



National Pollutant Inventory

Emission Estimation Technique Manual

for

Aluminium Smelting

First Published in March 1999

**EMISSION ESTIMATION TECHNIQUES
FOR
ALUMINIUM SMELTING**

TABLE OF CONTENTS

1.0 INTRODUCTION.....	1
2.0 DO I NEED TO REPORT	2
2.1 SUBSTANCES TO BE REPORTED.....	2
3.0 EMISSION ESTIMATION TECHNIQUES	5
3.1 USE OF EMISSION FACTORS.....	6
3.2 MASS BALANCE TECHNIQUES	6
3.3 SOFTWARE MODELS	7
3.4 EMISSION ESTIMATION TECHNIQUES (EETs).....	7
4.0 LOCATING AND USING EET'S IN THIS MANUAL	9
5.0 EMISSIONS TO AIR.....	19
5.1 COMBUSTION SOURCES	19
5.2 EMISSIONS FROM MATERIALS HANDLING AND STORAGE.....	19
5.3 ESTIMATING VENT EMISSIONS	20
5.3.1 Vent Releases from Acid Storage Tanks	20
5.3.2 Vent Releases from Liquid Pitch.....	20
5.4 PROCESS EMISSIONS	20
5.4.1 Source Test Data.....	21
5.4.2 Emission Factors.....	21
5.4.3 Control Technologies	23
5.4.4 Sulfur Dioxide Emissions from the Process	24
5.5 PARTICULATE SPECIATION	24
5.6 VOC EMISSIONS	25
5.6.1 Total VOC Emissions	25
5.6.2 Speciated VOC Emissions	25
6.0 MASS BALANCE.....	29
6.1 OVERALL FACILITY MASS BALANCE.....	31
6.2 INDIVIDUAL UNIT PROCESS MASS BALANCE	33
7.0 MONITORING	33
8.0 RELEASES TO WATER.....	35
9.0 RELEASES TO LAND.....	39
9.1 GROUNDWATER MONITORING	39
9.2 SPILLS	40
9.3 ON SITE DISPOSAL	41
10.0 DISCUSSION	42
11.0 GLOSSARY	43
12.0 REFERENCES	45

ALUMINIUM SMELTING

LIST OF FIGURES & TABLES

Figure 1.	Raw Materials Handling	12
2.	Anode Set Up.....	13
3.	Rodding	13
4.	Alumina Reduction.....	14
5.	Casting	15
6.	Anode Recycling.....	16
7.	Maintenance and Renovation Operations	16
8.	Wastewater Treatment	17
Table 1.	Location of EETs in this Manual	10
2.	Acid Properties	20
3.	Particulate and Fluoride Emission Factors for Anode Production.....	22
4.	Emission Factors for Alumina Reduction.....	22
5.	Emission Factors for Alumina Reduction	23
6.	Speciation Data for Anode Baking	26
7.	Speciation of Fugitive VOCs from Anode Prebake	27
8.	Speciation of VOCs from Materials Handling	28
9.	Speciation of VOCs from Prebake Reduction Cell	28
10.	Speciation of Fugitive VOCs from Prebake Reduction Cell	29
11.	Measurement Data	38

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 the aluminium smelting industry.

EET MANUAL: Aluminium Smelting

HANDBOOK: Aluminium Smelting

ANZSIC CODE: 272 and 2722

The aluminium smelting activities covered in this manual include:

- Raw material handling and storage;
- Alumina processing (including anode baking, alumina reduction, casting and rodding);
- Ancillary operations including pot relining, 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.

This 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 Do I Need To Report?

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
- Which 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 of the thresholds for the substances listed under the NPI. A series of worksheets are provided in *The NPI Guide* to assist with this exercise.

2.1 Substances to Be Reported

On the basis of discussions with the Australian Aluminium Council (AAC) and its members, the NPI substances typically emitted from aluminium smelting facilities have been identified and are listed below. It is important to note that it is your responsibility to determine which NPI substances are to be reported. The information below is provided solely to assist you to make a considered assessment.

Category 2a and 2b Substances:

- Arsenic & compounds;
- Beryllium & compounds;
- Cadmium & compounds;
- Carbon monoxide (CO);
- Chromium (III) & compounds;
- Chromium (VI) & compounds;
- Copper & compounds;
- Fluoride compounds;
- Hydrochloric acid;
- Lead & compounds;
- Magnesium oxide fume;
- Mercury & compounds;
- Nickel & compounds;
- Nickel carbonyl;
- Nickel subsulfide;
- Oxides of nitrogen;
- PM₁₀;
- Polychlorinated dioxins and furans;
- PAHs;
- Sulfur dioxide; and
- Total VOCs.

Category 1 and 1a Substances

In addition, it is expected that all aluminium smelting facilities are likely to trigger reporting thresholds for the following Category 1 Substances (note that the Category 2a and 2b Substances listed above that are also Category 1 substances are not included in the following list):

- Ammonia;
- Antimony & compounds;
- Benzene;
- Boron & compounds;
- 1,3-butadiene;
- Carbon disulfide;
- Chlorine;
- Cobalt & compounds;
- Cyanide (inorganic compounds);
- Manganese & compounds;
- Sulfuric acid;
- Selenium & compounds;
- Toluene;
- Xylenes; and
- Zinc & compounds.

NB: For the metal species listed above, consideration of whether or not a reporting threshold is triggered requires that consideration be given to trace metals in the feedstock. For a smelter processing 500,000 tonnes of alumina per annum, you would need 20 ppm of trace metal to trigger reporting for that substance.

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.

Category 3 Substances

Reporting may be triggered for the following Category 3 substances:

- Total nitrogen; and
- Total phosphorous.

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 EET's, 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.

In developing an inventory of emissions, it is important to utilise the best information available to develop emission estimates. Ideally, this data is obtained through the source testing of emission points, although it is recognised that in many situations sampling data is not available.

In the specific context of aluminium smelting, there are a range of EETs available. The EETs presented in this Manual as alternatives to direct measurement are:

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

Each of these EETs is 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 burning a particular fuel type). 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. However, as 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 equation 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 releases to the environment, or as part of the facility waste. Mass balance is particularly useful when the input and output streams can be quantified. 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. Section 6 of this Manual provides more guidance, as well as a worked example on the application of mass balance techniques.

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) can result in large errors in the final emissions estimates. Additionally, if sampling of input or output materials is conducted, failure to use representative samples will also contribute to the uncertainty of the result.

3.3 Software Models

Software models are available that predict emission rates for fugitive releases, 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, which require site-specific data. A range of other information is also often required to utilise software packages (eg for the chemical and/or physical characterisation of specific substances). Where relevant in this Manual, the use of these software packages for the purposes of characterising and estimating emissions is discussed.

While software models frequently require an initial investment of time, they can provide long term benefits because of their relative ease to use, and the speed with which estimations can be made.

3.4 Emission Estimation Techniques (EETs)

Section 4.0 provides an overview of the unit processes/activities covered by this Manual. This section also details where different EETs are considered in this Manual.

The National Environment Protection Measure (NEPM) 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 emission of a substance to the environment from landfill, sewage treatment plants, and tailings dams but does not include:

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

The NPI Guide lists all of the reportable substances and the associated reporting thresholds. This Guide should be consulted to ascertain whether your facility handles, manufactures, or otherwise uses any of the substances presented in the list, and determine whether any thresholds are exceeded. If the facility is found to trigger any thresholds, then releases to air, water, and land must be quantified. You should note, however, that although a particular threshold may be triggered, an emission estimation technique may not be found in this Manual because of a lack of available emission estimation data.

