH_3 \text{ emitted per year}$$

Where a facility uses a 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 in effluent streams, which is itself a listed substance and require reporting where annual emissions total 10 tonnes or more.

Wastewater treatment may precipitate the reportable chemical in a sludge. Facilities are often required to obtain data on the concentration of metals or other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge multiplied by the concentrations of the substance in the sludge. 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.

For many chemicals used and emitted during chemical processes, some degradation in treatment may occur so that all the chemical is not transferred to the sludge. Facilities can estimate the amount of reportable compounds 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.

3.3 Using Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source to some common activity associated with those emissions. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted divided by the unit weight, volume, distance, or duration of the activity emitting the substance, eg. kilograms of ammonia emitted per tonne of synthetic ammonia.

Equation 10 is used to estimate a facility's emissions from application of emission factors.

Equation 10

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

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 of pollutant i, %.

Emission control technologies, such as electrostatic precipitators, fabric filters or baghouses, and wet scrubbers, are commonly installed to reduce the concentration of particulates in process off-gases before stack emission. Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been used in emission estimation, the collection efficiency of the abatement equipment needs to be considered.

With regards to emission controls for PM_{10}, in the absence of measured data, or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 90% should be used in the emission factor equation to calculate actual mass emissions. This default should only be used if there is no other available control efficiency.

Application of Equation 10 is illustrated by Example 5.

Example 5 - Using Emission Factors

Table 6 shows that 1.1 kg of ammonia is emitted from the condensate steam stripper for each tonne of synthetic ammonia produced. It is assumed that the facility operates for 5 400 hours per year and activity rate is 2 t/hr.

$$EF_{Ammonia} = 1.1 \text{ kg/t}$$
$$E_{kpy,Ammonia} = A * OpHrs * EF_{Ammonia} * [1-CE_i / 100]$$
$$= 2 * 5\,400 * 1.1$$
$$= 11880 \text{ kg } NH_3 \text{ per year}$$

Table 4 - Emission Factors for Volatile Organic Compounds (VOCs) from Synthetic Ammonia Manufacturing[a, b]

Type of Operation	Substance	CASR[c] Number	Emission Factor (kg/tonne)
Feedstock desulfurisation	*n*-Hexane	110-54-3	0.00432
Primary reformer: External combustion boiler: *Natural gas*	*n*-Hexane	110-54-3	0.00006
	Cyclohexane	110-82-7	0.00006
	Formaldehyde	50-00-0	0.00048
	Benzene	71-43-2	0.00024
	Toluene	108-88-3	0.00012
Residual oil	*n*-Hexane	110-54-3	0.01000
	Formaldehyde	50-00-0	0.08000
	Acetone	67-64-1	0.05320
Carbon dioxide (CO_2) Regeneration	*n*-Hexane	110-54-3	0.000624
Condensate steam stripper	*n*-Hexane	110-54-3	0.00072

Source: USEPA, VOC / PM Speciation data system, October 1992.
[a] Emission Factors Rating: E
[b] Factor units are kg of substance emitted per tonne of ammonia produced.
[c] CASR = Chemical Abstract Service Registry.

Table 5 - Emission Factors for Non-Organics from Synthetic Ammonia Manufacturing[a,b]

Type of Operation	Substance	Emission Factor (kg/tonne)
Primary reformer: External combustion boiler:		
Natural gas	Boron (B)	0.007
Residual oil	Boron (B)	0.044
	Chlorine (Cl)	0.0065
	Manganese (Mn)	0.0005
	Zinc (Zn)	0.0005

Source: USEPA, VOC / PM Speciation data system, October 1992.
[a] Emission Factor Rating: E
[b] Factor units are kg of substance emitted per tonne of ammonia produced.

Table 6 - Uncontrolled Carbon Monoxide (CO), Total Volatile Organic Compounds (VOCs), Sulfur Dioxide (SO2) and Ammonia (NH3) Emission Factors for a Typical Ammonia Plant[a,b]

Emission Point	Emission Factor			
	CO kg/tonne	Total VOCs kg/tonne	SO_2 kg/tonne	NH_3 kg/tonne
Desulfurisation unit regeneration	6.9	2.7[e]	0.0288[c]	NA
Carbon dioxide (CO_2) regenerator	1.0	0.39[e]	NA	1.0
Condensate steam stripper	NA	0.6[d]	NA	1.1

Source: USEPA, AP-42 Section 8.1, July, 1993.
[a] Emission Factor Rating: E
[b] Factor units are kg of substance emitted per tonne of ammonia produced.
[c] Normalised to a 24-hour emission factor. Total sulfur is 0.0096 kg per tonne.
[d] Mostly methanol.
[e] Total VOCs adjusted from total organic compounds (TOCs) emission factors using CARB, 1991.
NA = not applicable

Emission factors developed from measurements for a specific process can sometimes be used to estimate emissions at other sites. Should a company have several processes of similar operation and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources. You are required to have the emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

3.4 Using Engineering and Site-Specific Equations

Theoretical and complex equations or *models* can be used for estimating emissions from synthetic ammonia manufacturing. 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 synthetic ammonia manufacturing processes 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 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. For details of the use of vapour pressure and mass transfer based equations, refer to the *Emission Estimation Technique Manual for Fugitive Emissions*

3.4.1 Fugitive Emissions

Many engineering equations presented in the *Emission Estimation Technique Manual for Fugitive Emissions* are for estimating emissions from organic liquids. 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 synthetic ammonia manufacturing, it may be necessary to estimate emissions of inorganic compounds for NPI-reporting purposes. This is particularly the case for mineral acids and ammonia in the gas/vapour phase.

