National Pollutant Inventory

Emission Estimation Technique Manual

for

Nickel Concentrating, Smelting and Refining

First published in June 1999

EMISSION ESTIMATION TECHNIQUES
FOR
NICKEL CONCENTRATING, SMELTING AND REFINING

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Nickel Concentrating, Smelting & Refining

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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 nickel concentrating, smelting and refining.

The scope of this document is to outline methods that can be used by the nickel concentrating, smelting and refining industry to:

- identify which substances they are required to report as part of the National Pollutant Inventory (NPI); and
- estimate emissions of NPI substances to air, water and land from their facilities.

This handbook covers the concentrating, smelting and refining of nickel commencing from the delivery of ore to the processing facilities for crushing and milling, through smelting and to the production of +99% pure nickel at the refinery, for the nickel sulfide and nickel/cobalt laterite processes.

It does not include extraction of ore, which is covered by the *EET Manual for Mining*.

Ancillary activities (eg. power generation, and ammonium sulfate and sulfuric acid production) are likewise not covered in this handbook but may be reportable under the NPI. These activities are covered by separate EET manuals.

The emission of NPI substances from processing facilities Tailings Storage Facilities (TSFs), waste management sites and sewerage systems are included in the reporting requirements of the NPI, and are covered by this manual.

EET MANUAL:	Nickel Concentrating, Smelting & Refining
HANDBOOK:	Basic Non-Ferrous Metal Manufacturing
ANZSIC CODE :	2729

The scope of this manual is presented diagrammatically in Figure 1.
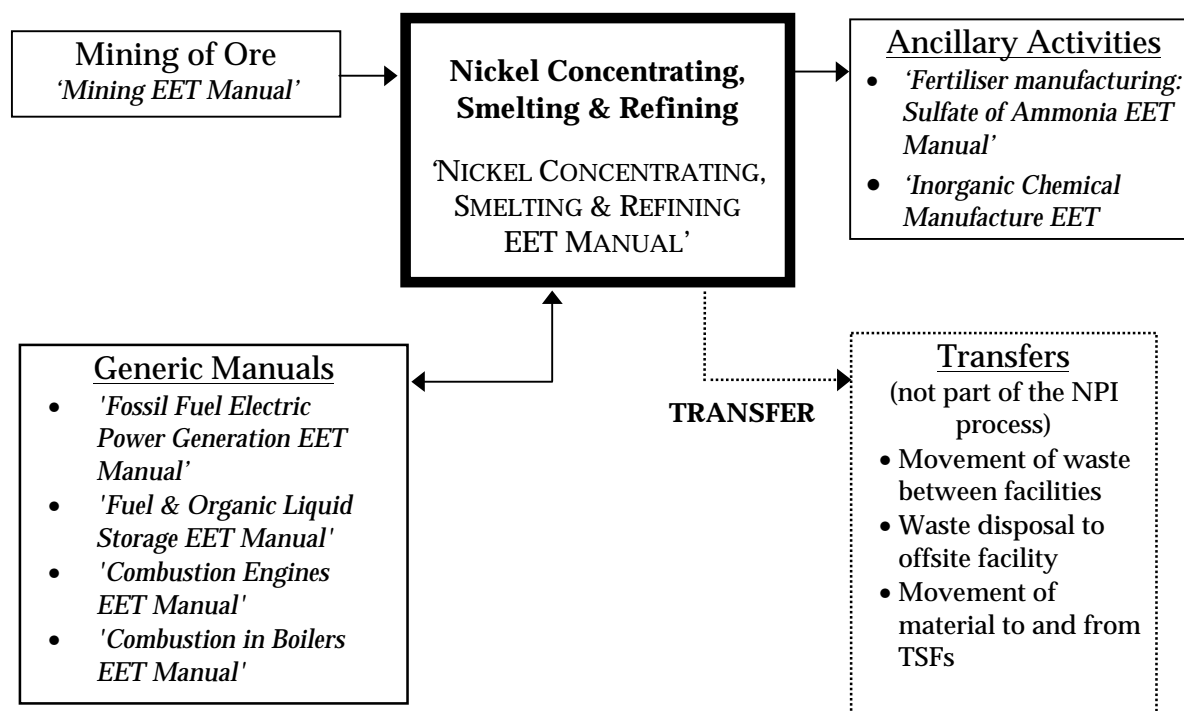
Figure 1 - **Scope of the 'Nickel Concentrating, Smelting and Refining EET Manual'
and its Relationship with Other EET Manuals**

Context and use of the manual

The NPI manual provides a "how to" guide for the application of various methods to estimate emissions as required by the NPI. It is recognised that the data that is generated in this process will have varying degrees of accuracy with regards to the actual emissions from nickel processing facilities. In some cases, there will necessarily be a large potential error due to inherent assumptions in the various emissions estimation techniques (EETs) and/or a lack of available information of chemical processes.