4.0 Locating and Using EETs in this Manual

Once the substances that require reporting have been identified (see Section 2.0 of this Manual), the next step is to establish which substances are released to the environment. Figures 1 to 8 (below) show the raw material inputs to, and outputs from each of major operations that comprise aluminium smelting operations. Table 1 identifies the location of the EETs relevant to each of these operations.

In reviewing Table 1, it is clear that there are many activities for which EETs are not currently available. A working group has been established by the aluminium smelting industry to:

1. Further review the EETs presented in this Manual; and
2. Develop EETs for those activities for which EETs are not currently available.

Table 1. Location of EETs in this Manual ^{a,b}

NPI Substance	Raw Materials	Anode Set Up	Alumina Reduction	Anode Recycling	Casting	Maintenance and Renovation Operation	Wastewater
Heavy metals & compounds (arsenic, beryllium, cadmium, chromium (III, VI), cobalt, copper, lead, magnesium, manganese, mercury, nickel, nickel carbonyl, nickel subsulfide, selenium, zinc)	<i>Air</i> Section 5.5	<i>Air</i> Section 5.5	<i>Air</i> Section 5.5	<i>Air</i> Section 5.5	N/A	N/A	<i>Water</i> Section 8.0
NPI Category 1 Substances (carbon monoxide, PM ₁₀ , sulfur dioxide, oxides of nitrogen) [Note that some additional specific guidance on characterising emissions on PM ₁₀ and SO ₂ is also provided in this Manual – see below]	N/A	<i>Air</i> Section 5.4	<i>Air</i> Section 5.4	N/A	<i>Air</i> Section 5.4	N/A	N/A
Polychlorinated dioxins and furans	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Polycyclic aromatic hydrocarbons (PAHs)	<i>Air</i> Section 5.6.2	<i>Air</i> Section 5.4.2 and/or 5.6.2	<i>Air</i> Section 5.4.2 and/or 5.6.2	N/A	<i>Air</i> Section 5.6.2	N/A	N/A

Table 1. Location of EETs in this Manual ^{a,b} cont'

NPI Substance	Raw Materials	Anode Set Up	Alumina Reduction	Anode Recycling	Casting	Maintenance and Renovation Operation	Wastewater
Total volatile organic compounds (VOCs) ^c	<i>Air</i> Section 5.6	<i>Air</i> Section 5.6	<i>Air</i> Section 5.6	N/A	<i>Air</i> Section 5.6	<i>Air</i> Section 5.6	N/A
Other Organics ^c (such as benzene, 1,3-butadiene, ethylbenzene, formaldehyde, toluene and xylenes (individual or mixed isomers))	<i>Air</i> Section 5.4 and/or 5.6.2	<i>Air</i> Section 5.4 and/or 5.6.2	<i>Air</i> Section 5.4 and/or 5.6.2	N/A	<i>Air</i> Section 5.4 and/or 5.6.2	<i>Air</i> Section 5.4 and/or 5.6.2	N/A
Fluoride compounds	N/A	N/A	<i>Air</i> Section 5.4	N/A	N/A	N/A	N/A
Chlorine	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Hydrochloric acid	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sulfuric acid	<i>Air</i> Section 5.3	N/A	N/A	N/A		N/A	N/A

Table 1. Location of EETs in this Manual ^{a,b} cont'

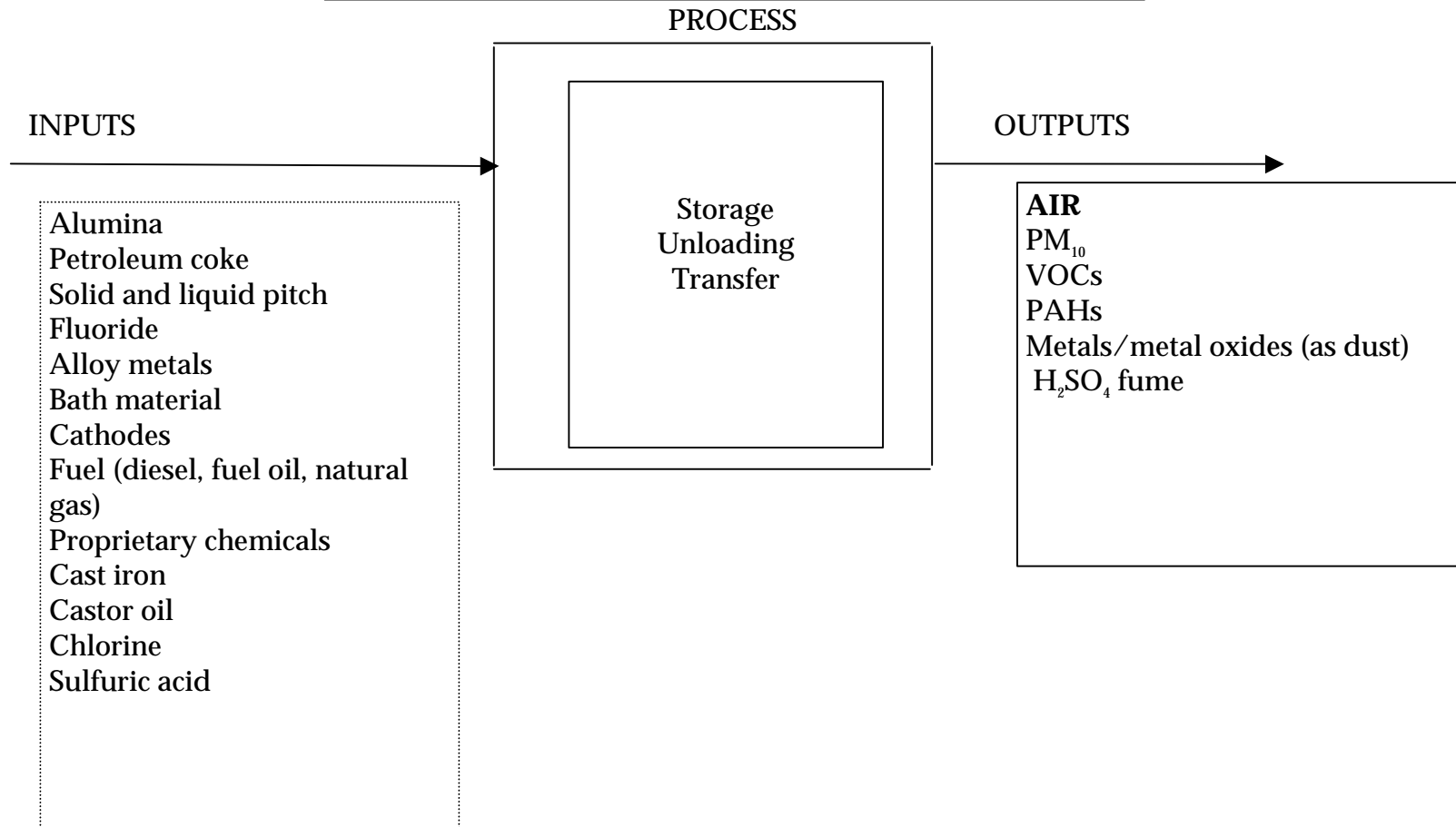
NPI Substance	Raw Materials	Anode Set Up	Alumina Reduction	Anode Recycling	Casting	Maintenance and Renovation Operation	Wastewater
Particulate matter (PM₁₀)	<i>Air</i> Section 5.4	<i>Air</i> Section 5.4	<i>Air</i> Section 5.4	<i>Air</i> Section 5.4	<i>Air</i> Section 5.4	N/A	N/A
Sulfur dioxide	N/A	<i>Air</i> Section 5.4.4	<i>Air</i> Section 5.4.4	<i>Air</i> Section 5.4.4	N/A	N/A	N/A
Total nitrogen Total phosphorous	N/A	N/A	N/A	N/A	N/A	N/A	N/A

^a As noted in Section 4, a working group has been established by the aluminium smelting industry. It is expected that this working group will develop additional EETs that are suitable for use by the Australian aluminium smelting industry for emission estimation.

