



National Pollutant Inventory

Emission Estimation Technique Manual

for

Alumina Refining

First Published in March 1999

**EMISSION ESTIMATION TECHNIQUES
FOR THE
ALUMINA REFINING INDUSTRY**

TABLE OF CONTENTS

1.0	INTRODUCTION	1
2.0	REPORTABLE SUBSTANCES.....	2
3.0	EMISSION ESTIMATION TECHNIQUES.....	4
	3.1 Use of Emission Factors.....	5
	3.2 Mass Balance Techniques	5
	3.3 Software Models.....	6
4.0	LOCATING EETS IN THIS MANUAL.....	7
	4.1 Assessing Emissions from Your Facility	7
	4.2 Using this Manual	7
	4.3 Alumina Refining Inputs/Outputs.....	8
5.0	IDENTIFICATION OF INDUSTRY EMISSIONS.....	13
	5.1 Combustion Sources	13
	5.2 Aggregate Handling and Storage	14
	5.2.1 Bauxite.....	14
	5.2.2 Limestone and Other Aggregate.....	15
	5.3 Bulk Chemical Handling and Storage.....	16
	5.4 Bauxite processing.....	16
	5.4.1 Grinding.....	16
	5.4.2 Digestion.....	17
	5.4.3 Precipitation and Clarification	18
	5.4.4 Classification	18
	5.5 Drying/Calcining	19
	5.6 Spent Process Material Storage.....	19
	5.7 Maintenance and Support Functions.....	20
6.0	EMISSIONS TO AIR	21
	6.1 Combustion Sources	21
	6.1.1 NPI-Listed Substances	21
	6.1.1.1 SO ₂ Emissions Using Mass Balance.....	22
	6.1.1.2 Emissions of NPI-Listed Substances Using Emission Factors.....	22
	6.1.2 Organic Compound Emissions.....	25
	6.1.3 Trace Elements from Combustion Sources.....	25
	6.1.3.1 Mass Balance	26
	6.1.3.2 Emission Factors.....	26
	6.2 Emissions from Materials Handling and Storage	28
	6.3 Process Sources	28

6.3.1 Emission Factors	28
6.3.2 Control Technologies	29
6.4 VOC Emissions	30
6.4.1 Total VOC Emissions	30
6.4.2 VOC Speciation.....	30
6.4.2.1 Speciation Based on Process Stream Composition	30
6.4.2.2 Speciation Using Developed Weight Fraction Data	31
6.5 Materials Storage	32
6.5.1 Acid Storage	31
6.5.2 Organic Liquids Storage.....	32
6.6 Trace Element Speciation.....	33
7.0 MASS BALANCE	34
7.1 Overall Facility Mass Balance	34
7.2 Individual Unit Process Mass Balance	37
8.0 MONITORING	38
9.0 EMISSIONS TO WATER.....	40
10.0 EMISSIONS TO LAND.....	44
10.1 Groundwater Monitoring	44
10.2 Spills.....	45
10.3 On-Site Disposal.....	46
11.0 ASSUMPTIONS AND DISCUSSION	47
Combustion Sources	47
Trace Elements.....	47
12.0 REFERENCES.....	48
APPENDIX A: NPI SUBSTANCES RELEVANT TO ALUMINA REFINING	49
APPENDIX B: PROCESS DESCRIPTION AND FLOW DIAGRAM.....	53

ALUMINA REFINING

LIST OF FIGURES & TABLES

Figure 1. Raw Materials Handling.....	9
2. Digestion.....	10
3. Drying and Calcining.....	10
4. Liquor Purification	11
5. Maintenance and Renovation Operations	12
6. Water Management.....	12
Table 1. Activities with the Potential to Trigger NPI Reporting	2
2. NPI Substances Emitted from Combustion.....	14
3. NPI Emissions from Bauxite Storage and Handling.....	15
4. NPI Emissions from Lime/Limestone Storage and Handling.....	15
5. NPI Emissions from Bulk Chemical Storage.....	16
6. NPI Emissions from Grinding of Bauxite	19
7. NPI Emissions from Digestion.....	17
8. NPI Emissions from Precipitation and Clarification	18
9. NPI Emissions from Calcining.....	19
10. NPI Emissions from Spent Material Processing.....	20
11. NPI Emissions from Maintenance and Support Functions	20
12. NPI-Listed Substances Emission Factors for Fuel Oil Combustion	26
13. NPI-Listed Substances Emission Factors for Gas Combustion	27
14. Emission Factors For Organic Emissions from Oil Combustion.....	28
15. Emission Factors For Organic Emissions from Gas Combustion.....	29
16. Emission Factors For Trace Elements From Fuel Oil Combustion.....	30
17. Emission Factors For Trace Elements From Gas Combustion.....	31
18. Emission Factors for Alumina Refining Processes.....	29
19. Speciation of VOCs for Alumina Refining.....	31
20. Acid Properties	31
21. Speciation Data from Alumina Refining	33
22. Example 2: Measurement Data	43

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 the alumina refining industry.

EET MANUAL: Alumina Refining

HANDBOOK: Alumina Production

ANZSIC CODE: 2721

The alumina refining activities covered by this Manual include:

- Raw material handling and storage;
- Bauxite processing (including grinding, digesting, precipitating, and drying);
- Ancillary operations including descaling, residue storage, and associated maintenance activities; and
- On-site combustion.

This Manual was drafted by Pacific Air & Environment, in conjunction with the NSW Environment Protection Authority, 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. Particular thanks are due to the Australian Aluminium Council and its members for their comments, advice, and information.

2.0 Reportable Substances

The NPI Guide at the front of this Handbook provides guidance to help you determine:

- Whether you are required to report under the NPI; and
- What substances are to be reported.

Section 2 of *The NPI Guide* details the necessary steps to be taken to assess whether your facility triggers any thresholds for the substances listed under the NPI. A series of worksheets are provided to assist with this exercise.

Steps 1 to 4 below provide some general guidance on the substances that are likely to require reporting.

Step 1: Identify activities that trigger thresholds

Review the activities that have the potential to trigger reporting based on the threshold criteria in *The NPI Guide*. Table 1 presents the activities associated with alumina refining that have the potential to trigger thresholds.

Table 1. Activities with the Potential to Trigger NPI Thresholds.^a

Activity	Threshold Trigger Category
Combustion (fuel type and usage) ^{b,d}	Category 2a and 2b substances
Storage/use of bauxite ^{c,d}	Category 1
Storage/use of bulk chemicals ^e	Category 1
Maintenance and Support ^e	Category 1

^a Appendix A of this Manual lists the NPI substances that are expected to be emitted from alumina refining facilities.

^b Due to the amount of fuel consumed, it is likely that all alumina refineries will be required to report on the listed Category 2a and 2b substances.

^c The trace metals present in bauxite may lead to reporting thresholds being exceeded. For example, an alumina refinery handling 500,000 tonnes of bauxite annually would need 20 ppm of an NPI-listed substance in the bauxite to trigger reporting for that substance.

^d When reviewing each operation, ensure that all feedstock is reviewed for trace metals that may be present.

^e Material Safety Data Sheets (MSDSs) can be reviewed to determine the composition of other products used on site.

Step 2: Calculate the quantity of each substance to ascertain if reporting threshold has been triggered

Using data on the composition of each substance (ie. MSDS, laboratory analysis, or other), multiply the concentration of each NPI-listed substance present by the annual usage. For example, if you know the trace metal composition of the bauxite, multiply the concentration of NPI-listed metals by the total annual tonnage used. This should be done for each aggregate (and other relevant raw materials) used in the refining process. If the total quantity of any NPI-listed substance exceeds 10 tonnes, then you must report the emissions of that substance wherever it is released in the facility.

Step 3: Identify activities associated with the emission of each NPI substance

Section 5 of this Manual identifies the unit activities that produce (or may produce) emissions of NPI-listed substances. It is important to recognise that, for each substance, there may be more than one activity that leads to its emission.

Step 4: Identify appropriate EETs for use in quantifying emissions

Once you have identified each activity that has the potential to release the substances, the next step is to identify an appropriate EET for the estimation of emissions. EETs for air, water, and land are provided in Sections 6, 9, and 10 of this Manual respectively. Specific guidance on the application of mass balance, and monitoring to emissions estimation are provided in Sections 7 and 8 respectively.

Additional guidance on the interpretation of ‘transfers’ as it applies to alumina refining is provided in Section 4.

NPI Substances

Category 1 and 1a Substances

The reporting criteria for Category 1 and 1a substances, as detailed in Clause 10 of the NPI NEPM, are:

- a Category 1 listed substance is only reportable if 10 tonnes or more of the substance is used per annum;
- the only Category 1a substance is Total Volatile Organic Compounds (VOCs) for which the throughput threshold is 25 tonnes per annum;
- “use” means processed (eg. crude oil throughput, production chemicals, drilling fluids), or coincidental production (eg substances contained in produced formation water, emissions from dehydrator regeneration etc); and
- substances in proprietary mixtures are not reportable unless the substance is specified in a Material Safety Data Sheet or, in the case of any other material, the occupier of the facility could reasonably be expected to know that the substance is contained in the material.

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.

The total amount of each Category 1 and 1a substance ‘used’ must be calculated in order to determine whether the threshold is exceeded. This involves developing a cumulative total for the use of each NPI substance from various sources.

3.0 Emission Estimation Techniques

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 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.

There is a range of EETs available for the estimation of emissions from alumina refining. The EETs presented in this Manual as alternatives to direct measurement are:

- emission factors;
- mass balance; and
- software models.

Each of these EETs are discussed briefly in Sections 3.1 to 3.3 below.

3.1 Use of Emission Factors

Emission factors are generally developed through the testing of a particular source population (eg. various boilers combusting a particular fuel). This information is used to relate the quantity of a pollutant emitted to some general measure of the activity. For example, boiler emission factors are typically expressed as emissions per quantity of fuel consumed. Because emissions estimated using emission factors are not derived through testing the actual source, they are subject to uncertainty.

Emission factors require ‘activity data’, which is combined with the factor to generate the emission estimates. The generic formula is:

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

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, %.

For example, if the emission factor has units of ‘*kg pollutant/m³ of fuel burned*’, then the activity data required would be ‘*m³ fuel burned/hr*’, thereby generating an emission estimate of ‘*kg pollutant/hr*’.

3.2 Mass Balance Techniques

Mass balance involves the quantification of total materials into and out of a process, with the difference between inputs and outputs being accounted for in terms of emissions to the environment, or as part of the facility waste. Mass balance is particularly useful when the input and output streams can be quantified, and this is most often the case for individual process units and operations.

Mass balance techniques can be applied across individual unit operations, or across an entire facility. These techniques are best applied to systems with prescribed inputs, defined internal conditions, and known outputs. It is essential to recognise that the estimates derived using mass balances are only as good as the values used in performing the calculations. For example, small errors in data or calculation parameters (eg. pressure, temperature, stream concentration, flow, control efficiencies etc) can result in large errors in the final emission estimations. In addition, if sampling of input or output materials is

conducted, failure to use representative samples will also contribute to the uncertainty of the result. Section 7 of this Manual provides additional guidance on the application of mass balance techniques, as well as a worked example.

3.3 Software Models

Software models are available that predict emission rates for fugitive emissions, landfills, lagoons, open dumps, waste piles, land treatment operations, and other source areas. These can be used either as a “screening” tool, or for in-depth investigations that require site-specific data. A range of information (eg. chemical and/or physical characteristics of specific substances) is typically also required to utilise such software packages. The use of these software packages has been included in this Manual (where relevant), for the purpose of characterising and estimating emissions.

While software models frequently require an initial investment of time, they can provide long term benefits because they can be used relatively easily and quickly to re-estimate emissions.