This difficulty is well illustrated by the example of emissions of cyanide from tailings storage facilities. Research in this area undertaken by the WA Chemistry Centre has shown that, for two TSFs with similar rates of leakage to groundwater, there was no movement of cyanide into groundwater at one site, while significant contamination of groundwater was detected for the second site. This dramatic difference was believed to be a result of particular site characteristics related to cyanide speciation, mineralogy and pH.

EETs should be considered as 'points of reference'

The EETs and generic emission factors presented in the manual should be seen as 'points of reference' for guidance purposes only. Each has associated error bands that are potentially quite large (eg. based on generic emission factors only) uncertainties of 100% are considered likely. Chapter 10 discusses the general reliability associated with the various methods. The potential errors associated with the different EET options should be considered on a case-by-case basis as to their suitability for a particular facility. Facilities may use EETs that are not outlined in this document. However, they must seek the consent of their relevant environmental authority to determine whether any 'in house' EETs are suitable for meeting their NPI reporting requirements.

Hierarchical approach recommended in applying EETs

The manual presents a number of different EETs, each of which could be applied to the estimation of NPI substances. The range of available methods should be viewed as a hierarchy of available techniques in terms of the error associated with the estimate. Each substance needs to be considered in terms of the level of error that is acceptable or appropriate with the use of the various estimation techniques. Also, the availability of pre-existing data and the effort required to decrease the error associated with the estimate will need to be considered. For example, if emissions of a substance are clearly very small no matter which EET is applied, then there would be little gained by applying an EET which required significant additional sampling.

The steps in meeting the reporting requirements of the NPI can be summarised as follows:

- for Category 1 and 1a substances identify which reportable NPI substances are used (or handled by way of their incidental presence in ore or materials, or exceeds the bulk storage capacity for 1a), and determine whether the amounts used or handled are above the "threshold" values and therefore trigger reporting requirements;
- for Category 2a and 2b substances determine the amount and rate of fuel (or waste) burnt each year, the annual power consumption and the maximum potential power consumption, and assess whether the threshold limits are exceeded;
- for Category 3 substances determine the annual emissions to water and assess whether the threshold limits are exceeded; and
- for those substances above the threshold values, examine the available range of EETs and determine emission estimates using the most appropriate EET.

Generally it will be appropriate to consider various EETs as alternative options whose suitability should be evaluated in terms of:

- the associated reliability or error bands; and
- the cost/benefit of using a more reliable method.

The accuracy of particular EETs is discussed in Chapter 10 - Emission Factor Rating.

NPI emissions in the environmental context

It should be noted that the NPI reporting process generates emission estimates only. It does not attempt to relate emissions to potential environmental impacts, bioavailability of emissions, natural background levels etc.

Facilities may undertake 'Ancillary Activities', such as the production of hydrochloric acid or ammonium sulfate, either as a process input or through processing of waste steams. When estimating emissions a facility should ensure that emissions are not 'double accounted' (See Section 4) and process maps should be used to minimise the potential for this.

The manual is structured to allow facilities to work through the manual addressing issues in a structured and coherent manner.

Likely emissions from facilities are discussed in Section 3, while Section 4 discusses the approach to emissions estimation and those elements of the environment where emissions may result.

Sections 5, 6, 7, 8 and 9 address the EETs likely to be used by the industry. This approach has been adopted in order to demonstrate how an EET may be applied to estimating emissions of a substance and supported by other EETs. For example facilities may choose to use a mass balance approach to their estimation of cyanide emissions. However the mass balance EET is likely to be supported by direct monitoring data and emission factors.

This manual has been prepared by PPK Environment & Infrastructure Pty Ltd on behalf of the WA Department of Environmental Protection. Funding for the project was provided by Environment Australia. It has been developed through a process of national consultation involving State and Territory environmental authorities, and industry groups. Particular thanks are due to Western Mining Corporation for its' comments, advice and information.