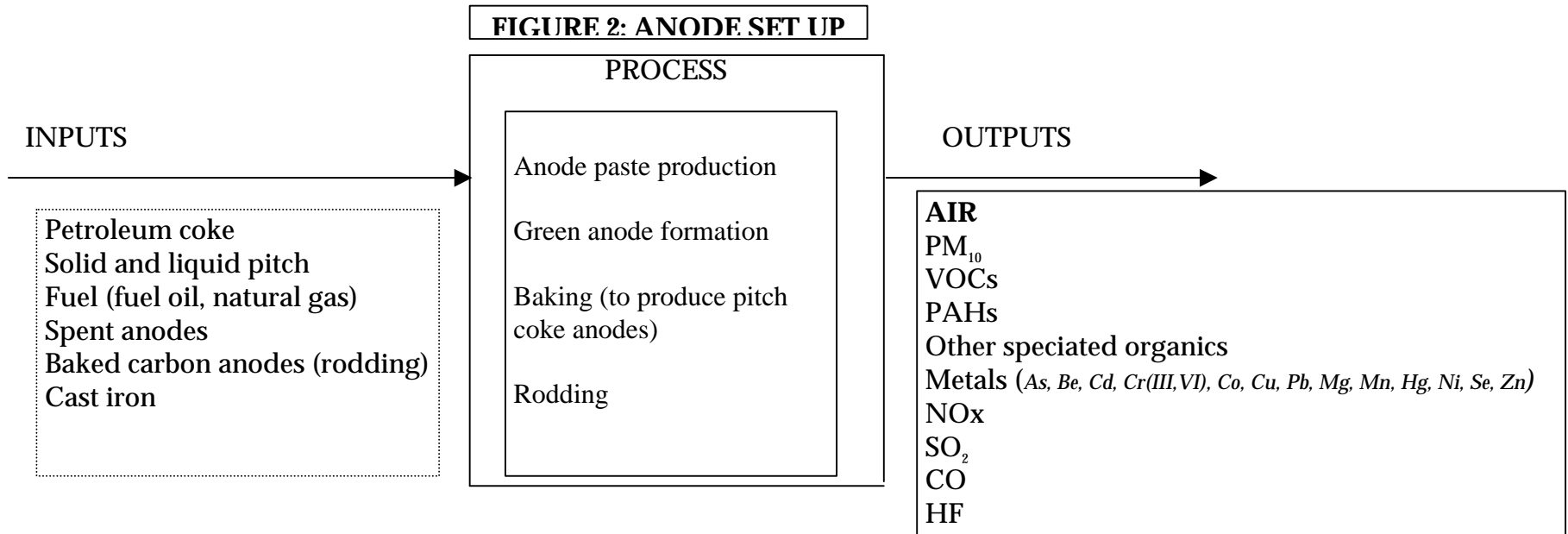
^b N/A = no EET currently available. It should be noted that in situations where there is no EET available, it is the responsibility of the reporting facility to develop a suitable emission estimation technique, and to obtain the consent of the relevant environmental authority for the use of the EET.

^c It should be noted that the generic category, Total VOCs, also encompasses these organic species.

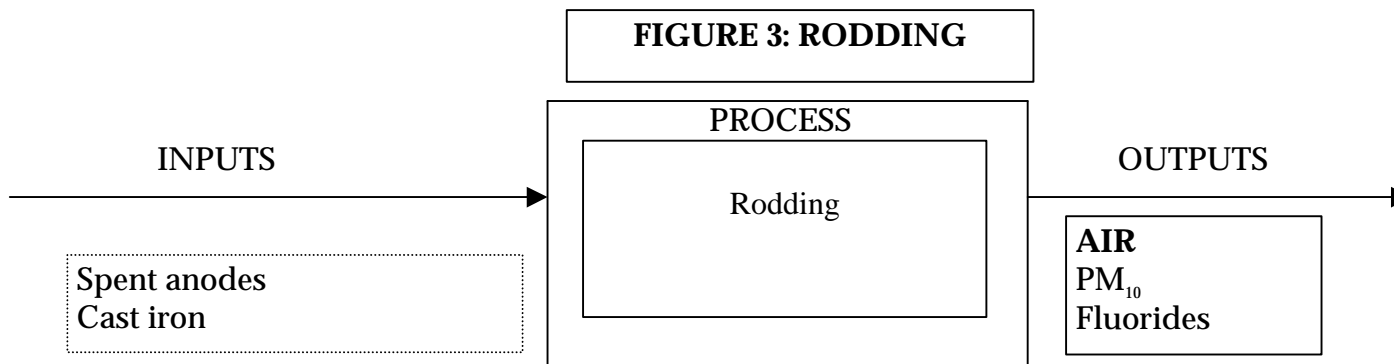
FIGURE 1: RAW MATERIALS HANDLING



Raw material inputs are transferred from the carrier (in some cases, this may be a marine vessel), or directly from the alumina refinery to the site storage via conveyor. The material is stockpiled on-site, and transferred to pot-rooms for conversion into aluminium. The outputs list the NPI substances potentially released.

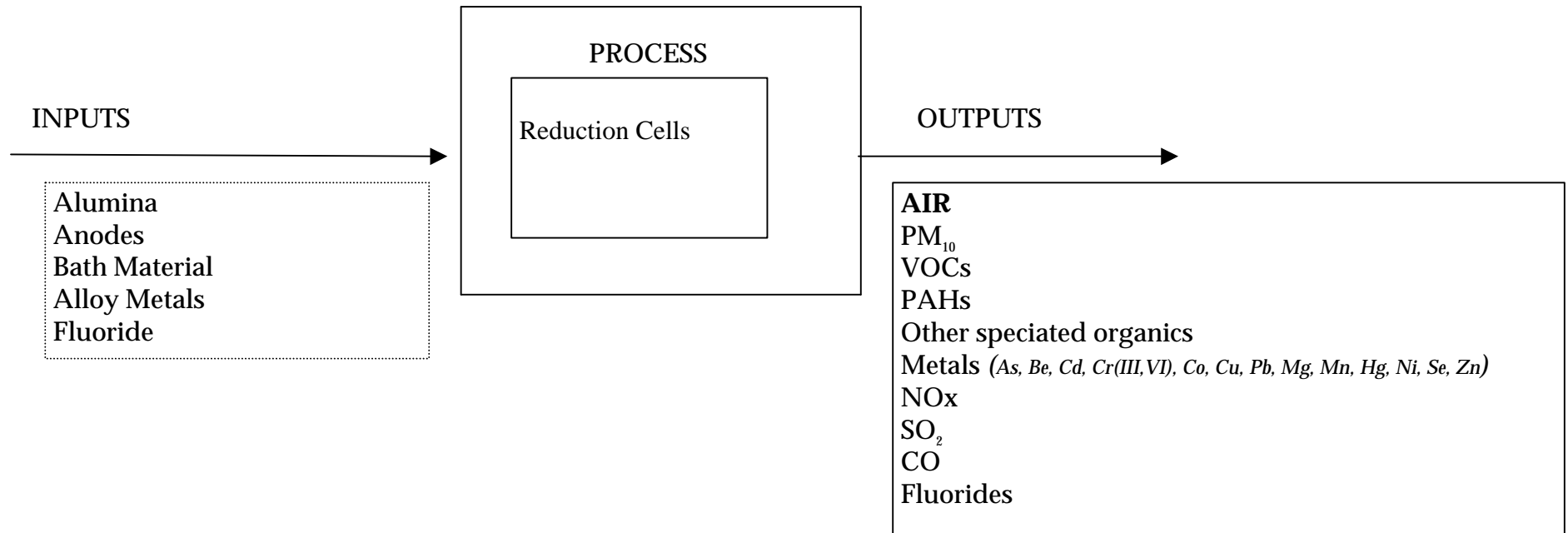


The anode paste plant (also known as the “green mill”) produces green pressed anodes. Multiple anodes are formed and baked prior to use, and the anodes are consumed in the reduction process.