4.0 Locating EETs in this Manual

4.1 Assessing Emissions from your Facility

In this Manual, Emission Estimation Techniques (EETs) are presented in the following sections:

- Section 6: Emissions to Air;
- Section 9: Emissions to Water; and
- Section 10: Emissions to Land.

Section 6 (emissions to air) is subdivided into defined activities within refining operations, and where possible, EETs have been identified. However, you should note that there are substances for which emission estimation techniques are not currently available. In some cases, it may be possible to use mass balance or available emissions monitoring data to characterise emissions. You should refer to Sections 7 and 8 of this Manual for additional guidance on the application of these EETs. If you are unable to estimate emissions using these EETs, you will need to develop your own EET and have it approved by your State or Territory Environmental Authority.

Section 9 provides an overview of those emissions to water that are to be reported to the NPI.

In a similar manner, Section 10 provides some general guidance on those emissions to land that are reportable to the NPI.

It is important to remember that the Measure for the NPI defines an emission as an emission of a substance to the environment whether in pure form, or contained in other matter, and whether in solid, liquid, or gaseous form. It includes the emission of a substance to the environment from landfill, sewage treatment plants, and tailings dams, but does not include:

- (a) deposit of a substance into landfill; or
- (b) discharge of a substance to a sewer or a tailings dam; or
- (c) removal of a substance from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

4.2 Using this Manual

The NPI Guide at the front of this Handbook lists all of the substances reportable under the NPI and the associated reporting thresholds. *The NPI Guide* should be consulted to ascertain whether your facility handles, manufactures, or otherwise uses any of the substances presented in the list, and to determine whether any thresholds are exceeded. If the facility is found to trigger any thresholds, then emissions to air, water, and land must be quantified. Once the reportable substances have been identified, the next step is to establish the substances that are emitted from each activity. Section 5 highlights the NPI substances potentially emitted from each activity, and indicates whether the emission is to air, water and/or land. It should be noted that reporting is not required for transfers.

Once you have reviewed your operations and listed the substances emitted from each activity, turn to the appropriate section (ie Section 6 for emissions to air, Section 9 for emissions to water and Section 10 for emissions to land) and apply the EETs as described. *(NB. Note: The information provided in this Manual is comprehensive. However, there are cases where no EETs are currently available.)*

Example 1

For example, Chromium (III) and compounds are NPI-listed substances and reporting is triggered through fuel use ('Category 2b') and compositional make up of bauxite ('Category 1'). To quantify emissions of chromium (III) and compounds, you need to perform the following steps:

Step 1: Identify the activities on site with the potential to emit chromium

The following activities are associated with the emission of chromium (III):

- Combustion (air and, if using coal, also ground and groundwater through presence of leachate from the ash storage);
- Bauxite handling and storage;
- Bauxite processing; and
- Spent material processing

Step 2: Locate the EETs

EETs for each of the above sources are presented in the following sections:

Air Emissions: Section 6

Section 6.1: Combustion (Section 6.1.3 deals with trace metals);

Section 6.2: Emissions from aggregate handling and storage;

Sections 6.3 and 6.4: Emissions from bauxite processing;

Water Emissions: Section 9

Bauxite storage has the potential for generation of diffuse runoff.

Spent processing material also has the potential to generate runoff.

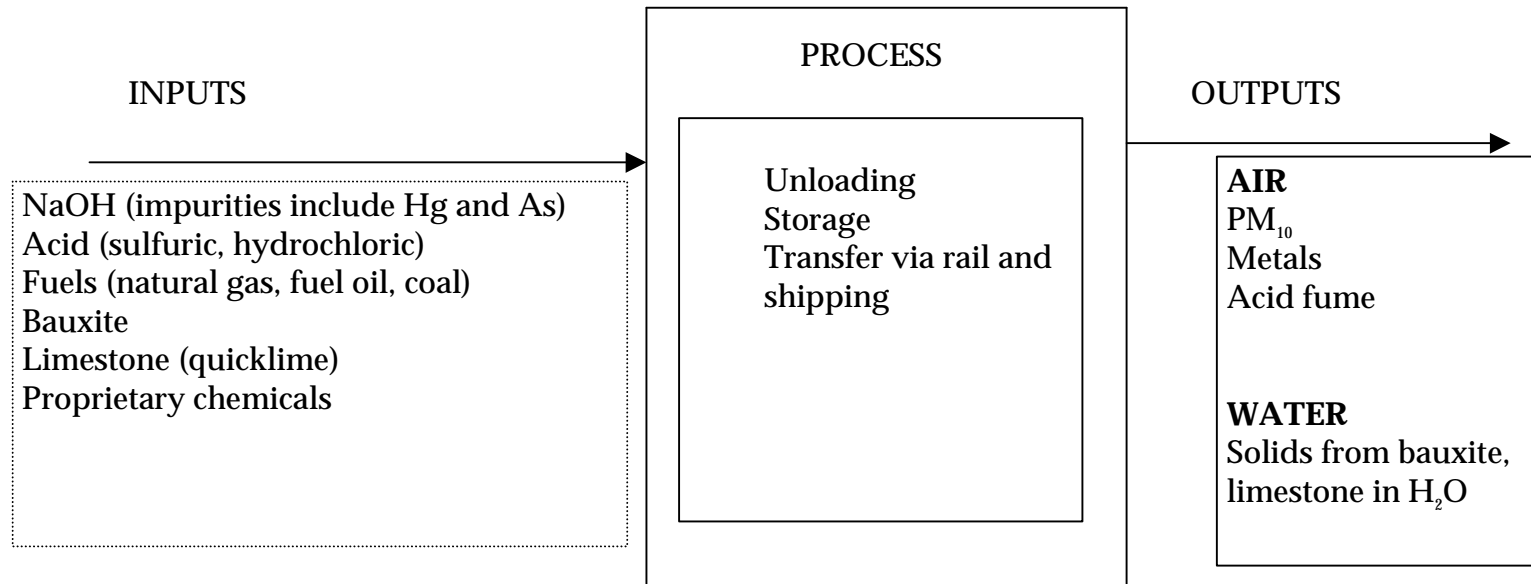
Land Emissions: Section 10

Leachate from the storage of red mud and ash (if coal is used).

4.3 Alumina Refining Inputs/Outputs

Figures 1 to 6 below show the raw materials inputs to, and outputs from, the various alumina refining processes expected to result in the emission of NPI-listed substances.

FIGURE 1: RAW MATERIALS HANDLING



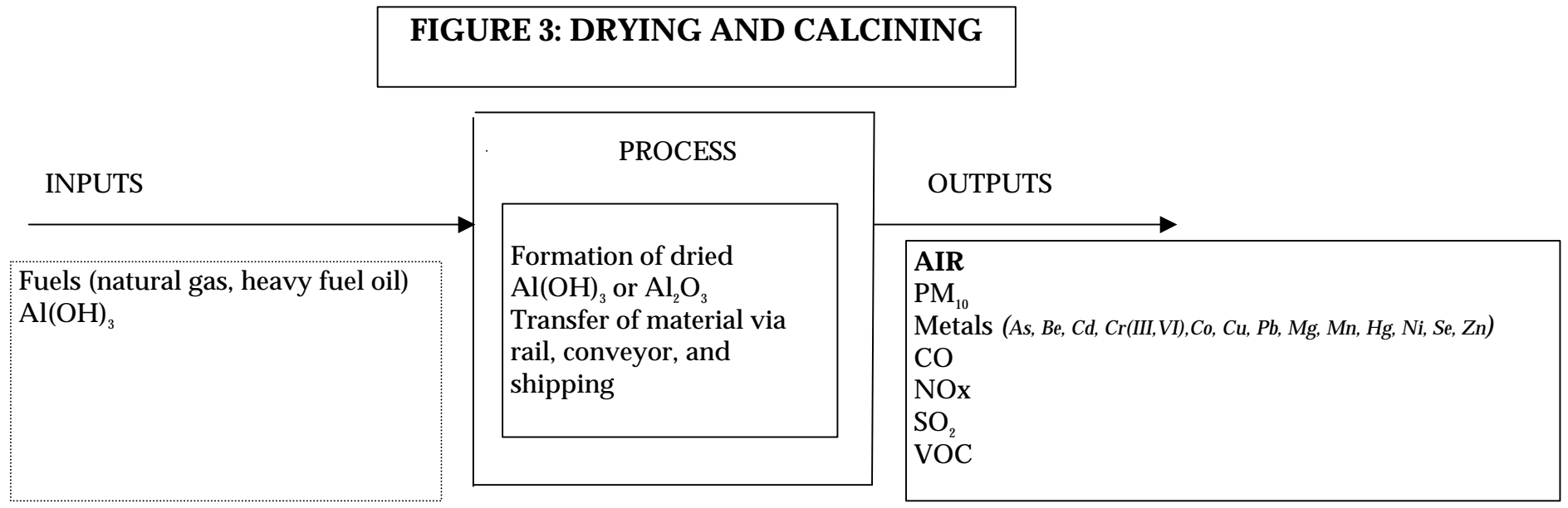
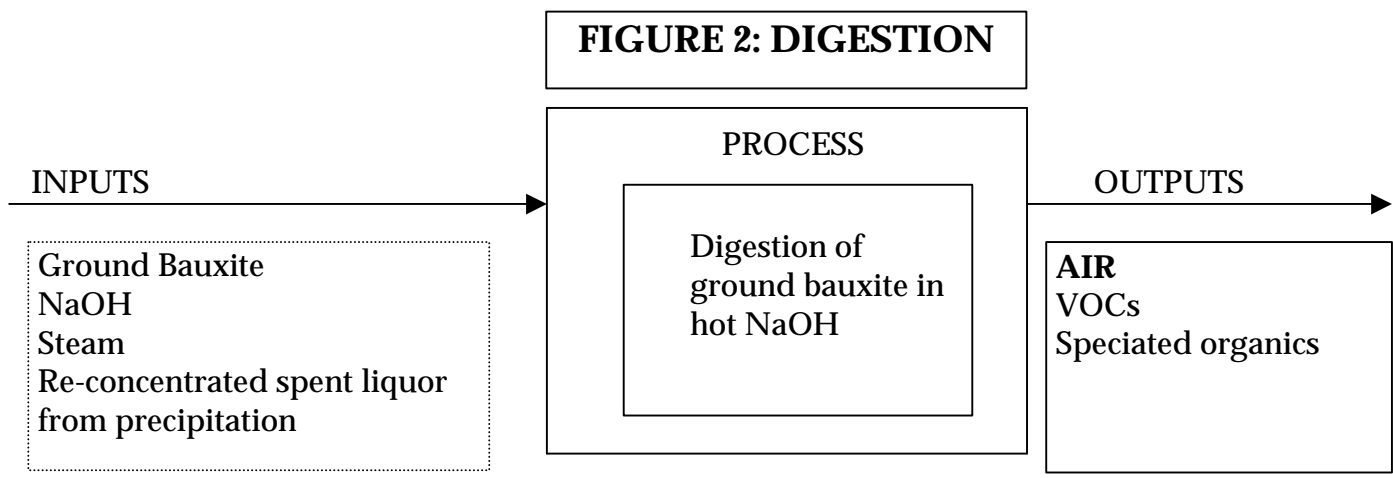