2.0   Process Description

2.1   General

Australia supplies 10% of world nickel production, most of which comes from Western Australia.

Nickel occurs naturally in two forms; as sulfide ores or laterite (oxide) ores.

- **Sulfide ores** are generally deep, hard rock deposits, which may be mined by a combination of open-cut and underground mining techniques.

- In **laterite ores** the weathering process has converted the nickel sulfides to oxide ores within the near-surface weathering zone. Laterite deposits are clay-rich "soft" deposits, extracted by open-cut mining.

Distinct processes are applied to the concentrating, smelting and refining of the ores from these sources.

Representative processes are discussed below and example process maps/flowsheets are presented as a source of reference. Refining processes at facilities across Australia will vary, and the flowsheets presented in this manual are not intended to be a comprehensive analysis of nickel processing techniques

As it is not possible to address the specific processes used at all Australia based nickel processing facilities in this manual, facilities are advised to use their own process maps/flow sheets to assist in structuring and addressing NPI reporting requirements.

2.2   Nickel Sulfide Processing

Nickel sulfide processing can be separated into the three processing stages: concentrating, smelting and refining. These stages are often carried out at distinct facilities and as such have been presented in this manner to simplify appreciation of operational issues.

2.2.1   Concentrating

The nickel sulfide concentrating process is presented in Figure 2.

Concentration. Ore is crushed to a powder and mixed with water. The slurry is fed into a rotating mill, where heavy steel rods or balls grind the rock to a fine pulp. The pulp from the mills is fed into a flotation cell where the mixture is agitated with compressed air. The agitation, together with the compressed air, causes bubbles to form. Nickel sulfide particles attach to the bubbles and float to the surface, producing a concentrated nickel froth. The froth is collected from the surface of the cell and retreated in the same way a number of times, increasing the grade of concentrate each time. Over 90% of the nickel in the initial ore is recovered into a concentrate that contains around 10% to 20% nickel, which is then filtered and dried prior to dispatch to a smelter as a fine powder.