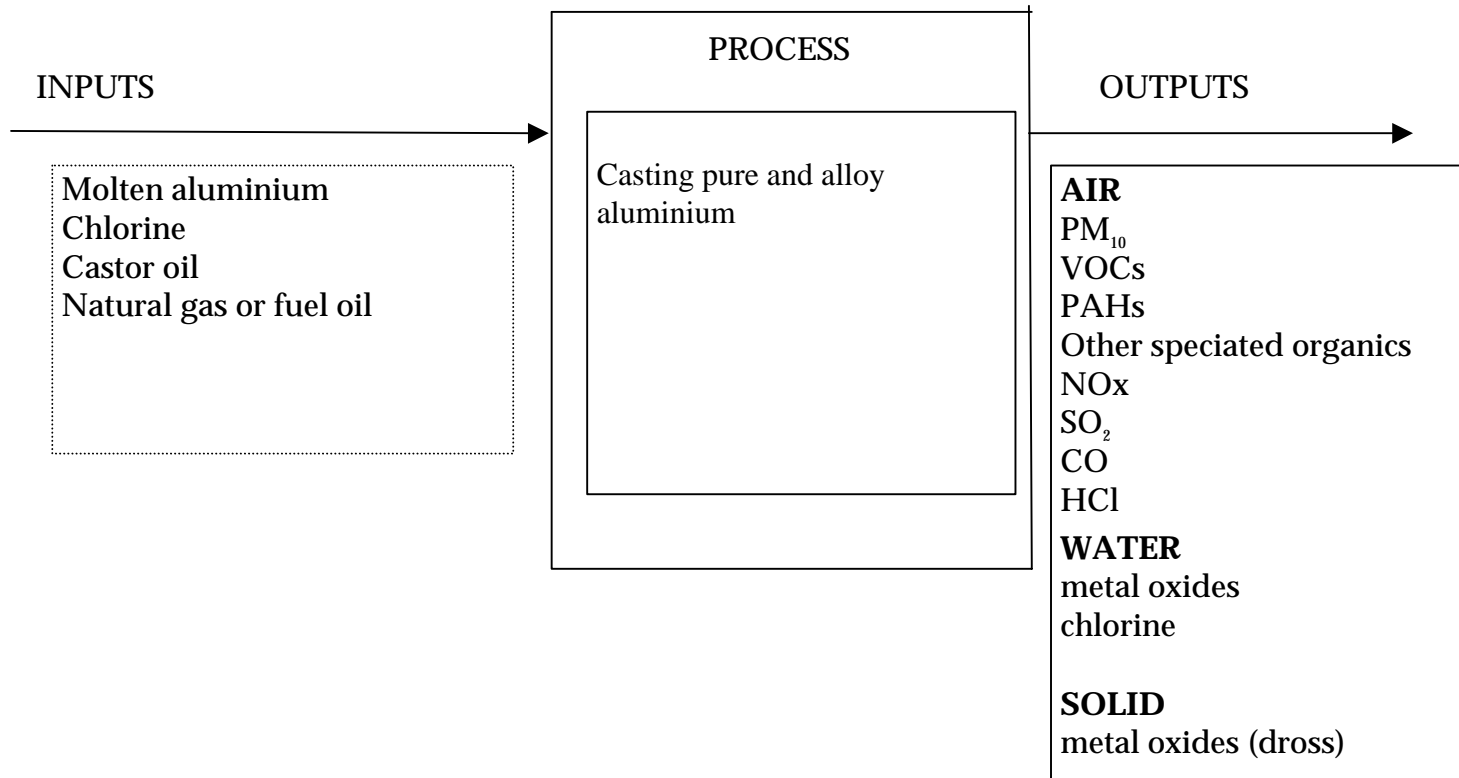
Spent anodes removed from the potlines are recycled in the rodding area. The spent anodes and residual material are returned to the green anode plant for processing.

FIGURE 4: ALUMINA REDUCTION



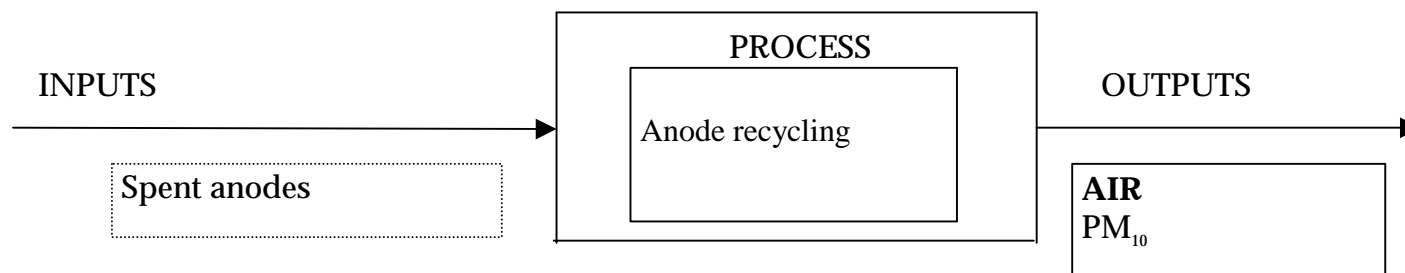
Electrolytic reduction of alumina occurs in shallow rectangular cells, or “pots”, which are steel shells lined with carbon. Carbon electrodes extending into the pot serve as the anodes, and the carbon lining as the cathode. Molten cryolite (Na_3AlF_6 ie. “bath”) functions as both the electrolyte, and the solvent for the alumina.

FIGURE 5: CASTING



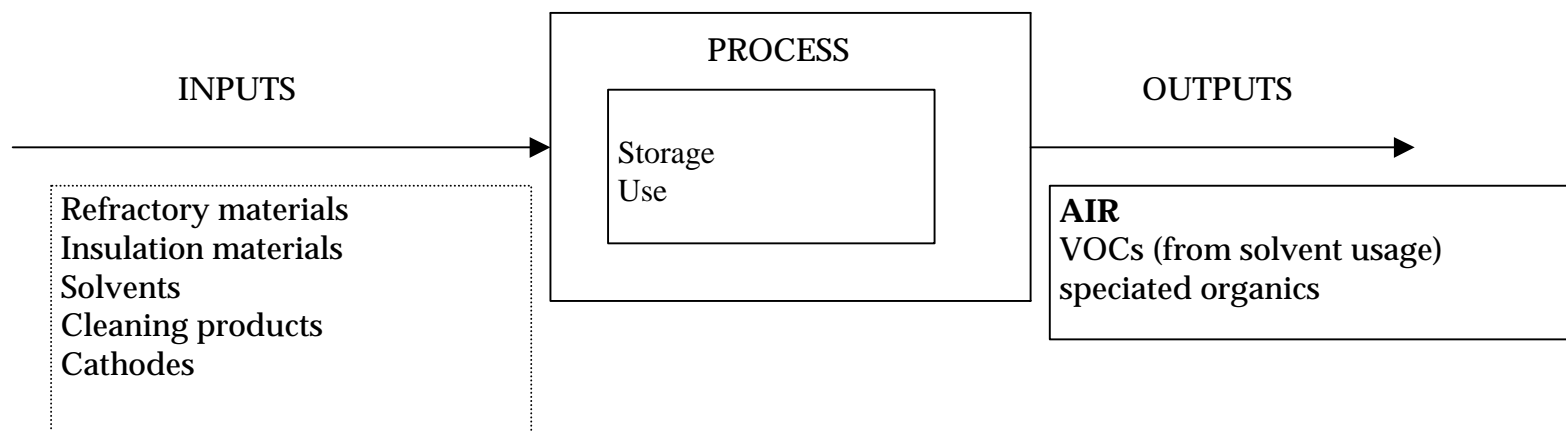
Molten aluminium is batch treated in furnaces to remove oxide, gaseous impurities, and active metals such as sodium and magnesium.