FIGURE 4: LIQUOR PURIFICATION

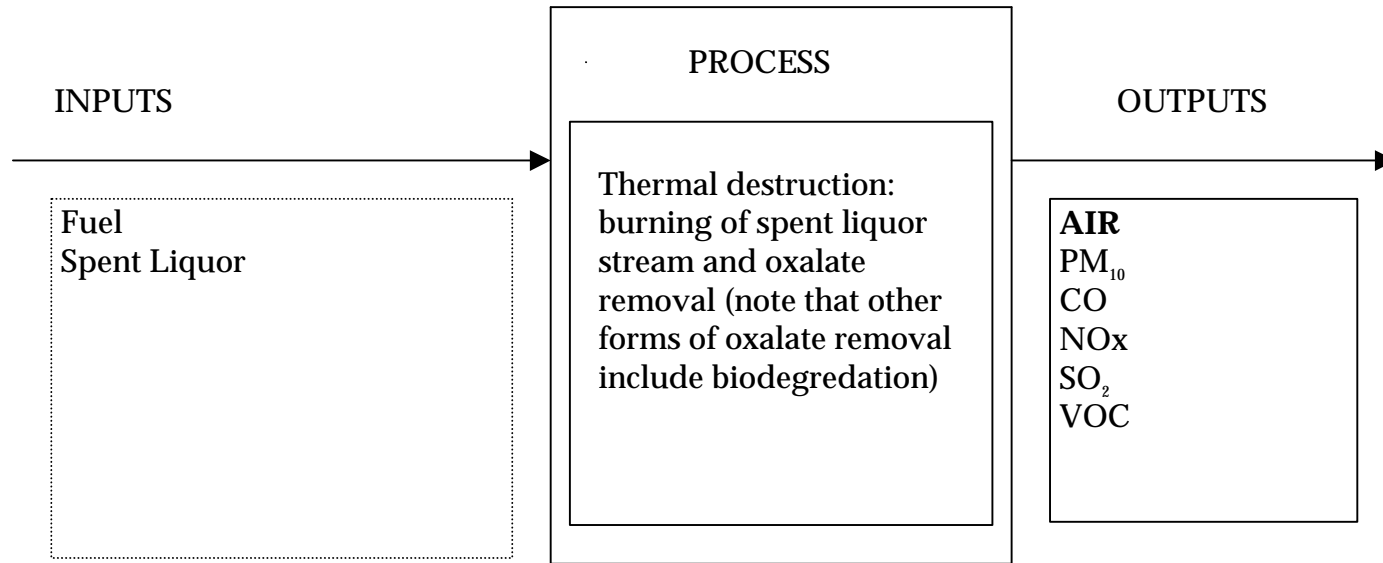


FIGURE 5: MAINTENANCE AND RENOVATION OPERATIONS

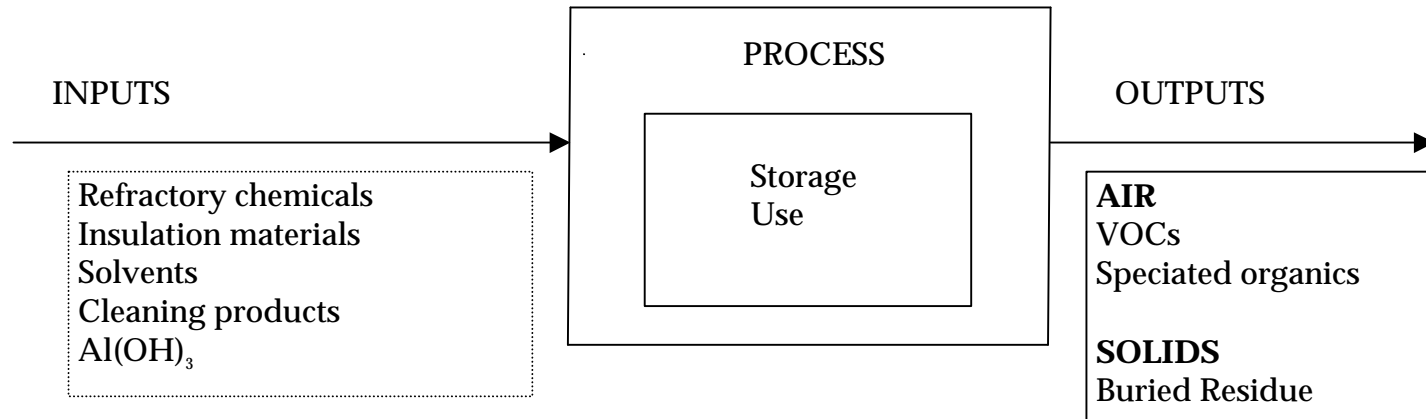
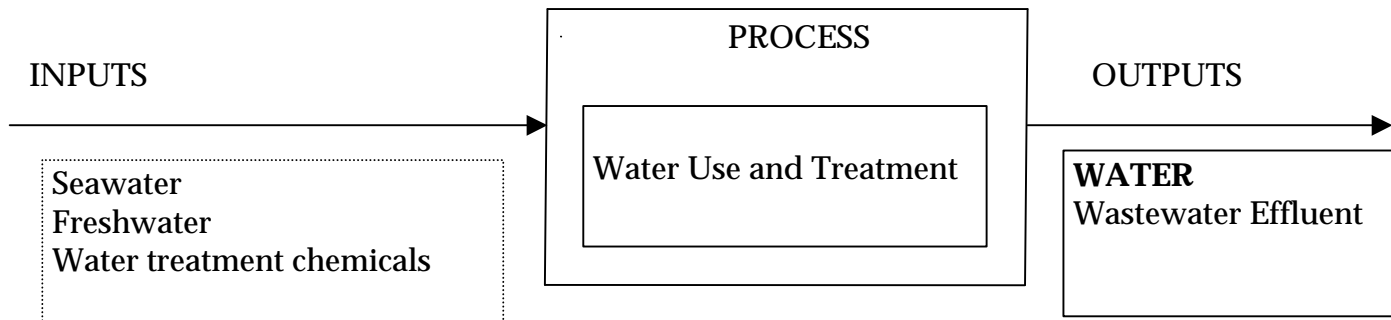


FIGURE 6: WATER MANAGEMENT



5.0 Identification of Industry Emissions

This section identifies the basic generic sources that may be relevant to your facility. A detailed process description and flow diagram are included in Appendix B.

The NPI-listed substances emitted (or expected to be emitted) from the various activities associated with alumina refining are found in the following sections:

- Section 5.1: Combustion sources
- Section 5.2: Aggregate storage and handling
- Section 5.3: Bulk chemical handling and storage
- Section 5.4: Bauxite processing
- Section 5.5: Drying/Calcining
- Section 5.6: Spent material storage
- Section 5.7: Maintenance and support functions

5.1 Combustion Sources

Many facilities generate heat (for further use in the process), energy and/or steam on-site through combustion of natural gas, fuel oil, and/or coal. Air emissions are the key emissions from combustion of natural gas and fuel oil. Coal also gives rise to air emissions, as well as coal ash from the combustion process. Emissions of NPI substances to air from combustion sources are likely to include the various compounds listed in Table 2.

Table 2. NPI Substances Emitted from Combustion

NPI Substances Potentially Emitted	Emissions to Air	Land Emissions
Oxides of Nitrogen SO ₂ CO VOCs including but not limited to: Benzene toluene xylenes ethylbenzene PAHs formaldehyde acetone n-hexane acetaldehyde phenol PM ₁₀ giving rise to the following speciated substances: antimony and compounds arsenic and compounds beryllium and compounds cadmium and compounds chromium (III) compounds chromium (VI) compounds cobalt and compounds copper and compounds lead and compounds fluoride compounds manganese and compounds nickel and compounds selenium and compounds zinc and compounds mercury and compounds (fume)	EETs for oil and gas are presented in Section 6 of this Manual. EETs for coal combustion presented in <i>Emission Estimation Technique Manuals for Combustion in Boilers and Fossil Fuel Electric Power Generation</i> .	Potential for leachate from ash storage (See Section 10 of this Manual).

5.2 Aggregate Handling and Storage

5.2.1 Bauxite

Bauxite is transferred from the carrier (in some cases this may be a marine vessel), or directly from the bauxite mine to the site storage via conveyor. The material is stockpiled on site and transferred to the bauxite processing area for conversion into alumina. Each facility may have a different set up. A typical bauxite handling and storage scenario would include the following:

- Unloading or “transporting to processing site” via conveyor;
- Stockpiling; and
- Transfer from stockpile to bauxite processing.

Potential emissions are provided in Table 3.

Table 3. NPI Emissions from Bauxite Storage and Handling

NPI Substances Potentially Emitted	Emissions to Air	Water Emissions
PM ₁₀ giving rise to the following speciated substances: arsenic and compounds boron and compounds chromium (III) compounds chromium (VI) compounds cobalt and compounds copper and compounds fluoride compounds manganese and compounds selenium and compounds zinc and compounds	Fugitive dust (EETs in Section 6)	Potential for diffuse runoff due to rain (EET in Section 7).

5.2.2 Limestone and other Aggregate

Lime or limestone is transferred on-site and stockpiled. A typical scenario would include the following:

- Unloading;
- Stockpiling; and
- Transfer to bauxite processing

Potential emissions of NPI substances are provided in Table 4.

Table 4. NPI Emissions from Lime/Limestone Storage and Handling

NPI Substances Potentially Emitted	Emissions to Air	Emissions to Water
PM ₁₀	Fugitive dust (EETs in Section 6)	Potential for diffuse runoff due to rain (EET in Section 7)

5.3 Bulk Chemical Handling and Storage

Bulk chemicals stored on site in tanks for use in the process may include:

- hydrochloric acid;
- sulfuric acid;
- diesel;
- petrol;
- LPG;
- chlorine;
- biocides;
- flocculants; and
- defoamers

Note: Other Category 1 substances may also be used in quantities that may trigger the 10 tonne reporting threshold. These will need to be identified and assessed on a facility by facility basis.

As indicated in Table 5, these substances may be released to air. However, there is also the potential for emissions to land from spills.

Table 5. NPI Emissions from Bulk Chemical Storage

NPI Substances Potentially Emitted	Emissions to Air	Emissions to Land
Hydrochloric acid; Sulfuric acid; VOCs and speciated organics released from the handling/storage of hydrocarbons	Storage of these substances in fixed roof tanks may give rise to fugitive emissions into the atmosphere (EETs in Section 6)	Section 10 provides a discussion on spills, and how these may be characterised

5.4 Bauxite processing

Bauxite processing includes grinding, digestion, drying, and calcining. These processes give rise to air emissions, and the formation of spent process material.

5.4.1 Grinding

The bauxite is crushed and finely ground in a mill prior to the digestion process. The grinding process gives rise to air emissions as indicated in Table 6. The use of a control technology, such as a spray tower, floating bed scrubber, or cyclone, can help reduce particulate emissions. Where grinding is carried out using wet milling, no dust emissions would be expected.

Table 6. NPI Emissions from Grinding of Bauxite

NPI Substances Potentially Emitted	Emissions to Air
Particulate (including PM ₁₀) giving rise to the following speciated substances: arsenic and compounds; boron and compounds; chromium (III) compounds; chromium (VI) compounds; cobalt and compounds; copper and compounds; fluoride compounds; manganese and compounds; selenium and compounds; and zinc and compounds.	Air emissions through mill ventilation (EETs in Section 6).

5.4.2 Digestion

Finely ground bauxite is slurried with sodium hydroxide solution and lime and reacted at high pressure and temperature to remove the iron oxides, and most of the silicon oxides. The pressure, temperature, and retention time in the digester is a function of the mineral composition of the bauxite. Sodium aluminate is formed, and the silicon, iron, titanium, and calcium oxides form the insoluble components of the solid waste residual.

During the digestion process, volatile organic components of the ore are vented and emitted to air as fugitives. Table 7 provides a list of possible NPI substances emitted from the digestion process.

Table 7. NPI Emissions from Digestion

NPI Substances Potentially Emitted	Emissions to Air
VOCs including, but not limited to: Methanol; Ethanol; Acetaldehyde; Acetone; Benzene; Cyclohexane; Ethylbenzene; Xylenes (all isomers); Styrene; Chloroform; Trichloroethane; and PAHs. Other compounds, including: Hydrogen Sulfide; Carbon Disulfide; and Sulfur Dioxide.	Fugitive emissions of organic volatiles and other compounds (EETs in Section 6).