Ore

Soda Ash or
Lime

Crushing & Milling

Metals, PM_{10}

Collector (Xanthate), frother, activator,
depressant, lime, CaO, cyanide

Flotation

CS_2, HCN

Power/Fuel

Thickening & Drying

Products of combustion, CS_2

Hydrocyclone	→ Coarse sand used for mine backfill

Thickener

TSFs

PM_{10}, cyanide, metals

**Nickel Sulfide
Concentrate
(13 - 20%)**
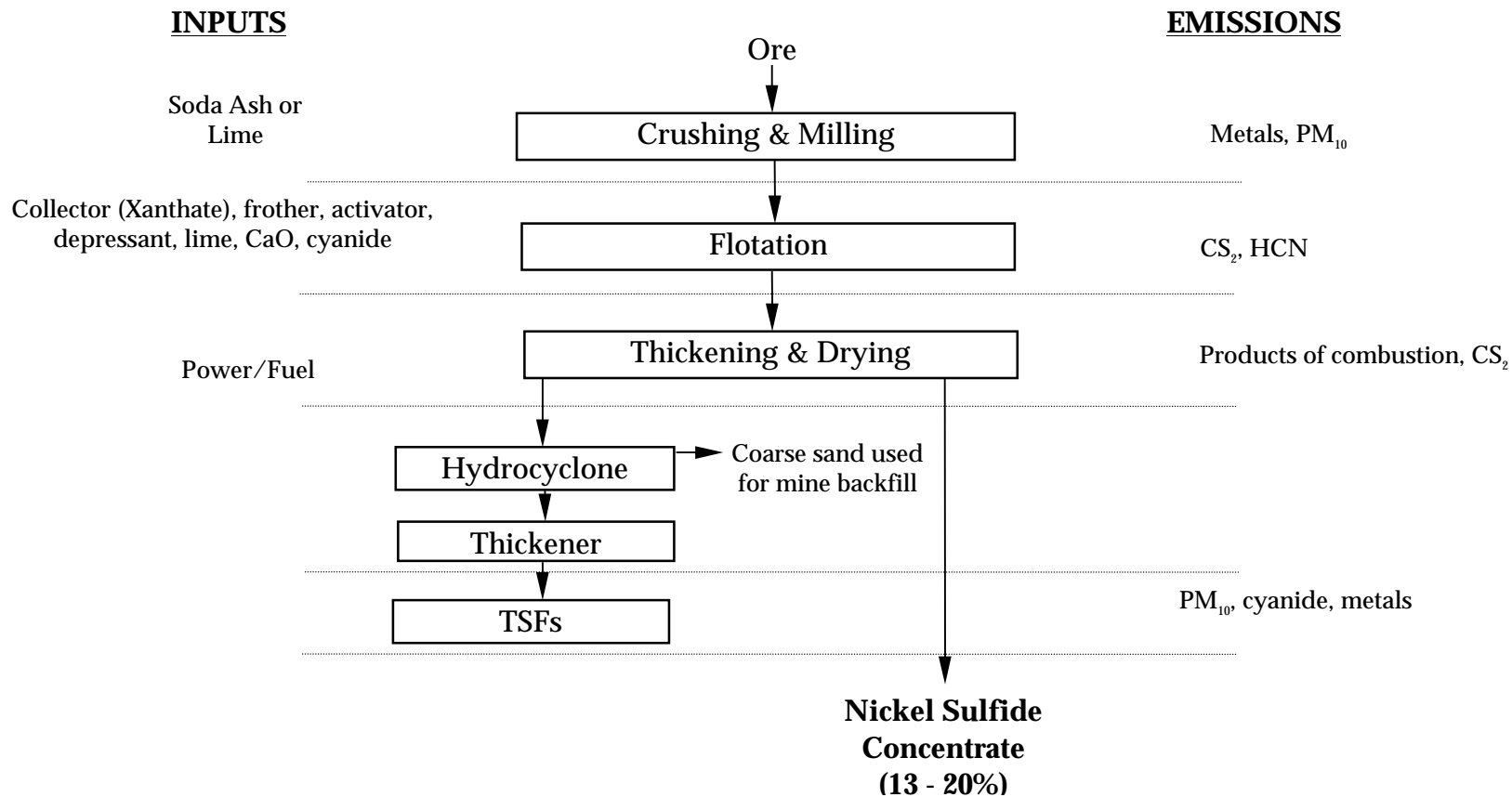
Figure 2 - Nickel Sulfide Concentrating Process Inputs and Emissions

Flotation: Mill pulp is fed into mechanically agitated flotation cells where chemical reagents (an activator, a collector, a pH modifier and a depressant) are added and air is injected to create froth on the surface. The activator promotes flotation of the slower floating pyrrhotite (Fe_nS_{n+1}) mineral; the collector collects these nickel-rich particles, attaches them to the air bubbles and floats them to the surface; the pH modifier helps produce a higher grade of concentrate; and the depressant coats the waste materials to make them sink. The froth that floats to the surface contains most of the nickel and iron sulfides.

Thickening: Thickening involves gravity separation of water from the heavier mineral-rich component. The method often used is counter-current decantation (CCD), in which the slurry is cycled through two thickening tanks and liquid is progressively poured off for water recovery.

2.2.2 Smelting

The smelting flowsheet is presented in Figure 3.

Flash Furnace: Dry concentrate is mixed with flux (silica sand) and recycled furnace dust and fed into the reaction shaft of the flash furnace. In the shaft this mixture reacts with oxygenated hot air and oxidises (flashes) almost instantaneously. The fused mixture falls into a settler bath where the matte and slag are separated. The nickel 'matte' sinks to the bottom and the remaining material called 'slag' floats to the top. The exothermic reaction provides most of the heat requirement; the balance may be supplied by natural gas.

Converter: The converter upgrades the nickel content of the matte by blowing air into it to oxidise the remaining iron sulfides.

Concentrate

Power/Fuel, coke, lime,
sand, reverts

| Flash Furnace |

PM$_{10}$, metals, products of
combustion

| Slag Heap |

PM$_{10}$, metals, SO$_2$

| Electrostatic Precipitator |

Limestone, NaOH, HCl,
H$_2$SO$_4$

| Sulfur Recovery |

H$_2$SO$_4$ product

H$_2$SO$_{4,}$
SO$_2$, NO$_x$, CO

| Residue or storage
ponds |

PM$_{10}$, metals

Power/Fuel, flux
materials

| Converter |

PM$_{10}$, metals, products of
combustion

| Granulator, Dryer &
Packing |

PM$_{10,}$ H$_2$S, metals

Nickel matte
(65 - 74%)

Figure 3 - **Nickel Sulfide Smelting Process Inputs and Emissions**

2.2.3 Refining

An example nickel refining flowsheet is presented in Figure 4. Figure 4 is representative of one refining process. Facilities utilising other processes should refer to their facility-specific flowsheets.