FIGURE 6: ANODE RECYCLING



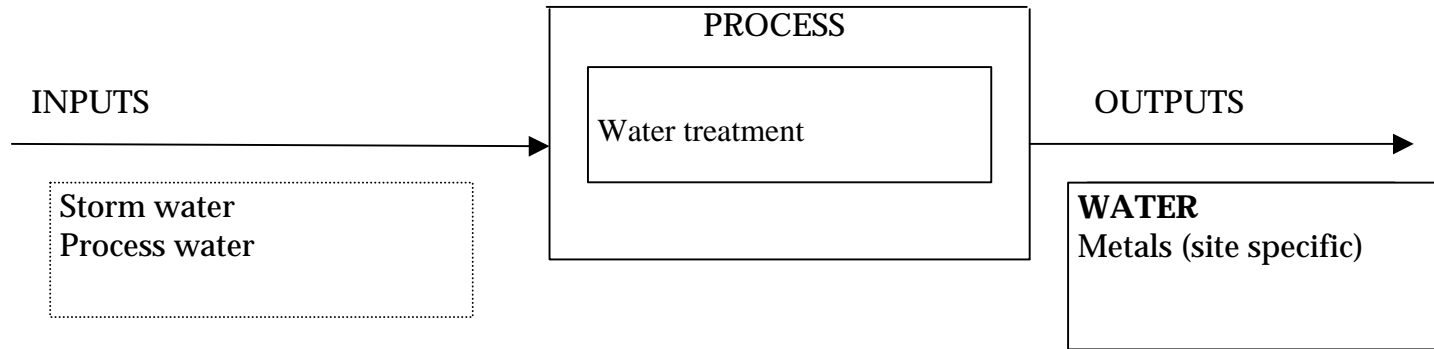
HF emissions originate from the recycling of anode butts, when fluorides not removed during cleaning of the butts are volatilised in the furnace and removed with the flue gas stream.

FIGURE 7: MAINTENANCE AND RENOVATION OPERATIONS



Maintenance and renovation operations are unlikely to require the reporting of NPI substances because of the quantities involved.

FIGURE 8: WASTEWATER TREATMENT



NB: Refer to Sewage and Wastewater Treatment EET Manual.

5.0 EMISSIONS TO AIR

Emissions to the atmosphere can be divided into generic categories and are presented in this Manual as follows:

- Section 5.1: Combustion sources (ie. furnaces and boilers);
- Section 5.2: Emissions from materials handling and storage;
- Section 5.3: Vent emissions from bulk storage; and
- Section 5.4: Process emissions

Sections 5.5 and 5.6, 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 to emissions estimation are discussed in Sections 6 (Mass Balance) and 7 (Monitoring) of this Manual respectively.

5.1 Combustion Sources

Emission estimation techniques for combustion systems can be found in the following EET Manuals:

- *Emission Estimation Technique Manual for Fossil Fuel Electric Power Generation*; and
- *Emission Estimation Technique Manual for Combustion in Boilers*.

Emissions from holding furnaces can also be calculated using the EETs presented in these Manuals. However, the emission factors presented in these Manuals do not account for the metal fume or PM_{10} associated with this process. There is no published data available on emissions of metal fume. These emissions would need to be characterised on a site by site basis.

5.2 Emissions from Materials Handling and Storage

In the specific context of aluminium smelting operations, no EETs are currently available for emissions of particulate matter. However, emission estimation techniques for similar operations are presented in the *Emission Estimation Technique Manual for Mining*.

5.3 Estimating Vent Emissions

5.3.1 Vent Releases from Acid Storage Tanks

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 calculated. You should note that sulfuric acid is likely to be the only NPI substance of concern in terms of bulk acid storage at aluminium smelting facilities.

Table 2. Acid Properties^a

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

^a Source: Perry & Green (1997)

^b Based on 1 atm (101.3 kPa) and 20°C. Note that Table 2-14 on page 2-82 of Perry & Green (1997) presents 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').

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

$$E = 0.042 * MW * V_{vs} * (Vol\%/100) \quad (2)$$

Where:

- E: = Mass of acid released during filling in (kg)
- MW = Molecular weight of acid (Sulfuric Acid = 98 kg/kmol)
- V_{vs} : = Volume of the vapour space in the tank (ie. the volume of acid added (m³))
- Vol% = Volume percent, refer to Table 2.

5.3.2 Vent Releases from Liquid Pitch

No EETs are currently available for emissions from the storage of liquid pitch. However, some facilities may have monitoring data that can be used for emission estimation.

5.4 Process Emissions

Data pertaining to emissions from process sources (eg. reduction, anode paste, baking) are limited. The available data (in the form of emission factors, or other simple estimation techniques) is presented in the following Sections. As noted in Table 1, however, a range of other NPI substances are likely to be emitted from process sources. In this situation, it is your responsibility to quantify these emissions for the purposes of NPI reporting (even if no EETs are available). Emissions may be characterised using other EETs presented in this Manual, such as a mass balance across a particular process/activity (see Section 6.0 of this Manual), or an overall

facility mass balance using available monitoring and process data (Sections 6 and 7 of this Manual).

5.4.1 *Source Test Data*

Aluminium smelting facilities in Australia collect source specific data on emissions as part of compliance monitoring on a state/territory-specific basis. There is likely to be some commonality between the various operations (eg most facilities are likely to have data relating to emissions of fluoride and NPI-listed substances). Individual facilities may also perform monitoring for specific substances (eg. PAHs) as part of licensing or other requirements. Any monitoring data that is currently collected should be used, where possible, to characterise emissions of NPI-listed substances. Section 7 (Monitoring) of this Manual provides a further discussion on the use of monitoring data to characterise emissions.

5.4.2 *Emission Factors*

Emission factors available in the literature are provided in this Section. You should note that although the number of NPI-listed substances presented in the following Tables is limited, it is likely that other compounds are also emitted (see Table 1). In addition, it should be noted that these emission factors are based principally on US data, and that there are limitations associated with applying this data to Australian facilities (this issue is discussed further in Section 10). The general equation for the use of emission factors appears in Section 3.1.

Emission factors for particulate and fluoride emissions from anode production and alumina reduction are presented in Table 3 and Table 4 respectively. However, most data available in the literature pertains to total particulate matter rather than the NPI-listed PM_{10} . In the absence of better data, the total particulate data can be used to provide conservative upper levels for PM_{10} emissions. In addition, you can refer to Section 5.5 for information regarding the speciation of particulate emissions.

There is limited information available on emissions of organic compounds from process operations. Section 5.6 of this Manual discusses VOC emissions further, and provides additional information regarding the speciation of VOC emissions.

Emission factors are provided in the following tables for both point, and fugitive sources. In applying the emission factors in these Tables, point and fugitive emissions should be calculated separately, and then added to provide total emissions. Furthermore, it is important to note that the control technologies specified in the following tables relate to point source emissions only.