5.4.3 Precipitation and Clarification

The hot slurry is usually cooled by flash evaporation, producing steam that is used to preheat the incoming slurry. The slurry is then processed in a series of clarification steps designed to separate the solid residual from the liquor. The steps can include the following:

- Passage of slurry through hydrocyclones to remove grit;
- Addition of flocculant (ie. starch or other settling agents) to settle fine particles;
- Filtration of clear overflow;
- Washing of underflow in thickeners to remove caustic, which is then sent on as spent product;
- Sending of filtrate (containing sodium aluminate) to precipitator; and
- Crystallisation and precipitation of aluminum hydroxide.

As indicated in Table 8, the precipitator may also give rise to fugitive emissions of volatile organic substances similar to the substances identified for the digester.

Table 8. NPI Emissions from Precipitation and Clarification

NPI Substances Potentially Emitted	Emissions to Air
VOCs including, but not limited to: Methanol; Ethanol; Acetaldehyde; Acetone; Benzene; Cyclohexane; Ethylbenzene; Xylenes (all isomers); Styrene; Chloroform; Trichloroethane; and PAHs. Other compounds including: Hydrogen sulfide; Carbon disulfide; and Sulfur dioxide.	Organic volatiles and other compounds released through process vents (EETs in Section 6).

5.4.4 Classification

After precipitation, the slurry (containing trihydrate crystals) is sent to classification where the product is classified according to crystal size. The coarse particles are:

- washed to remove excess sodium hydroxide;
- dewatered on vacuum filters; and
- sent to calcination.

The finer crystals are recycled to the precipitation process as seed, thereby providing nucleation sites for precipitation to occur. Spent liquor from the precipitators is recycled to the digesters.

5.5 Drying/Calcining

The coarse alumina is calcined in rotary kilns or fluid-bed calciners at about 1000°C. During calcination, water is driven off. Calciners produce hot flue gases containing alumina and water vapour. Two types of kilns are used in the refining industry: oxalate, and liquor burning. CO is produced in the oxalate process.

Typical control equipment includes cyclonic separators, followed by ESPs. The control equipment can also be used to recover product as well as to minimise emissions. Typical emissions are provided in Table 9. You should note that the emissions associated with this activity depend on the specific fuel being used.

Table 9. NPI Emissions from Calcining

NPI Substances Potentially Emitted	Emissions to Air
VOCs PAHs CO NO _x SO ₂ PM ₁₀ giving rise to the following speciated substances: arsenic and compounds; boron and compounds; chromium (III) compounds; chromium (VI) compounds; cobalt and compounds; copper and compounds; fluoride compounds; manganese and compounds; selenium and compounds; and zinc and compounds.	Stack emissions from the kiln (EETs in Section 6).

5.6 Spent Process Material Storage

The following spent process material is generated during the refining process:

- red mud from precipitator and clarifier;
- refractory linings (linings from furnaces, and reactors, etc);
- descaling waste (scrapping out vessel); and
- coal ash from coal combustion.

Since these materials are processed on-site, they do not need to be reported under the NPI. The potential for emission of NPI substances occurs under the following circumstances:

- leachate is emitted into the ground and/or groundwater; and/or
- runoff from the site is emitted into a water body; and/or
- fugitive air emissions are emitted into the atmosphere.

An indication of the possible NPI emissions and associated sources are provided in Table 10.

Table 10. NPI Emissions from Spent Material Processing

NPI Substances Potentially Emitted	Source	Emissions to Air	Emissions to Water	Emissions to Land
PM ₁₀ giving rise to the following speciated substances: arsenic and compounds; boron and compounds; chromium (III) compounds; chromium (VI) compounds; cobalt and compounds; copper and compounds; fluoride compounds; manganese and compounds; selenium and compounds; and zinc and compounds. Organics (see precipitation)	Red mud from alumina processing	Fugitive emissions from the surface (storage) as well as handling (EETs in Section 6)	Surface runoff (EETs in Section 9)	Leachate (EETs in Section 10)
Chromium (III) and Chromium (VI) compounds	Refractory waste	Refractory waste	Refractory waste	Refractory waste
See above (red mud)	Descaling waste	Descaling waste	Descaling waste	Descaling waste
Organics Metals as per red mud	Coal ash	Coal ash	Coal ash	Coal ash

5.7 Maintenance and Support Functions

Maintenance and support functions are unlikely to trigger the reporting of NPI substances because of the quantities of materials handled. However, a substance may be reportable as a result of other activities that do trip thresholds and hence, maintenance and support emissions will need to be included as indicated in Table 11.

Table 11. NPI Emissions from Maintenance and Support Functions

NPI Substances Potentially Emitted	Source	Emissions to Air
See Appendix A for listing of potential solvents	Solvent usage for maintenance	EET in Section 6

6.0 Emissions to Air

Emissions to the atmosphere are divided into the following generic categories:

- Section 6.1: Combustion sources (ie. furnaces and boilers);
- Section 6.2: Materials handling and storage;
- Section 6.3: Process emissions (eg. precipitation, digestion etc.); and
- Section 6.6: Vent emissions from bulk storage.

Sections 6.4 and 6.5 respectively, provide guidance on the speciation of emissions of particulate matter, and VOCs. In addition to the EETs discussed in this Section, the general application of mass balance techniques and monitoring for emission estimations are discussed in Section 7 and Section 8 of this Manual.

6.1 Combustion Sources

Combustion is a process used in alumina refining. Natural gas and fuel oil combustion emissions are considered in this section.

NB: Air emissions from coal combustion are handled separately in the 'Emission Estimation Technique Manual for Combustion in Boilers' and the 'Emission Estimation Technique Manual for Fossil Fuel Electric Power Generation'.

For the purposes of this Manual, the NPI substances emitted from combustion processes are divided as follows:

- Section 6.1.1: NPI-Listed Substances (NO_x , SO_2 , PM_{10} , CO and total VOCs);
- Section 6.1.2: Organic compound speciation; and
- Section 6.1.3: Trace elements from Combustion Sources (including metals and compounds such as fluorides, ammonia, carbon disulfide, etc.).

Holding furnaces are also included in the 'combustion category'.

6.1.1 NPI-Listed Substances

The NPI-listed substances released by combustion sources are:

- Oxides of nitrogen (NO_x);
- Sulfur dioxide (SO_2);
- Particulate matter less than 10 micrometres (PM_{10});
- Carbon monoxide (CO); and
- Volatile organic compounds (VOCs).

Emission factors are provided for the estimation of these pollutants with the exception of SO_2 , for which the preferred estimation technique is mass balance based on the sulfur content of the fuel.

6.1.1.1 Emissions of SO₂ Using Mass Balance

Estimates of SO₂ emissions can be made using the following equation, which assumes 100% conversion of sulfur to SO₂:

$$\text{Emission of SO}_2 \text{ (kg/hr)} = \text{Fuel Usage (kg/hr)} * (\text{wt}\%S/100) * 2 \quad (2)$$

Where:

Fuel Usage = the feed rate of fuel (ie. oil or gas) to the combustion system in kg/hr
wt%S = the weight percent of sulfur (as elemental S) in the fuel

6.1.1.2 Emissions of NPI-Listed Substances Using Emission Factors

Table 12 and Table 13 below provide emission factors for use in estimating emissions of the NPI-listed substances from oil, and gas combustion sources respectively. The general term 'boiler' is used in these tables, however, the emission factors also apply to furnaces. In addition, the term 'uncontrolled' indicates that the emission factors assume that no pollution control devices are used to reduce the respective pollutants (eg. baghouse or ESP for PM₁₀, Low NO_x Burners for NO_x reduction, etc).

Table 12. NPI-Listed Substances Emission Factors for Fuel Oil Combustion ^{a, b}

Oil Type and Firing Configuration	Emission Factors (kg/m ³ oil fired)			
	NO _x ^c	CO	PM ₁₀ ^d	VOC
<i>Boilers > 30 MW</i>				
No. 6 oil fired, normal firing	5.6	0.6	0.71A+1.5	0.091
No. 6 oil fired, normal firing, LNB ^e	4.8	0.6	0.71A+1.5	ND
No. 6 oil fired, tangential firing	3.8	0.6	0.71A+1.5	0.091
No. 6 oil fired, tangential firing, LNB ^e	3.1	0.6	0.71A+1.5	ND
No. 5 oil fired, normal firing	5.6	0.6	0.71A+1.5	0.091
No. 5 oil fired, tangential firing	3.8	0.6	0.71A+1.5	0.091
No. 4 oil fired, normal firing	5.6	0.6	0.71A+1.5	0.091
No. 4 oil fired, tangential firing	3.8	0.6	0.71A+1.5	0.091
No.2 oil fired	2.9	0.6	1.54	ND
No.2 oil fired, LNB/FGR ^c	1.2	0.6	1.54	ND
<i>Boilers < 30 MW</i>				
No. 6 oil fired	6.6	0.6	0.86A+1.5	0.034
No. 5 oil fired	6.6	0.6	0.86A+1.5	0.034
No. 4 oil fired	2.4	0.6	0.86A+1.5	0.024
Distillate oil fired	2.4	0.6	1.54	0.024

^a Source: USEPA (1998a). The oil type categories are defined as follows:

No. 5 and 6 Fuel Oil: These are very heavy fuel oils containing significant quantities of nitrogen, sulfur, and ash. No. 6 fuel oil is sometimes referred to as Bunker C.

No. 4 Fuel Oil: This is typically a mixture of distillate and residual oils.

Distillate Oil: This is more volatile and less viscous than the other oils, has negligible nitrogen and ash contents, and usually contains less than 0.3 percent sulfur.

^b These emission factors apply to uncontrolled sources, unless otherwise indicated.

^c NO_x emission factors are expressed as NO₂. A more accurate method for estimating NO_x emissions from industrial boilers (i.e. < 30 MW) is to apply the following equation:

kg NO₂ / m³ oil fired = 2.47 + 12.53(N), where N is the weight percent of nitrogen in the oil.

^d Particulate emission factors for residual oil combustion without emission controls are typically a function of fuel oil grade, and sulfur content:

No. 6 oil: A = 1.12(S) + 0.37 kg/m³, where S is the weight percent of sulfur in the oil.

No. 5 oil: A = 1.2 kg/m³

No. 4 oil: A = 0.84 kg/m³

Depending on the fuel type burned, the appropriate factor for 'A' should be substituted where known into the relevant PM₁₀ factor in the table.

^e LNB = Low NO_x Burners, FGR = Flue Gas Recirculation

Table 13. NPI-Listed Substances Emission Factors for Gas Combustion ^a

Combustion System Type	Emission Factors (kg/10 ⁶ m ³ gas fired)			
	NO _x ^b	CO	PM-10	VOC
<i>Wall Fired Boilers > 30 MW</i>				
Uncontrolled	4480	1344	122	88
Controlled – Low NOx burners	2240	1344	122	88
Controlled – Flue gas recirculation	1600	1344	122	88
<i>Boilers < 30 MW</i>				
Uncontrolled	1600	1344	122	88
Controlled – Low NOx burners	800	1344	122	88
Controlled – Flue gas recirculation	512	1344	122	88
<i>Tangential-Fired (All Sizes)</i>				
Uncontrolled	2720	384	122	88
Controlled – Flue gas recirculation	1216	1568	122	88

^a Source: USEPA (1998b). These emission factors are based on the fuel gas at 15 degrees C and 1 atm.

^b NO_x emission factors are expressed as NO₂.

Scaling Emissions According to Heating Value

The emission factors presented in **Table 12** and **Table 13** are based on the volumetric quantity of fuels burned in each boiler/furnace. These factors are based on fuels with the standard heating values listed below:

- Fuel oil No. 4, 5 and 6: 41.8 GJ/m³
- Fuel oil No. 2 and distillate: 39 GJ/m³
- Fuel gas: 37.2 MJ/m³

While it is stated in AP-42 (USEPA, 1997a) that the gas heating value is the higher heating value, no information of this nature is specified with regards to the oil heating values. However, as the gas data refers to the higher heating value, it is assumed that this also applies to the oil heating values.