Emission estimates of inorganic compounds can be obtained for synthetic ammonia manufacturing processes by the following methods:

- 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 7 and Equation 11; or
- Use the emission factors from Table 8.

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 process lines at synthetic ammonia plants. Equation 11 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 8. An example of this estimation technique is given at Example 6.

Equation 11

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

where:

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

ER_i = emission rate, kg/hr/source

C_i = concentration of pollutant i in the equipment, %

OpHrs= operating hours, hr/yr

Table 7 - 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/source)		Correlation Equation (kg/hr/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 which is the actual mass emission rate of a leak.

[a] SV is the screening value (ppmv) measured by a monitoring device and is an indication of the concentration level of any leaking material at the leak interface. 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 6 - Calculating Fugitive Chemical Leaks

A synthetic ammonia plant operates a light-liquid pump on an 80 percent ammonia solution storage tank. The pump is run for 8 760 hours during the year.

For a Screening Value of zero ppmv

OpHrs = 8 760 hr / yr

SV (screening value) = 0 ppmv

Default-zero emission rate = $7.5 * 10^{-6}$ kg / hr / source

NH_3 emissions = $ER_i * (C_i / 100) * OpHrs$

= $7.5 * 10^{-6} * (80 / 100) * 8\ 760$

= $5.26 * 10^{-2}$ kg / yr / source

For a Screening Value of 20 ppmv

OpHrs = 8 760 hr / yr

SV (screening value) = 20 ppmv

NH_3 emissions = $1.90 * 10^{-5} (SV)^{0.824}$

= $1.90 * 10^{-5} (20)^{0.824}$

= $2.24 * 10^{-4}$ kg / hr / source

NH_3 emissions = $2.24 * 10^{-4} * 8\ 760 * (80 / 100)$

= 1.68 kg NH_3 / yr / source

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 8, 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 12 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 8.

Equation 12

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

where:

$E_{kpy,i}$ = emission rate of pollutant x from all equipment in the *stream* of a given equipment type, kg/yr
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 7 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 7 - 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 8 and Equation 12. 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} / 100) * OpHrs * N

Stream A

$E_{kpy,NH3}$ = 0.0199 * (80 / 100) * 8 760 * 15

= 2 092 kg NH_3 / yr

Stream B

$E_{kpy,NH3}$ = 0.0199 * (100 / 100) * 4 380 * 12

= 1 046 kg NH_3 / yr

Table 8 - 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	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0104
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.

4.0 Emission Estimation Techniques: Acceptable Reliability and Uncertainty

This section is intended to give a general overview of some of the inaccuracies associated with each of the techniques. Although the National Pollutant Inventory does not favour one emission estimation technique over another, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions from synthetic ammonia manufacturing facilities. The technique chosen is dependent on available data, available resources, and the degree of accuracy sought by the facility in undertaking the estimate. In general, site-specific data that is representative of normal operations is more accurate than industry-averaged data, such as the emission factors presented in Section 3.0 of this Manual.

4.1 Direct Measurement

Use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions from synthetic ammonia manufacturing facilities. However, collection and analysis of 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 one 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 all aspects of production of synthetic ammonia.

In the case of CEMS, instrument calibration drift can be problematic and uncaptured data can create long-term incomplete data sets. However, it may be 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 Mass Balance

Calculating emissions from a synthetic ammonia manufacturing facility using mass balance appears to be a straightforward approach to emission estimations. However, it is likely that few Australian industries consistently track material usage and waste generation with the overall accuracy needed for application of this method. 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.

4.3 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from synthetic ammonia manufacturing processes.

Use of emission equations to estimate emissions from synthetic ammonia manufacturing facilities is a more complex and time-consuming process than the use of emission factors. Emission 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.

4.4 Emission Factors

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks. They 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 5.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

When using emission factors, you 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/process selected in applying the factor, and the target equipment/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

5.0 References

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USEPA, March 1990, *AIRS Facility Subsystem Source Classification Codes And Emission Factor Listing For Criteria Pollutants,* EPA-450/4-90-003, United States Environmental Protection Agency, Research Triangle Park, NC, USA.

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USEPA, July 1993, *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42, Section 8.1 Synthetic Ammonia*, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, USA.
http://www.epa.gov/ttn/chief/ap42.html

The following Emission Estimation Technique Manuals are available at the NPI Homepage and from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Phosphate Manufacturing;
- Emission Estimation Technique Manual for Urea Manufacturing;
- Emission Estimation Technique Manual for Ammonium Sulfate Manufacturing; and
- Emission Estimation Technique Manual for Sewage and Wastewater Treatment.