Table 3. Particulate and Fluoride Emission Factors for Anode Production ^a

Operation	Total Particulate ^{b,c,d,e} (kg/tonne)	Gaseous Fluoride ^b (kg/tonne)	Particulate Fluoride ^b (kg/tonne)
Anode baking furnace			
Uncontrolled	1.5	0.45	0.05
Spray tower	0.375	0.02	0.015
ESP	0.375	0.02	0.015
Dry alumina scrubber	0.03	0.004	0.001
Fugitive	ND	ND	ND

^a Source: USEPA (1995).

^b Units are kilograms (kg) of pollutant/tonne of molten aluminum produced.

^c Includes particulate fluoride, but does not include condensable organic particulate.

^d As noted above, the emission factors pertain to total particulate matter, rather than PM₁₀. In the absence of better data, the total particulate data can be used to provide conservative upper levels 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.

Table 4. Emission Factors for Alumina Reduction ^a

Operation	Total Particulate ^{b,c,d,e} (kg/tonne)	Gaseous Fluoride ^b (kg/tonne)	Particulate Fluoride ^b (kg/tonne)
Prebake cell			
Uncontrolled	47	12	10
Emissions to collector	44.5	11.4	9.5
Crossflow packed bed	13.15	3.25	2.8
Multiple cyclones	9.8	11.4	2.1
Spray tower	8.9	0.7	1.9
Dry ESP plus spray tower	2.25	0.7	1.7
Floating bed scrubber	8.9	0.25	1.9
Dry alumina scrubber	0.9	0.1	0.2
Coated bag filter dry scrubber	0.9	1.7	0.2
Dry plus secondary scrubber	0.35	0.2	0.15
Fugitive	2.5 ^f	0.6	0.5

^a Source: USEPA (1995).

^b Units are kilograms (kg) of pollutant/tonne of molten aluminum produced.

^c Includes particulate fluoride but does not include condensable organic particulate.

^d As noted above, the emission factors pertain to total particulate matter, rather than PM₁₀. In the absence of better data, the total particulate data can be used to provide conservative upper levels 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.

^f 58 percent of these emissions are < PM10.

Table 5. Emission Factors for Alumina Reduction ^a

Substance	Source	Emission Factor (kg/tonne) ^b
Phenol	Reduction	0.15
PAH ^c	Reduction	0.40
Hydrogen Fluoride	Reduction	2.5
	Anode Baking	0.26

^a Source: USEPA FIRE Database (1995).

^b Emission factor units are - mg/tonne Al produced.

^c Note that only the following four compounds had emission factor information: Naphthalene, Benz(a)anthracene, Benzo(a)pyrene, Chrysene, and Fluoranthene. There are other compounds that are classified as 'PAHs' (the USEPA typically considers 16 compounds in total). However, no data was available for these.

Anode Production

The following information was supplied by Hydro Aluminium (Hydro Aluminium, 1998) regarding PAH emissions from anode production:

- PAH emissions from anode production range from 0.005 - 0.25 kg/tonne anodes produced. Based on this data, the recommended emission factor for anode production is 0.13 kg/tonne (ie an average of the lower, and upper bounds).

Holding Furnaces

Holding furnace emissions can be calculated using the EETs for combustion (see Section 5.1 of this Manual). However, the EETs presented do not account for metal fume, and PM₁₀ emissions associated with such processes. There is currently no published data on emissions of metal fume, and very little information pertaining to particulate emissions from activities such as casting and rodding. The following data has been supplied by Hydro Aluminium (Hydro Aluminium, 1998) regarding emissions of total particulate from casting operations:

- Total particulate emissions from casting range from 0.03 - 0.2 kg/tonne anodes produced. Based on this data, the recommended emission factor for total particulate matter is 0.12 kg/tonne (ie an average of the lower, and upper bounds). In a similar manner to the other particulate matter sources above, this emission factor can be used to derive conservative estimates of PM₁₀ emissions from this operation.

5.4.3 Control Technologies

As shown in Tables 3 to 5 above, emission factors are available for both uncontrolled and controlled releases.

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 may be combined with an 'uncontrolled' emission estimate using Equation 1, and an example is presented below.

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

Where an emission factor for the controlled emission is available, the control efficiency automatically defaults to zero.

Example 1

An anode baking furnace operates with a spray tower to control emissions. It operates for 5000 hours per year, with a throughput of 0.2 tonnes/hr. Table 3 provides the controlled emission factor: 0.375 kg/tonne. The controlled PM₁₀ emission is calculated as follows:

$$\begin{aligned} E_{\text{kpy,PM10}} &= A * O_{\text{phrs}} * EF_i * (1 - CE_i/100) \\ &= 0.2 * 5000 * 0.375 * (1-0) \\ &= 375 \text{ kg/yr} \end{aligned}$$

5.4.4 Sulfur Dioxide Emissions from the Process

SO₂ emissions from the reduction process and anode production can be estimated using a mass balance. These emissions are separate to the SO₂ generated from the combustion process.

The most conservative estimates of SO₂ releases from the anode production and smelting operation can be made using the following simple equation, (supplied by the Australian Aluminium Council (AAC)), that assumes 100% conversion of sulfur to SO₂ :

$$\text{Emission (kg/hr)} = 2 * [(M_{\text{PITCH}} * S_{\text{PITCH}}/100) + (M_{\text{COKE}} * S_{\text{COKE}}/100)] \quad (3)$$

Where:

$$\begin{aligned} M_{\text{PITCH}} &= \text{Consumption of pitch at the smelter (kg/hr)} \\ S_{\text{PITCH}} &= \text{Sulfur content of pitch (weight percent)} \\ M_{\text{COKE}} &= \text{Consumption of coke at the smelter (kg/hr)} \\ S_{\text{COKE}} &= \text{Sulfur content of coke (weight percent)} \end{aligned}$$

5.5 Particulate Speciation

Metals can be speciated based on trace analysis data, or MSDS 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.

$$X_{\text{kpy,i}} = (m)(c_i) \quad (4)$$

Where:

$$\begin{aligned} X_{\text{kpy,i}} &= \text{mass emission of component i (kg/yr)} \\ m &= \text{mass emission rate of total particulate matter (kg/yr)} \\ c_i &= \text{mass fraction of component i (dimensionless)} \end{aligned}$$

You should that this methodology is most applicable to emissions from low temperature sources, such as stockpiles. This is because this methodology intrinsically assumes that all metals are contained in the released particulate matter. While this may be a reasonable assumption for metals with very low vapour pressures, more volatile metals (eg. mercury) are likely to be partially present in vapour form. However, insufficient information is currently available to produce better estimates, other than through source testing.

With regards to emission controls for PM_{10} , and 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.

5.6 VOC Emissions

5.6.1 Total VOC Emissions

Very little data is available to estimate total VOC emissions from smelting operations. However, based on discussions with the aluminium smelting working group, EETs will be developed for total VOC releases from various operations. If VOC data is available, speciation can be performed using the methodology outlined in the following section.

5.6.2 Speciated VOC Emissions

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 using generic weight fractions developed by the USEPA. In addition, the speciation data from the USEPA is limited and, therefore, a combination of these two methodologies may be required.

5.6.2.1 Speciation Based on Process Stream Composition

This methodology involves using the composition data for each process stream (ie obtained from analytical procedures 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)(kg/hr)
- WP_i = The concentration of NPI substance "i" in weight percent
- WP_{VOC} = The VOC concentration in weight percent.

5.6.2.2 Speciation Using Developed Weight Fraction Data

In the absence of analytical data, the default VOC speciation data presented in Tables 6 to 10 can be used to characterise emissions of NPI-listed substances. (Note that some emission factors are also available for emissions of organic compounds from anode production and alumina reduction operations, as presented in Section 5.4.2.) Applying this speciation data requires the use of an equation similar to that in Section 5.6.2.1:

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

Where:

- E_i = The mass emissions of NPI substance "i" from the equipment (kg/hr)
- E_{VOC} = The estimated total VOC mass emission rate (kg/hr)
- WP_i = The weight percent of the relevant compound in the VOC emission (as provided in Tables 6 through 10).