Emissions calculated using the emission factors provided in **Table 12** and **Table 13** must be scaled according to a ratio of the fuel's actual heating value, to the standard values supplied above. The emission factors provided in the tables should be applied using the following generic formula:

$$E_i = EF_i * Q_f * \text{Actual Heating Value/Standard Heating Value} \quad (3)$$

E_i = Emission, kg/hr

EF_i = Emission factor, kg/m³

Q_f = Fuel usage, m³/hr

6.1.2 Organic Compound Emissions

There are a range of organic compounds released during the combustion of fuel oil and gas. For those organic compounds on the NPI substance list, emission factors are presented in Table 14 and Table 15 for oil, and gas combustion respectively.

It is important to note that the emission factors presented in Table 14 and Table 15 reflect the data available in the literature. It is possible that other NPI substances are also emitted, but no information on such emissions is available. Refer to Section 11.0 for a discussion of these emission factors.

Table 14. Emission Factors for Organic Emissions from Oil Combustion ^a

NPI Substance	Emission Factor (kg/10 ⁶ m ³ oil fired)
Benzene	2.57 * 10 ⁻⁵
Toluene	7.44 * 10 ⁻⁴
Xylenes ^b	9.01 * 10 ⁻⁴
Ethylbenzene	7.63 * 10 ⁻⁶
PAH's	1.43 * 10 ⁻⁴
Formaldehyde	3.96 * 10 ⁻³
Acetone ^c	1.01 * 10 ⁻²
n-Hexane ^c	1.80 * 10 ⁻³

^a Source: USEPA (1998a), unless otherwise indicated.

^b Source: USEPA (1997b).

^c Source: USEPA (1993).

Table 15. Emission Factors for Organic Emissions from Gas Combustion ^a

Organic Compound	Emission Factor (kg/10 ⁶ m ³ gas fired)
Benzene	3.4 * 10 ⁻²
Toluene	5.4 * 10 ⁻²
Acetaldehyde ^b	0.13
Formaldehyde	1.2
Phenol ^b	0.062
PAH's	1.1 * 10 ⁻²
n-Hexane	29

^a Source: USEPA (1998b), unless otherwise indicated.

^b Source: USEPA (1997b).

You should note that, in a similar manner to the estimation of emissions of NPI-listed substances resulting from the combustion of oil and gas, the emissions calculated using the emission factors provided in Table 14 and Table 15 must be scaled, based on the fuel's actual heating value. (See Section 6.1.1.2 for a further discussion of this).

6.1.3 Trace Elements from Combustion Sources

Emissions of certain trace elements can be estimated using mass balance when fuel composition data is available. If such data is unavailable, default emission factors can be used. This Section is divided into two categories, with the first examining emission estimation using mass balance (ie. where and how it is applicable), and the second relating to emission factors.

6.1.3.1 Mass Balance

Mass balance is the preferred methodology for estimating ‘uncontrolled’ emissions of metals resulting from fuel and gas combustion. This approach assumes that 100 percent of the trace elements present in the fuels are released into the atmosphere upon combustion (this assumption is discussed further in Section 11.1.2).

To use this mass balance methodology, the two key data requirements are:

1. The metal content of the fuels utilised in each boiler and furnace; and
2. The fuel consumption rate for each combustion source.

The above inputs can then be applied using the following equation:

$$ER = Q_f * \text{Metal Content of Fuel (wt\%)} / 100 \quad (4)$$

ER = Emission rate, kg/hr

Q_f = Fuel usage, kg/hr

Example 2

The following data is known about the fuel and its usage at a refinery:

- the cadmium (Cd) content of the fuel oil is approximately 0.3 ppmwt (parts per million by weight); and
- the fuel oil usage of the boiler is approximately 1100 kg/hr.

Therefore, the emission rate of ‘cadmium and compounds’ (assuming that 100 percent of the cadmium entering the boiler is released in the flue gases) is derived as follows:

$$1100 \text{ kg/hr fuel oil} * 0.3 \text{ kg Cd} / 10^6 \text{ kg fuel oil} = 3.3 * 10^{-4} \text{ kg/hr}$$

The *uncontrolled* emission rate of cadmium and compounds is, therefore, $3.3 * 10^{-4}$ kg/hr.

6.1.3.2 Emission Factors

In the event that insufficient data is available to derive emission estimates of metals using mass balance, the emission factors presented in Table 16 and Table 17 may be used for oil and gas combustion respectively. The oil types relating to Table 16 are discussed in Section 6.1.1.2. The general use of emission factors is discussed in Section 3.1.

Table 16. Emission Factors for Trace Elements from Fuel Oil Combustion ^a

Trace Element (and Compounds)	Distillate Oil Combustion ^b (kg/m ³)	Residual Oil Combustion ^c (kg/m ³)
Antimony	ND ^d	6.3 * 10 ⁻⁴
Arsenic	6.71 * 10 ⁻⁵	1.5 * 10 ⁻⁴
Beryllium	5.03 * 10 ⁻⁵	3.3 * 10 ⁻⁶
Cadmium	5.03 * 10 ⁻⁵	4.8 * 10 ⁻⁵
Chromium (III) ^e	ND	7.2 * 10 ⁻⁵
Chromium (VI)	ND	3.0 * 10 ⁻⁵
Cobalt	ND	7.2 * 10 ⁻⁴
Copper	1.01 * 10 ⁻⁴	2.1 * 10 ⁻⁴
Lead	1.51 * 10 ⁻⁴	1.8 * 10 ⁻⁴
Manganese	1.01 * 10 ⁻⁴	3.6 * 10 ⁻⁴
Mercury	5.03 * 10 ⁻⁵	1.4 * 10 ⁻⁵
Nickel	5.03 * 10 ⁻⁵	1.0 * 10 ⁻²
Selenium	2.52 * 10 ⁻⁴	8.2 * 10 ⁻⁵
Zinc	6.67 * 10 ⁻⁵	3.5 * 10 ⁻³
Fluoride	ND	4.5 * 10 ⁻³

^a Source: USEPA (1997a).

^b 'Distillate' also includes No. 2 fuel oil (refer to Section 6.1.1.2).

^c 'Residual' includes fuel oil No. 4, 5 and 6 (refer to Section 6.1.1.2).

^d 'ND' = No data available.

^e Data was supplied for total Cr and Cr(VI). The estimate for Cr(III) was derived by assuming that after subtracting Cr(VI), all remaining Cr is trivalent (ie. Cr(III)).

Table 17. Emission Factors for Trace Elements from Gas Combustion ^a

Trace Element (and Compounds)	Emission Factor (kg/10 ⁶ m ³)
Arsenic	3.2 * 10 ⁻³
Beryllium	1.9 * 10 ⁻⁴
Chromium (VI) ^b	1.1 * 10 ⁻³
Cobalt	1.3 * 10 ⁻³
Copper	1.4 * 10 ⁻²
Cadmium	1.8 * 10 ⁻²
Lead	8.0 * 10 ⁻³
Manganese	6.1 * 10 ⁻³
Mercury	4.2 * 10 ⁻³
Nickel	3.4 * 10 ⁻²
Selenium	3.8 * 10 ⁻⁴
Zinc	4.6 * 10 ⁻¹

^a Source: USEPA (1998a) unless otherwise indicated.

^b Source: USEPA (1997b)

You should note that reporting is only required for those substances that trigger reporting thresholds. It is possible that these thresholds are *not* triggered for all of the compounds listed in the tables above. Refer to *The NPI Guide* at the front of this Handbook for more information.

6.2 Emissions from Materials Handling and Storage

In the specific context of alumina refining, no EETs are currently available to quantify emissions from these operations. However, many of the materials handling and storage activities conducted at alumina refineries are similar to those found at mine sites (see the *Emission Estimation Technique Manual for Mining* for further details).

6.3 Process Sources

Emission estimation techniques for grinding, precipitation, digestion, drying and calcining will vary depending on the type of data available. The intent of the NEPM and the Memorandum of Understanding is that no additional monitoring of emissions will be required over and above that already conducted by facilities (eg. for licensing, and/or other regulatory requirements). If source testing is performed for other compliance programs, then the results can be used for emissions estimation.

You should note that in addition to the EETs discussed in this Section, emissions can be estimated using other methodologies provided in this Manual such as mass balance (refer Section 7) and/or monitoring data (refer Section 8).

6.3.1 Emission Factors

An alternative to direct measurement or mass balances is the use of emission factors. You should note that although the number of NPI-listed substances presented in this Section is limited, other NPI-listed compounds may also be emitted.

Emission factors for particulate and fluoride emissions from grinding and calcining operations are presented in Table 18. In addition, you should refer to Section 6.4 of this Manual for additional guidance regarding the speciation of particulate emissions.

There is limited information available on emissions of volatile organic compounds (VOCs) from process operations. Section 6.6 of this Manual discusses VOC emissions further, and provides additional information regarding the speciation of VOC emissions.

Table 18. Emission Factors for Alumina Refining Processes ^a

Operation	Total Particulate ^{d,e} (kg/tonne)
Bauxite grinding ^b	
Uncontrolled	3
Spray tower	0.9
Floating bed scrubber	0.85
Quench tower and spray screen	0.5
Aluminum hydroxide calcining	
Uncontrolled ^c	100
Spray tower	30
Floating bed scrubber	28
Quench tower	17
ESP	2

^a Source: USEPA, (1997a). For bauxite grinding, factors expressed as kg/tonne bauxite processed. For aluminium calcining, factors expressed as kg/tonne of alumina produced.

Neg = negligible

^b Note that many Australian alumina refineries use wet milling. In this situation, the dust emissions are expected to be zero.

^c After multicyclones

^d The data available in the literature pertains to total particulate rather than the NPI-listed PM₁₀. In the absence of better data, the total particulate data can be used to provide conservative upper bounds for PM₁₀ emissions.

^e With regards to emission controls for PM₁₀, 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.

6.3.2 Control Technologies

As shown in Table 18 above, emission factors are available for both uncontrolled and controlled emissions.

Where available however, it is preferable to use the actual pollutant reduction efficiencies of control technologies, rather than the defaults provided above. 'Actual' control efficiency data can be combined with an 'uncontrolled' emission estimate using Equation 1, an example is presented below.

This equation can be applied when uncontrolled emissions and the control efficiency associated with the particular control equipment utilised are known.

Example 3

The 'uncontrolled' emission estimate for PM₁₀ from calcining is 5000 tonnes per year. A wet scrubber, with a known reduction efficiency of 90 percent, is used to aid in controlling emissions. Therefore, using Equation 1, the 'controlled' emission estimate is derived as follows:

$$\begin{aligned}\text{Controlled Emission} &= 5000 * (1-90/100) \\ &= 5000 * 0.1 \\ &= 500 \text{ tonnes/annum}\end{aligned}$$

Thus, the particulate emission after considering the particulate emission control is 500tonnes/annum.

6.4 VOC Emissions

6.4.1 Total VOC Emissions

Very little data is available to estimate total VOC emissions from alumina refining operations. Currently, emissions can only be estimated using source test data collected at refining facilities, if such data is available. Total VOC emission estimates can then be speciated using the methodologies outlined in the following section.

6.4.2 VOC Speciation

Once total VOC emissions have been estimated, these emissions can be speciated into NPI-listed substances using either:

1. Process stream composition data; and/or
2. Available speciation data (in the form of weight fractions) from the USEPA.

The first methodology is likely to give more accurate estimates than those derived by using generic weight fractions developed by the USEPA. The speciation data from USEPA is limited and, therefore, a combination of these two methodologies may be required.

Each of these VOC speciation methods will be discussed in greater detail in the following sections.

6.4.2.1 Speciation Based on Process Stream Composition

This methodology involves using the compositional data for each process stream (ie. obtained from analytical procedure such as GC/MS), and applying this data to approximate the vapour phase composition.

This EET relies on the following equation to speciate emissions from a single source:

$$E_i = E_{\text{VOC}} * (WP_i / WP_{\text{VOC}}) \quad (5)$$

Where:

- E_i = The mass emissions of NPI substance "i" (kg/hr)
- E_{VOC} = The total VOC mass emission rate from a source (fugitive or stack)
- WP_i = The concentration of NPI substance "i" in weight percent
- WP_{VOC} = The VOC concentration in weight percent.

6.4.2.2 Speciation Using Developed Weight Fraction Data

In the absence of analytical data, the default VOC speciation data presented in Table 19 can be used to characterise emissions of NPI-listed substances. As previously mentioned, only limited VOC speciation data has been found in the literature. Applying this speciation data requires the use of an equation similar to that in Section 6.4.2.1, as follows:

$$E_i = E_{\text{VOC}} * (WP_i / 100) \quad (6)$$

Where:

- E_i = The mass emissions of NPI substance "i" from the source (kg/hr)
- E_{VOC} = The total VOC mass emission rate (kg/hr)
- WP_i = The weight percent of the relevant compound in the VOC emission (as provided in Table 19).

Table 19. Speciation of VOCs for Alumina Refining^a

Substance	M Wt	Weight Percent
Cyclohexane	84.16	2.3
Formaldehyde	30.03	18.2
Benzene	78.11	9.1
Toluene	92.13	4.5

^aSource: USEPA (1990).

A much greater range of compounds was originally supplied, with the weight fractions all summing to 100%. The compounds shown in the table above are those present on the NPI substance list.

The degree of speciation that can be performed using this method is limited, and it is possible that other compounds present on the NPI substance list will be identified in the VOCs emitted.

6.5 Materials Storage

6.5.1 Acid Storage

Emissions from the storage of acids can be estimated by assuming that the vapour space within the storage tank is saturated, and at atmospheric pressure. Using the following table, and assuming ideal gas properties, an estimate can be derived.

Table 20. Acid Properties^a

Acid	Partial Pressure (kPa)	Volume Percent
Sulfuric Acid ^b	$0.277 * 10^{-5}$	$2.73 * 10^{-6}$
Hydrochloric Acid ^c	1.41	1.4

a Source: Perry & Green (1997). Based on 1 atm and 20C

b Note that Table 2-14 on page 2-82 of Perry & Green (1997) provides an extensive table specifying the properties of sulfuric acid at various storage temperatures and solution concentrations. The term 'Vol%' above (and in the equation below) is derived by dividing the partial pressure taken from this table, by the ambient pressure of 101.3 kPa (note that the pressure data as read from the table in Perry's is in units of 'bars').

c Concentration = 30%. Similarly to footnote b, Table 2-10 on page 2-76 in Perry & Green (1997) provides relevant hydrochloric acid properties.

To estimate emissions during filling operations to acid storage tanks, the following formula can be used (based on the ideal gas law):

$$E = 0.042 * MW * V_{vs} * (Vol\%/100) \quad (7)$$

Where:

E = Mass of acid emitted during filling (kg)

MW = Molecular Weight of acid (for Hydrochloric Acid = 36.5 kg/kmol;
Sulfuric Acid = 98 kg/kmol)

V_{vs} = Volume of the vapor space in the tank = volume of acid added (m³).

Vol% = Volume percent from above table.

6.5.2 Organic Liquids Storage

EETs for the storage of organic liquids (eg. fuels) can be found in the *Emission Estimation Technique Manual for Fuel and Organic Liquid Storage*.

6.6 Trace Element Speciation

Metals can be speciated based on trace analysis data, or MSDS information provided by the vendor. This data can be combined with particulate emissions data (ie. collected as source test results and/or calculated by other estimation techniques) using the equation below:

$$E_{kpy,i} = (m)(c_i) \quad (8)$$

Where:

$$\begin{aligned} E_{kpy,i} &= \text{mass emission of component i (kg/yr)} \\ m &= \text{mass emission rate of particulate (kg/yr)} \\ c_i &= \text{mass fraction of component i (mg/kg *10}^{-6}\text{), see Table 21.} \end{aligned}$$

You should note that this methodology is most applicable to emissions from low temperature sources, such as stockpiles. This is because this methodology is based on the intrinsic assumption that all metals are contained by the released particulate matter. While this may be a reasonable assumption for metals with very low vapour pressures, more volatile metals such as mercury are likely to be partially present in vapour form at increased temperatures. However, insufficient information is currently available to produce better estimates than those derived by source testing.

In addition, metals can be speciated in bauxite and red mud using data presented in the literature, as provided in Table 21. This data can be combined with particulate emission data using the equation provided above.

Table 21. Speciation Data from Alumina Refining^{a,b,c,d}

NPI Substance	Bauxite (mg/kg)	Red Mud (mg/kg)
Antimony	0.2	0.3
Arsenic	16.6	29.0
Beryllium	0.4	0.7
Cadmium	2.6	4.5
Chromium	179.0	314.0
Cobalt	12.6	22.0
Copper	15.4	27.0
Lead	5.7	10.0
Manganese	94.0	165.0
Mercury	<0.03	<0.05
Nickel	<3.0	<5.0
Selenium	<6.0	<10.0
Zinc	18.3	32.0
Boron	<12.0	<20.0
Fluorine	645.0	1130.0

^a Source: Department of Agriculture, WA (1993)

^b Based on the ratio 3.5 tonnes bauxite yields 2 tonnes red mud

^c A large Refinery can generate 3.5 Mt/annum

^d WA figures for speciation may not represent all bauxite. It is acknowledged that the mineralogy and processing efficiencies vary from site to site.

7.0 Mass Balance

Mass balances involve examining a process to determine whether emissions can be characterised based on an analysis of operating parameters, material composition, and total material usage. Mass balance involves the quantification of total materials into and out of a process with the difference between inputs and outputs being accounted for as an emission to the environment (to air, water, land), or as part of the facility's waste. Mass balance is particularly useful when the input and output streams can be readily characterised, and this is most often the case for small processes and operations.

Mass balance can be applied across an entire facility or across individual unit operations. Mass balance techniques and engineering estimates are best used where there is a system with prescribed inputs, defined internal conditions, and known outputs.

It is essential to recognise that the emission values produced when using mass balance are only as good as the values used in performing the calculations. For example, small errors in data or calculation parameters (eg. pressure, temperature, stream concentration, flow, control efficiencies) can result in potentially large errors in the final estimates. In addition, when sampling of input and/or output materials is conducted, the failure to use representative samples will also contribute to uncertainty. In some cases, the combined uncertainty is quantifiable, and this is useful in determining if the values are suitable for their intended use.

7.1 Overall Facility Mass Balance

Mass balances can be used to characterise emissions from a facility, providing that sufficient data is available pertaining to the process and relevant input and output streams. Mass balances can also be applied to an entire facility (see the example below). This involves consideration of material inputs to the facility (purchases), and materials exported from the facility in products and wastes, where the remainder is considered as a 'loss' (or an emission to the environment).

The mass balance calculation can be summarised by:

$$\text{Total mass into process} = \text{Total mass out of process}$$

In the context of the NPI, this equation could be written as:

$$\text{Inputs} = \text{Products} + \text{Transfers} + \text{Emissions}$$

Where:

Inputs: All incoming material used in the process.

Emissions: Emissions to air, water, and land (as defined under the NPI). Emissions include both routine and accidental emissions, as well as spills.

Transfers: As defined under the NPI NEPM, transfers include substances discharged to sewer, substances deposited into landfill and substances removed from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

Products: Products and materials exported from the facility.

Applying this to an individual NPI substance (substance 'i'), the equation may be written as:

Input of substance 'i' = Amount of substance 'i' in product + amount of substance 'i' in waste + amount of substance 'i' transformed/consumed in process + emissions of substance 'i'.

The mass balance approach can be used for any NPI-listed substance for which the facility is required to provide a report. Emissions to air, water and land can then be estimated. A simple example of the application of mass balance is presented below.

Example 4

A process uses 10 000 tonnes of raw material A, 5 000 tonnes of raw material B, and 20 000 tonnes of water to produce 22 000 tonnes of product, and 4 000 tonnes of by-product annually, where A and B are NPI-listed substances (NB. You are required to quantify NPI-listed substances only). What is the total amount of waste emitted from the process? How much of this should be reported under the NPI?

The general calculation process is presented as a series of steps:

Step 1: Calculate Total Inputs to Process

Total inputs:

$$\begin{aligned} &= \text{mass of A} + \text{mass of B} + \text{mass of water} \\ &= 10\,000 + 5\,000 + 20\,000 \\ &= 35\,000 \text{ tonnes} \end{aligned}$$

Step 2: Calculate Total Outputs from Process

Total outputs:

$$\begin{aligned} &= \text{mass of product} + \text{mass of by-product} \\ &= 22\,000 + 4\,000 \\ &= 26\,000 \text{ tonnes} \end{aligned}$$

Step 3: Calculate Total Amount of Waste Produced

Total quantity of waste produced:

$$\begin{aligned} &= \text{mass of inputs} - \text{mass of outputs} \\ &= 35\,000 - 26\,000 \\ &= 9\,000 \text{ tonnes per annum.} \end{aligned}$$

Step 4: Identify Transfers and Spills

The facility will need to identify those wastes that are classed as transfers under the NPI. For example, of the 9000 tonnes per annum of waste produced, 2800 tonnes may be collected and sent for offsite disposal (ie. reporting not required), while approximately 6000 tonnes may be sent to an on-site water treatment facility prior to discharge to sewer (ie. reporting not required). This would then indicate that 200 tonnes of waste has been released into the environment (in the present example, the release is to atmosphere, but could also be a release direct to a water body). If the approximate proportions of substances A and B in the waste stream are known, the quantity of A and B released to the atmosphere can be determined. It is important to note that you should take into account the efficiency of any pertinent emission controls (eg. the waste may be routed through an incinerator that destroys most, or all of substances A and B before they are released to the atmosphere).

7.2 Individual Unit Process Mass Balance

The general mass balance approach described above can also be applied to individual unit processes. This requires that information is available on the inputs (eg. flow rates, concentrations, densities) and outputs of the unit process.

The following general equation can be used (NB. scm is an abbreviation for standard cubic metres – refer to Section 8):

$$E_i = \sum Q_f W_{fi} P_i - \sum Q_o W_{oi} P_o \quad (9)$$

Where:

- E_i = loss rate of component i to unknown stream (kg/hr)
- Q_f = Volumetric flow rate of inlet stream, i (scm/hr)
- Q_o = Volumetric flow rate of outlet stream, o (scm/hr)
- W_{fi} = Weight fraction of component i in inlet stream i
- W_{oi} = Weight fraction of component i in outlet stream o
- P_i, P_o = Density of streams i and o respectively (kg/scm)

Information on process stream input and output concentrations is generally known because this information is required for process control. The loss E_x will be determined through analysis of the process. You should note that it is then necessary to identify the environmental medium (or media) to which emissions occur.

8.0 Monitoring

Many facilities conduct monitoring as part of the existing regulatory requirements. Usually, the monitoring is tied directly to the conditions of an environmental licence and will vary from site to site.

It is important to recognise that facilities also collect a range of other information (beyond that derived from stack or liquid effluent testing), which can be used in characterising emissions for the NPI. Typical data collected includes:

- volumetric flow rates (eg. products, wastes, wastewater treatment);
- mass flowrates;
- stream composition;
- product and waste composition; and
- production and waste quantities.

In most situations, the use of monitoring data as a basis for calculating emissions will provide the most representative emissions information for a facility, and if available, this data should be used for emission calculations.