It is acknowledged that not all facilities will trigger thresholds for all compounds listed in the following Tables, but the emission factors have been provided for completeness.

Table 6. Speciation of VOCs from Anode Baking^a

Substance	Molecular Weight	Weight Percent
Hexane	86.17	0.45
Benzene	78.11	0.5
Toluene	92.13	0.52
Ethylbenzene	106.16	0.14
Xylenes	106.16	0.23
Phenol	94.11	3.35
PAHs	128.17	41.86

^a Source: USEPA (1993).

Table 7. Speciation of Fugitive VOCs from Anode Prebake ^a

Substance	Molecular Weight	Weight Percent
1,3-butadiene	54.09	0.72
Hexane	86.17	1.48
Cyclohexane	84.16	0.97
Methanol	32.04	1.51
Ethanol	46.07	1.47
Methyl methacrylate	100.13	0.50
Formaldehyde	30.03	1.67
Acetaldehyde	44.05	0.91
Acetone	58.08	1.59
Methyl ethyl ketone	72.1	1.32
Methyl isobutyl ketone	100.16	0.60
Ethylene oxide	44.05	0.41
Dichloromethane	84.94	0.81
Chloroform	119.39	0.55
Tetrachloroethylene	165.83	0.76
1,1,2-trichloroethane	133.42	0.38
Trichloroethylene	131.4	0.46
Vinyl chloride	62.5	0.45
Benzene	78.11	3.04
Toluene	92.13	2.20
Ethylbenzene	106.16	0.70
Xylenes	106.16	1.68
Cumene	120.2	0.41
Styrene	104.14	1.30
Phenol	94.11	0.47
PAHs	128.17	0.37

^a Source: USEPA (1993).

Table 8. Speciation of VOCs from Materials Handling ^a

Substance	Molecular Weight	Weight Percent
1,3-butadiene	54.09	0.72
Hexane	86.17	1.48
Cyclohexane	84.16	0.97
Methanol	32.04	1.51
Ethanol	46.07	1.47
Methyl methacrylate	100.13	0.50
Formaldehyde	30.03	1.67
Acetaldehyde	44.05	0.91
Acetone	58.08	1.59
Methyl ethyl ketone	72.1	1.32
Methyl isobutyl ketone	100.16	0.60
Ethylene oxide	44.05	0.41
Dichloromethane	84.94	0.81
Chloroform	119.39	0.55
Tetrachloroethylene	165.83	0.76
1,1,2-trichloroethane	133.42	0.38
Trichloroethylene	131.4	0.46
Vinyl chloride	62.5	0.45
Benzene	78.11	3.04
Toluene	92.13	2.20
Ethylbenzene	106.16	0.70
Xylenes	106.16	1.68
Cumene	120.2	0.41
Styrene	104.14	1.30
Phenol	94.11	0.47
PAHs	128.17	0.37

^a Source: USEPA (1993).

Table 9. Speciation of VOCs from Prebake Reduction Cell ^a

Substance	Molecular Weight	Weight Percent
Hexane	86.17	0.45
Benzene	78.11	0.5
Toluene	92.13	0.52
Ethylbenzene	106.16	0.14
Xylenes	106.16	0.23
Phenol	94.11	3.35
PAHs	128.17	41.86

^a Source: USEPA (1993).

Table 10. Speciation of Fugitive VOCs from Prebake Reduction Cell ^a

Substance	Molecular Weight	Weight Percent
1,3 butadiene	54.09	0.72
Hexane	86.17	1.48
Cyclohexane	84.16	0.97
Methanol	32.04	1.51
Ethanol	46.07	1.47
Methyl methacrylate	100.13	0.50
Formaldehyde	30.03	1.67
Acetaldehyde	44.05	0.91
Acetone	58.08	1.59
Methyl ethyl ketone	72.1	1.32
Methyl isobutyl ketone	100.16	0.60
Ethylene oxide	44.05	0.41
Dichloromethane	84.94	0.81
Chloroform	119.39	0.55
Tetrachloroethylene	165.83	0.76
1,1,2-trichloroethane	133.42	0.38
Trichloroethylene	131.4	0.46
Vinyl chloride	62.5	0.45
Benzene	78.11	3.04
Toluene	92.13	2.20
Ethylbenzene	106.16	0.70
Xylenes	106.16	1.68
Cumene	120.2	0.41
Styrene	104.14	1.30
Phenol	94.11	0.47
PAHs	128.17	0.37

^aSource: USEPA (1993).

6.0 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 a release 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.

6.1 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 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	=	Releases to air, water, and land (as defined under the NPI). Emissions include both routine and accidental Releases, 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:

$$\text{Input of substance 'i'} = \text{Amount of substance 'i' in product} + \text{amount of substance 'i' in waste} + \text{amount of substance 'i' transformed/consumed in process} + \text{emissions of substance 'i'}$$

The mass balance approach can be used for each NPI-listed substance where there is a responsibility to report. Emissions can then be allocated to air, water, and land. A simple example of the application of mass balance is presented below.

Example 2

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. (Note: 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:
= mass of A + mass of B + mass of water
= 10 000 + 5 000 + 20 000
= 35 000 tonnes

Step 2: Calculate Total Outputs from Process

Total outputs:
= mass of product + mass of by-product
= 22 000 + 4 000
= 26 000 tonnes

Step 3: Calculate Total Amount of Waste Produced

Total quantity of waste produced:
= mass of inputs – mass of outputs
= 35 000 – 26 000
= 9000 tonnes per annum.

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, for example, 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 account must be taken 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).

6.2 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 (feed) (ie flow rates, concentrations, densities) and outputs of the unit process.

The following general equation can be used (note that scm is an abbreviation for standard cubic metres – refer to Section 7):

$$E_i = \sum Q_f W_{f,i} P_i - \sum Q_o W_{o,i} P_o \quad (7)$$

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)
- $W_{f,i}$ = Weight fraction of component i in inlet stream i
- $W_{o,i}$ = 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, as this information is required for process control. The loss E_i 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 releases occur.

7.0 Monitoring

Many facilities conduct monitoring as part of their existing regulatory requirements. Typically, the monitoring is tied directly to the conditions on 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 stack or liquid effluent testing, which may be used in characterising emissions for the NPI. Typical data collected includes:

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

In most situations, the use of such data as a basis for calculating emissions will provide the most representative emissions information for a facility and this data should be used, (where available), to calculate emissions.

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 account of the number of hours per year the source is discharging to the environment.

Stack data is typically 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);
- Nm³ – normal cubic metre (typically at 0°C and 1 atm);

It is essential to ascertain the conditions the source test data reflects before determining annual emission estimates. Typically, the measured concentrations and flue gas flows are presented on source test reports at the same conditions (ie. temperature and pressure).

Two examples of the use of sampling data to characterise annual emissions are presented below. Example 3 is based on the concentration of the compound being presented at the same conditions as the measured flow rate, while Example 4 is based on the concentration and flue gas flows being measured under different conditions.