Monitoring data can be expressed in a range of units. The following discussion may be of assistance when converting monitoring results into annual emission estimates for the purposes of the NPI. It is important to remember that the calculation of annual emissions must also take into account the number of hours per year the source is discharging to the environment.

Stack data is commonly presented in terms of either actual flow, or a 'normalised' flow. The difference is that normalised data is standardised to a particular temperature and pressure, typically 0°C and 1 atm respectively. However, sometimes it may be referenced to 25°C and 1 atm. The following terms may be used when presenting data:

- acm – actual cubic metre (at actual temperature and pressure);
- scm – standard cubic metre (typically at 25°C and 1 atm, although sometimes it may be at 20°C, or even 0°C); and
- Nm³ – normal cubic metre (typically at 0°C and 1 atm);

It is essential to know the conditions under which the source test data is collected before determining annual emission estimates. You should note that the measured concentrations and flue gas flows are usually presented on source test reports at the same conditions (ie. temperature and pressure).

Provided below are two examples of the use of sampling data to characterise annual emissions. Example 5 is where the concentration of the compound is presented at the same conditions as the measured flow rate. Example 6 is where the concentration and flue gas flows are measured under different conditions.

Example 5

The following example relates to a situation where the concentration of the compound is presented at the same conditions as the measured flow rate.

The following data is known:

- the flue gas flow from a stack is measured at 30 Nm³/sec;
- the measured concentration of cadmium in the flue gas is 0.01 mg/Nm³; and
- the stack operates 24 hours per day for 300 days per year.

First of all, the number of seconds per year the stack is emitting is determined:

$$\begin{aligned}\text{No. seconds/year} &= (3600\text{sec/hour}) * (24\text{hours/day}) * (300\text{days/year}) \\ &= 2.6 * 10^7 \text{ seconds/year}\end{aligned}$$

Using this data, the emission is derived as follows:

$$\begin{aligned}\text{Emission} &= (30\text{Nm}^3/\text{sec}) * (0.01\text{mg}/\text{Nm}^3) * (2.6 * 10^7 \text{ sec/year}) \\ &= 7.8 \text{ kg of cadmium per year.}\end{aligned}$$

Example 6

If the concentration and flue gas flows are measured under different conditions then additional calculations are required. For this example, the following data is known:

- the flue gas flow from a stack is measured at 100 acm/sec;
- the flue gas flow from a stack is measured at 100 acm/sec;
- the stack operates 24 hours per day for 300 days per year; and
- the conditions at the stack tip are approximately 150°C and 1 atm.

Using the actual stack data, the 'actual' flue gas flow can be converted to a normalised flow using a ratio of temperatures. You should note that the temperatures must be presented using the absolute temperature scale of Kelvin (ie. 0°C = 273 K). The conversion is then performed as follows (noting that the actual stack conditions are 150 + 273 = 423 K):

$$\begin{aligned}\text{Flue gas (Nm}^3/\text{sec)} &= 100 \text{ acm/sec} * (273/423) \\ &= 64.5 \text{ Nm}^3/\text{sec}\end{aligned}$$

The emission rate is then derived using the same methodology as outlined in Example 5.

$$\begin{aligned}\text{Emission} &= (0.01 \text{ mg}/\text{Nm}^3) * (64.5 \text{ Nm}^3/\text{sec}) * (2.6 * 10^7 \text{ sec/year}) \\ &= 16.8 \text{ kg of cadmium per year.}\end{aligned}$$

9.0 Emissions to Water

It is important to recognise that, for the purposes of the NPI, the following are classed as transfers and are not required to be reported (NEPM, Clause 3(3)).

- Discharge of substances to sewer;
- Deposit of substances into landfill; and/or
- Removal of substances from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

The first stage in characterising emissions to water therefore is, to identify those emissions that are classed as transfers under the NPI. These emissions do not need to be reported under the NPI. Other emissions however (eg. discharges to surface water bodies such as streams and rivers), do need to be reported.

Discharges to water are highly process and site-specific. As a consequence, most facilities perform some monitoring to characterise these emissions. While the NPI does not require facilities to conduct monitoring to characterise emissions, it is likely that most facilities that discharge to water will have at least some monitoring data that can be used to assist in the characterisation of emissions. Examples relating to the application of monitoring data for the calculation of emissions are provided below.

Where no monitoring information is available, guidance on the characterisation of wastewater emissions is provided in the *Emission Estimation Technique Manual for Sewage and Wastewater Treatment*.

Examples 7 & 8 will show how emissions can be estimated from point source discharges. The first example is relevant for wastewater streams that have a relatively constant daily flow rate, and the measured concentration of the relevant compound in the stream does not vary greatly. The second example is relevant for streams that have more variable flow rates and composition (eg. stormwater).

Example 7

The following information is known regarding the wastewater stream:

- the wastewater stream contains an average cadmium concentration of 500 mg/L;
- the stream is sent to an on-site wastewater treatment plant at a rate of 5 L/minute;
- the stream leaving the plant contains 25 milligrams/L of cadmium (and is discharged to a local water body); and
- the plant operates 24 hours per day for 330 days per year.

Using the data above, determine the quantity of cadmium released from the wastewater treatment plant.

STEP 1: Determine the annual quantity of wastewater discharged

$$\begin{aligned}\text{Volume} &= (5 \text{ L/min}) * (60 \text{ min/hour}) * (24 \text{ hour/day}) * (330 \text{ days/year}) \\ &= 2.4 \text{ million L/year}\end{aligned}$$

STEP 2: Determine the quantity of cadmium exiting the plant

$$\begin{aligned}\text{Quantity (OUT)} &= (2.4 \text{ million L/year}) * (25 \text{ mg/L}) \\ &= 60 \text{ kg/year}\end{aligned}$$

Therefore, based on the calculations above, 60 kg/year of cadmium is discharged from the plant annually, and is required to be reported under the NPI because the discharge is to a water body.

Example 8

This example is a little more complex than the previous one because it requires the analysis of all monitoring data collated in a year from which an average can be derived. In this example, samples are taken fortnightly to measure the discharge flow from a site, as well as the cadmium levels in the discharge. The data collected over a single year is presented in Table 22 below

The daily release is derived by multiplying the daily flow rate by the measured level of cadmium. The annual release can be determined by multiplying the average daily release shown in the table above, by the number of days the wastewater treatment plant discharges per year.

For this example, the plant is assumed to be operational for 300 days per year. Therefore, the annual emission estimate is derived as follows:

Annual release of cadmium

$$\begin{aligned} E_{\text{kpy,cadmium}} &= (1.17 \text{ kg/day}) * (300 \text{ days/year}) \\ &= 351 \text{ kg.} \end{aligned}$$

Therefore, it is estimated that 351 kg of cadmium is released from the site annually.

Table 22. Measurement Data

Measured Flow (10⁶ L/day)	Cadmium (µg/L)	Daily Release (kg)
1.660	918	1.52
1.576	700	1.10
1.668	815	1.36
1.760	683	1.20
1.456	787	1.15
1.360	840	1.14
1.828	865	1.58
1.696	643	1.09
1.852	958	1.77
1.656	681	1.13
1.904	680	1.29
1.724	628	1.08
1.476	807	1.19
1.568	729	1.14
1.292	964	1.25
1.208	722	0.87
1.432	566	0.81
1.288	510	0.66
1.320	630	0.83
1.288	630	0.81
1.632	652	1.06
1.768	649	1.15
1.424	695	0.99
1.560	758	1.18
1.692	658	1.11
1.948	970	1.89
	AVERAGE	1.17 kg/day

10.0 Emissions to Land

Under the NPI, facilities are required to report their emissions to land. Emissions to land have been defined by the NPI Implementation Working Group as:

All emissions of listed substances, except those which are directed to, and contained by, purpose built facilities are to be reported to the NPI. This applies irrespective of whether the substances' fate is within or outside a reporting facility boundary. With respect to receipt of NPI substances, such receiving facilities are to be operating in accordance with any applicable State or Territory government requirements.

Emissions to receiving facilities such as secure landfills, sewers, and tailings dams do not need to be reported. Similarly, the removal of a substance for transfer to another facility for destruction, treatment, recycling, reprocessing, recovery, or purification is not required to be reported. This means, for instance, that if an accidental release of a water-borne pollutant is directed to a temporary bund or into a watercourse then it must be reported, regardless of whether the emission is detectable at the boundary of the facility. If the release is directed to and stored in a purpose built facility, (eg. a rubber lined dam), then it does not need to be reported. However, all other emissions of NPI-listed substances except those that are directed to and contained by purpose built receiving facilities are to be reported under the NPI, irrespective of whether the substance's fate is within, or outside the reporting facility's boundary.

To characterise emissions to land, three general EETs are discussed here:

- groundwater monitoring;
- spills; and
- on-site disposal.

10.1 Groundwater Monitoring

Some facilities conduct monitoring of groundwater to characterise emissions from the facility. Where available, this monitoring data can be used to assist in the characterisation of emissions. This involves determining upstream and downstream concentrations, and using this information in conjunction with groundwater flow information, to determine the contribution of the facility to pollutant levels in the groundwater.

In terms of meeting NPI reporting requirements, this approach is reasonable in situations where there is no loss of substances (eg. due to evaporation) prior to the substance entering the groundwater, and where the time between the release occurring and the substance entering the groundwater is minimal. Therefore, for those facilities where groundwater monitoring captures all emissions to land, such monitoring can be used as a reasonable measure of emissions to the environment. If this is not the case, (eg. where the rate of transmission through the soil/clay is low, or when there are other routes where substances to land are carried off-site, such as evaporation or surface run-off), it will be necessary to characterise these emissions using the other EETs presented in this Manual.

10.2 Spills

For many facilities the primary source of emissions to land will be because of spills, including intentional spillage due to vessel washdown. Accidental spills can contribute to emissions to land directly, to water through runoff, and to air.

Unless spilled material is routed to a secure containment facility, the quantity of material spilled, less any material that is collected, must be reported under the NPI. In practical terms, a log of spillages could be maintained detailing the quantities spilled, and the composition of the spill (in particular, the quantities of NPI substances spilled). This log could then provide the basic information required for NPI reporting.

You should note that if the spill is a volatile liquid, it is reasonable to assume that all of the light end fraction is volatilised, and the remaining liquid is released into the ground. However, if the liquid is not volatile and no material is collected, it is reasonable to assume that all material is released to the land. The time, quantity of spill, temperature, and porosity of the soil all play an important part in the estimation of release.

The evaporation rate of compounds into the atmosphere is given by the following equation:

$$E_{\text{VAP}} = 1.2 * 10^{-10} (\text{MW}(P_{\text{vap},i})/T) U^{0.78} X^{0.89} Y \quad (10)$$

Where:

- E_{VAP} = Evaporation rate of substance “i” (g/s)
- U = Wind speed over the surface of the spill (cm/s)
- X = Downwind dimension (cm)
- Y = Crosswind dimension (cm)
- MW = Molecular weight of substance “i” (can be obtained from Perry & Green (1997) or other standard chemical engineering reference texts)
- $P_{\text{vap},i}$ = Vapour pressure of substance “i” at spill temperature T (dyne/cm² = 0.0001 kPa)
- T = Temperature (K)

Once losses to the atmosphere have been quantified, emissions to land can be estimated using the following equation:

$$ER_{LAND,i} = Qty_{SPILL} - ((time) * (E_i)) - Q_{Removed} \quad (11)$$

Where:

$ER_{LAND,i}$	=	The emission to the land of compound “i”
Qty_{SPILL}	=	The quantity of compound in the liquid spilled
$Q_{Removed}$	=	The quantity of pollutant cleaned up
E_i	=	The loss through evaporation of substance “i” as estimated using the evaporation equation above
Time	=	The time period between when the liquid was initially spilled, and eventual clean up

10.3 On-Site Disposal

Facilities with provision for on-site disposal of wastes will need to consider the discussion in Section 10.0 to determine whether the disposal is classed as a transfer, or as an emission to land under the NPI. If the disposal is not a transfer, reporting will be required under the NPI. In a similar approach as outlined for spills, the most effective EET involves maintaining a record of all such disposal to land and, in particular, the amount of NPI substances contained in the material disposed of in such a manner.

11.0 Assumptions and Discussion

Combustion Sources

The emission factors presented in Table 14 are based on residual oil combustion. In the absence of more appropriate data however, it may be assumed that this data also applies to distillate oil combustion.

Trace Elements

The following discussion relates to the principle behind the mass balance approach. USEPA (1989) suggests that because oil combustion does not generate any bottom ash, it can generally be assumed that 100 percent of the trace elements present in the fuel are released into the atmosphere. It is further stated that emissions of these trace elements would be independent of combustor design and combustion sector (ie. industrial, utility etc.). While similar comments were not made for gas combustion, it is safe to assume that these comments would also apply to it because gas combustion does not result in the generation of bottom ash either.

The emission factors provided in Table 6 indicate that emissions of beryllium and mercury from residual oil combustion are lower than those from distillate oil combustion. These emission factors have been checked with the source document (USEPA, 1998b) and are correct. However, no explanation can be provided for this discrepancy.

12.0 References

1. AWMA (1992) *Air Pollution Engineering Manual*, Air & Waste Management Association, Van Nostrand Reinhold, 1992.
2. Department of Agriculture, Western Australia, (1993), "*Use of Bauxite Residue in the Peel-Harvey Coastal Plain Catchment*", Public Environmental Review.
3. Perry, R.H. & Green, D.W. (1997), *Perry's Chemical Engineers' Handbook – Seventh Edition*, McGraw Hill, NY.
4. USEPA (1989), *Estimating Air Toxic Emissions from Coal and Oil Combustion Sources*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, (EPA-450/2-89-001)
5. USEPA (1990), *Air Emissions Species Manual – Volume 1 Volatile Organic Species Profiles, Second Edition*, Office of Air Quality Planning and Standards, Research Triangle Park, (EPA-450/2-90-001a).
6. USEPA (1993), *VOC/PM Speciation DBMS*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, 1993
7. USEPA (1997a), *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Sources, Fifth Edition*, Office of Air Planning and Standards, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, 1995 (AirChief CD-ROM, 1997, Version 5.0)
8. USEPA (1997b) *Factor Information Retrieval System (FIRE)*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, (AirChief CD-ROM, 1997, Version 5.0)
9. USEPA (1998a), *Fuel Oil Combustion*, March 1998 Revision to AP-42 Section 1.3.
10. USEPA (1998b), *Natural Gas Combustion*, September 1998 Revision to AP-42 Section 1.4
11. The following Emission Estimation Technique Manuals referred to in this Manual can be obtained 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 Mining;
 - Emission Estimation Technique Manual for Fossil Fuel Electric Power Generation; and
 - Emission Estimation Technique Manual for Sewage and Wastewater Treatment.

Appendix A

(List of NPI Substances)

Appendix A

NPI reportable substances relevant to the Alumina Refining Industry in Australia

NPI Substance	Table 1 (ie 36 substances)	Table 2 (ie 90 substances)	Alumina Refining
1. acetaldehyde		x	x (cat 1)
2. acetic acid (ethanoic acid)		x	
3. acetone	x	x	x (cat 1)
4. acetonitrile		x	
5. acrylamide		x	
6. acrylic acid		x	
7. acrylonitrile (2-propenenitrile)		x	
8. ammonia (total)		x	
9. aniline (benzenamine)		x	
10. antimony and compounds		x	
11. arsenic and compounds	x	x	x (cat 1, 2b)
12. benzene	x	x	x (cat 1)
13. benzene hexachloro (HCB)		x	
14. beryllium and compounds		x	x (cat 2b)
15. biphenyl (1,1-biphenyl)		x	
16. boron and compounds		x	x (cat 1)
17. 1,3-butadiene (vinyl ethylene)	x	x	
18. cadmium and compounds	x	x	x (cat 1,2b)
19. carbon disulfide		x	x (cat 1)
20. carbon monoxide	x	x	x (cat2a)
21. chlorine		x	x(cat 1)
22. chlorine dioxide		x	
23. chloroethane (ethyl chloride)		x	
24. chloroform (trichloromethane)		x	x (cat 1)
25. chlorophenols (di, tri, tetra)		x	
26. chromium (III) compounds		x	x (cat 1, 2b)
27. chromium (VI) compounds	x	x	x (cat 1, 2b)
28. cobalt and compounds	x	x	x (cat 1)
29. copper and compounds		x	x (cat 1,2b)

NPI Substance	Table 1 (ie 36 substances)	Table 2 (ie 90 substances)	Alumina Refining
30. cumene (1-methylethylbenzene)		x	
31. cyanide (inorganic compounds)	x	x	
32. cyclohexane		x	x (cat 1)
33. 1,2-dibromethane	x	x	
34. dibutyl phthalate		x	
35. 1,2-dichloroethane		x	
36. dichloromethane	x	x	
37. ethanol		x	x (cat 1)
39. 2-ethoxyethanol	x	x	
38. 2-ethoxyethanol acetate	x	x	
39. ethyl acetate		x	
40. ethyl butyl ketone		x	
41. ethylbenzene		x	x (cat 1)
42. ethylene glycol (1,2-ethanediol)	x	x	
43. ethylene oxide		x	
44. di-(2-ethylhexyl) phthalate (DEHP)		x	
45. fluoride compounds	x	x	x (cat 1,2a)
46. formaldehyde (methyl aldehyde)		x	
47. glutaredehyde	x	x	
48. n-hexane		x	
49. hydrochloric acid		x	x (cat 1, 2a)
50. hydrogen sulfide		x	x (cat 1)
51. lead and compounds	x	x	x (cat 1, 2b)
52. magnesium oxide fume		x	x (cat 2b)
53. manganese and compounds		x	x (cat 1)
54. mercury and compounds	x	x	x (cat 2b)
55. methanol	x	x	x (cat 1)
56. 2-methoxyethanol		x	
57. 2-methoxyethanol acetate		x	
58. methyl ethyl ketone	x	x	
59. methyl isobutyl ketone	x	x	

NPI Substance	Table 1 (ie 36 substances)	Table 2 (ie 90 substances)	Alumina Refining
60. methyl methacrylate	x	x	
61. 4,4-methylene bis 2,4 aniline (MOCA)		x	
62. methylenebis (phenylisocyanate)		x	
63. nickel and compounds		x	x (cat 2b)
64. nickel carbonyl	x	x	x (cat 2b)
65. nickel subsulfide	x	x	x (cat 2b)
66. nitric acid		x	
67. organo-tin compounds		x	
68. oxides of nitrogen	x	x	x (cat 2a)
69. particulate matter (pm ₁₀)	x	x	x (cat 2a)
70. phenol		x	
71. phosphoric acid		x	
72. polychlorinated dioxins and furans		x	x (cat 2b)
73. polycyclic aromatic hydrocarbons (PAHs)	x	x	x (cat 2a)
74. selenium and compounds		x	x (cat 1)
75. styrene (ethylbenzene)		x	x (cat 1)
76. sulfur dioxide	x	x	x (cat 1,2a)
77. sulfuric acid	x	x	x (cat 1)
78. 1,1,1,2-tetrachloroethane		x	
79. tetrachloroethylene	x	x	
80. toluene (methylbenzene)	x	x	
81. toluene-2,4-diisocyanate		x	
82. total nitrogen	x	x	x (cat 3)
83. total phosphorus	x	x	x (cat 3)
84. total volatile organic compounds		x	x (cat 2a)
85. 1,1,2-trichloroethane		x	
86. trichloroethylene	x	x	
87. vinyl chloride monomer		x	
88. xylenes (individual or mixed isomers)	x	x	x (cat 1)
89. zinc and compounds		x	x (cat 1)

Appendix B

(Process Description and Flow Diagram)

APPENDIX B PROCESS DESCRIPTION

The Refining Process

Metallic mineral processing typically involves the mining of ore from either open pit or underground mines, the crushing and grinding of ore, the separation of valuable minerals from matrix rock through various concentration steps, and at some operations, drying, calcining, or pelletizing of concentrates to ease further handling and refining.

The number of crushing steps necessary to reduce ore to the proper size varies with the type of ore. Softer ores, such as some uranium, bauxite, and titanium/zirconium ores, require little or no crushing. Final comminution of both hard and soft ores is often accomplished by grinding operations using media such as balls or rods of various materials. Grinding is most often performed with an ore/water slurry, which reduces particulate matter (PM) emissions to negligible levels.

After final size reduction, the beneficiation of the ore increases the concentration of valuable minerals by separating them from the matrix rock. Various physical and chemical processes are used to concentrate the mineral. Most often, physical or chemical separation is performed in an aqueous environment that eliminates PM emissions, although some ferrous and titaniferous minerals are separated by magnetic or electrostatic methods in a dry environment. The concentrated mineral products may be dried to remove surface moisture.

Alumina is produced from bauxite by the Bayer Process. In the Bayer Process, aluminum hydroxides or hydrates are selectively separated from other components by extracting them with sodium hydroxide to form sodium aluminate. Alumina is then precipitated from the sodium aluminate solution, washed, and calcined. The process is shown in Figure A.1.

To prepare bauxite for processing, mined ore is crushed and ground in ball mills to a finely divided state. Most bauxite as mined has a low moisture content. If the moisture content is high, then the bauxite must be dried in rotary kilns before it is sent to storage. The drying operation emits significant amounts of bauxite dust.

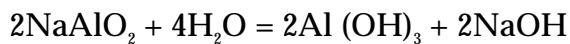
To produce high purity alumina suitable for aluminum reductions cells, finely divided bauxite containing 30-70% alumina is slurried with sodium hydroxide solution and reacted at high temperature and pressure in reactors called digesters. Sodium aluminate is formed leaving behind most of the silicon, iron, titanium, and calcium oxides as insoluble components in the solid waste residue. This is formed according to the following general equation:



The hot slurry is usually cooled by flash evaporation, producing steam that is used to heat incoming slurry. Next, the slurry is processed in a series of clarification steps designed not only to separate the solid residue from the liquor, but also to rid the solution of the

impurities that would lower the quality of the aluminum when the alumina later is electrolysed. These impurities are mainly oxides of silicon and iron.

If the bauxite contains coarse material (mainly sand), it is first removed from the slurry in hydrocyclones, and starch or some settling agent is added to the overflow before it enters a clarifier. Starch promotes agglomeration and settling of the fine particles, and the relatively clear overflow from the clarifier is filtered in either filter presses, or sand filters to remove any remaining suspended solids. The clarifier underflow is then washed in thickeners to remove as much caustic as possible before it is pumped to a bauxite residue pond. The filtrate containing sodium aluminate, now at 50°C to 70°C, is processed in precipitators where aluminum hydroxide crystallises and precipitates as shown in the following



After precipitation, the slurry containing trihydrate crystals is sent to classification, where the product is separated according to crystal sizes. The coarse product is washed to remove excess sodium hydroxide, dewatered on vacuum filters, and sent to calcination. The finer crystals are recycled to the precipitation process as seed, thereby providing nucleation sites for precipitation to occur. Spent liquor from the precipitators is recycled to the digesters.

The coarse alumina is calcined in rotary kilns or fluid-bed calciners at about 1800°F. During calcination, water (mechanically and chemically bound) is driven off. Calcination produces hot flue gases containing alumina and water vapour, and the usual types of control equipment consist of cyclonic separators followed by ESPs. The control equipment not only minimises air pollution, but recovers valuable product as well. Calcined alumina is stored for shipment to the smelter as feedstock for the aluminum electrolytic cells.



Figure B 1 - Bayer Process Flowsheet
 [Adapted from Air Pollution Engineering Manual]