Example 3

The following example relates to the 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 $30 \text{ Nm}^3/\text{sec}$;
- the measured concentration of cadmium in the flue gas is $0.01 \text{ mg}/\text{Nm}^3$; 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:

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

Using this data, the emission is derived as follows:

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

Example 4

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

- the flue gas flow from a stack is measured at $100 \text{ acm}/\text{sec}$;
- the measured concentration of cadmium in the flue is $0.01 \text{ mg}/\text{Nm}^3$;
- 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. Note, however, that the temperatures must be presented using the absolute temperature scale of Kelvin (ie. $0^\circ\text{C} = 273 \text{ K}$). The conversion is then performed as follows (noting that the actual stack conditions are $150 + 273 = 423 \text{ K}$):

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

The emission rate is then derived using the same methodology as outlined in Example 3 as follows:

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

8.0 Emissions to Water

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

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

The first stage in characterising releases to water therefore, is to identify those releases that are classed as transfers. These releases are not required to be reported for the purposes of reporting to the NPI. Other releases, (eg discharges to surface water bodies such as streams and rivers), are required to be reported.

Discharges to water are strongly related to process, and are site-specific in nature. As a consequence, most facilities perform some monitoring to characterise these emissions. While the NPI does not require facilities to conduct monitoring to characterise releases, 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 on the application of monitoring data to the calculation of emissions are provided below.

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

Examples

Examples 5 & 6 show how emissions can be estimated from point source discharges. Example 5 is relevant for wastewater streams that have a relatively constant daily flow rate, and where the measured concentration of the relevant compound in the stream does not vary greatly. Example 6 is relevant to streams that have more variable flow rates and composition (eg stormwater).

Example 5

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

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

Based on the calculations above, 60 kg/year of cadmium is therefore discharged from the plant annually (and is required to be reported under the NPI because the emission is to a water body).

Example 6

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 cadmium levels in the discharge. The data collected over a single year is presented in Table 11.

The daily release is derived by multiplying the daily flow rate, by the measured level of cadmium. The annual release can be determined by combining 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

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

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

Table 11. 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

9.0 Emissions to Land

Under the NPI, facilities are required to report on their emission 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, substances that are removed for transfer to another facility for destruction, treatment, recycling, reprocessing, recovery, or purification are 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 which 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

9.1 Groundwater Monitoring

Some facilities conduct monitoring of groundwater to characterise releases from the facility. Where available, this monitoring data can be used to assist in the characterisation of releases. 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 releases 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 offsite, such as evaporation, or surface runoff), it will be necessary to characterise these releases using the other EETs presented in this Manual.

9.2 Spills

For many facilities, the primary source of emissions will be as a result of spills (this may also include intentional spillage due to vessel washdown). Accidental spills can directly contribute to releases to land, 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 (ie. in particular, the quantities of NPI substances spilled). This log could then constitute the basic information required to meet NPI reporting requirements.

You should note that if the spill is a volatile liquid, it reasonable to assume that all of the light end fraction is volatilised, and that the remaining liquid is released into the ground. However, if the liquid is not volatile, and no material is collected, it may be 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:

$$E_{\text{VAP}} = 1.2 * 10^{-10} (MW(P_{\text{vap},i})/T) U^{0.78} X^{0.89} Y \quad (8)$$

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 (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:

$$ER_{\text{LAND},i} = \text{Qty}_{\text{SPILL}} - ((\text{time}) * (E_i) - Q_{\text{removed}}) \quad (9)$$

Where:

- $ER_{\text{LAND},i}$ = The emission to the land of compound “i”
- $\text{Qty}_{\text{SPILL}}$ = 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.

9.3 On-Site Disposal

Facilities with on-site disposal of wastes will need to consider the discussion in Section 8.0 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. In a similar approach to spills, the most effective EET is to maintain 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.

10.0 Discussion

Through discussions with the AAC, it has become apparent that there are significant differences between the aluminium smelting industry in the US, and the aluminium smelting facilities currently operating in Australia. It is believed that the US industry represents a cross section of both new and old technologies, while the Australian industry is essentially comprised of new technologies. The implication is that many of the emission factors developed by USEPA to characterise emissions from aluminium smelting facilities may not characterise emissions from the Australian industry adequately. However, there is no data currently available to confirm this hypothesis.

The information (in particular, the emission factors) presented in this Manual reflects the best data currently available. It is expected that the work of the aluminium smelting working group will, in time, provide better emission estimation techniques that can be used by the industry. Until this time, the emission factors presented in this Manual should be used for emission estimation.

11.0 Glossary

A glossary of terms commonly used in relation to aluminium smelting is presented below. Note however that not all of these terms are used in this Manual.

Alumina	Aluminium oxide (Al_2O_3); raw material; a fine white powder refined from bauxite
Anode	Positive electrode; in aluminium smelting, the carbon electrode consumed in the process
Anode effect	Disturbances to the smelting process caused when the concentration of alumina in the molten bath falls, causing increased electricity consumption, and fluoride emissions
Baghouse	Type of dust collector with bags in which dusts are filtered
Bath	Molten contents of a cell
Carbon bake furnace	Series of pits lined with refractory bricks, in which 'green' anodes are baked prior to use in cells
Cathode	Negative electrode; in aluminium smelting, the carbon lining of a pot
Cryolite	Sodium aluminium fluoride (Na_3AlF_6) added to the bath as a flux
Dross	Waste material removed from the surface of molten metal and consists of aluminium oxides, metal chlorides, and fluorides
Dry scrubbing	Removal of a contaminant from an air stream by passage through a solid phase medium; in aluminium smelting, removal of gaseous fluorides by contact with primary alumina
Dust collector	Air pollution control equipment designed to filter out particulate matter from a gas stream
Fugitive emissions	Atmospheric emissions not emitted from a designated stack. These are largely uncontrollable, usually emanating from a large leak, or spill.
Green carbon plant	Facility for the manufacture of anodes using a combination of petroleum coke, pitch, recycled butts, temperature, and pressure.
Net carbon ratio	Carbon consumption relative to aluminium production (usually expressed in tonnes)
Petroleum coke	Anode raw material obtained as a by-product of oil refining
Pitch	Anode raw material obtained as a by-product in the coking of coal to metallurgical coke, produced by the distillation of the coal tar
Reduction cell	A carbon and refractory lined steel vessel within which liquid aluminium is produced by the electrolytic reduction of alumina dissolved in an electrolyte (bath) consisting mainly of cryolite. This is a continuous process operating at 970°C

Reduction line	A row of reduction cells connected electrically in series
Ringlemann	Test used to determine the blackness of smoke emitted from a stack
Rodding	Joining of carbon anodes to copper bars with molten cast iron
Spent cell lining	Major hazardous waste material generated at the smelter resulting from the dismantling of reduction cells at the end of their useful life
Wet scrubbing	Removal of a contaminant from an air stream by passage through a liquid; in aluminium smelting, removal of gaseous fluoride and sulfur oxides by passage through alkaline solutions.

12.0 References

1. USEPA (1997) *Factor Information Retrieval System (FIRE)*, 1997, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, 1997 (AirChief CD-ROM, 1997, Version 5.0)
2. Perry, R.H. & Green, D.W. (1997), *Perry's Chemical Engineers' Handbook – Seventh Edition*, McGraw Hill, NY.
3. USEPA (1993) *VOC/PM Speciation DBMS (SPECIATE)*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, 1993
4. USEPA (1995) *Compilation of Air Pollutant Emission Factors AP-42, Volume I: Stationary Sources, Fifth Edition, 1995*, 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)
5. Hydro Aluminium (1998), Fax from Per Ravn, Hydro Aluminium, to Katrina Whitely, Tomago Aluminium, re National Pollutant Inventory, 25 September, 1998.
6. The following Emission Estimation Technique Manuals referred to in this Manual can be obtained from Environment Australia:
 - Emission Estimation Technique Manual for Combustion in Boilers
 - Emission Estimation Technique Manual for Fossil Fuel Electric Power Generation
 - Emission Estimation Technique Manual for Mining
 - Emission Estimation Technique Manual for Sewage and Wastewater Treatment.