INPUTS   **EMISSIONS**

Nickel matte

Grinding   Metals, PM_{10}

Ammonia (NH_3)   Leaching   Ammonia (NH_3)

Flocculants   Heating, Thickening & Filtering PM_{10}, CuS

Copper sulfide product

$FeSO_4$, H_2 Reduction

Flash Tanks H_2, Ni, $(NH_4)_2SO_4$

H_2S Liquor Stripping H_2S, SO_2, PM_{10}, mercaptans

Mixed sulfides   Ammonium sulfate $(NH_4)_2SO_4$

Washing, filtering & drying PM_{10}

Power/ Fuel   Briquetting PM_{10}, metals, products of combustion

Power/ Fuel   Sintering PM_{10}, H_2S, metals, products of combustion

Nickel Briquettes (+99%)

Figure 4 - **Nickel Sulfide Refining Process Inputs and Emissions**

Various processes exist to convert the nickel matte into marketable products. Essentially, residual iron sulfides are removed by leaching with ammonia, then valuable components are progressively removed by differential precipitation.

Leaching: Finely ground nickel matte is mixed with process liquor (recycled from the final leaching tank) and pumped into autoclaves for reaction with air and ammonia at high pressure. Leaching dissolves the valuable metals - nickel, copper and cobalt - but leaves iron as an insoluble residue.

Reduction: The process liquor undergoes a 5 day reduction cycle to precipitate nickel powder. The cycle commences with nucleation - the generation of fine seed particles - and ends with total discharge of the vessel. Nickel in solution is reduced to nickel metal and ferrous sulfate is oxidised to ferrous hydroxide. The nickel and liquor are separated by settlement.

Liquor Stripping: Reaction with hydrogen sulfide gas in a recirculating pipe reactor system precipitates a mixed sulfur product. This product typically contains 25% nickel, 25% cobalt and 30% sulfur.

2.3   Nickel Laterite Pressure Acid Leach Process

The process flow diagram for the nickel laterite pressure acid leach process is presented in Figure 5.

Pressure Leaching: Slurry is fed into autoclaves at high pressure following heating. The slurry reacts with sulfuric acid at high pressure and temperature. Leaching dissolves the valuable metals - nickel and cobalt - but leaves iron as an insoluble residue.

Sulfide Precipitation: Sulfide precipitation yields a 'cake' product following heating and injection with hydrogen sulfide to precipitate the nickel and cobalt.

Solvent Extraction: This process utilises an organic solvent to extract nickel from the product liquor, leaving cobalt. Nickel is subsequently stripped from the loaded solvent using a concentrated ammonia (NH_3) solution or sulfuric acid (H_2SO_4).

INPUTS　　　　　　　　　　　　　　　　　　　　　**EMISSIONS**

Laterite ores　　　　　　　　　　　　　　PM_{10}

LEACH

Preparation

Power/Fuel,　　**Pressure leaching**　　　　　　PM_{10}, products
$H\ SO$　　　　　　　　　　　　　　　　　　　of combustion

Counter current washing

Calcrete, CaO　　**Slurry neutralisation**　　　　PM_{10}

TSFs　　　　　　PM_{10},
　　　　　　　　seepage

REFINING

H_2S　　**Mixed sulfide precipitation**　　　　H_2S

O_2　　**Mixed sulfide pressure leach**

Solvents　　**Solvent extraction**　　　　Organic fugitives

NH_3　　**Metal separation**　　　　NH_3

Poly acrylic　　**Nickel**　　　**Cobalt**
acid, H　　　　**hydrogen**　　**hydrogen**
　　　　　　reduction　　**reduction**

　　　Nickel　　　**Cobalt**
　　　powder　　　**powder**　　　PM_{10}

Power, poly　　**Nickel**　　　**Cobalt**　　PM_{10}, metals,
acrylic acid　　**Briquetting**　**Briquetting**　products of
　　　　　　　　　　　　　　　　　combustion

Power, H_2　　**Nickel**　　　**Cobalt**　　PM_{10}, metals,
　　　　　　Sintering　　**Sintering**　products of
　　　　　　　　　　　　　　　　　combustion

　　Nickel　　　**Cobalt**
　　Briquettes　　**Briquettes**　　　PM_{10}
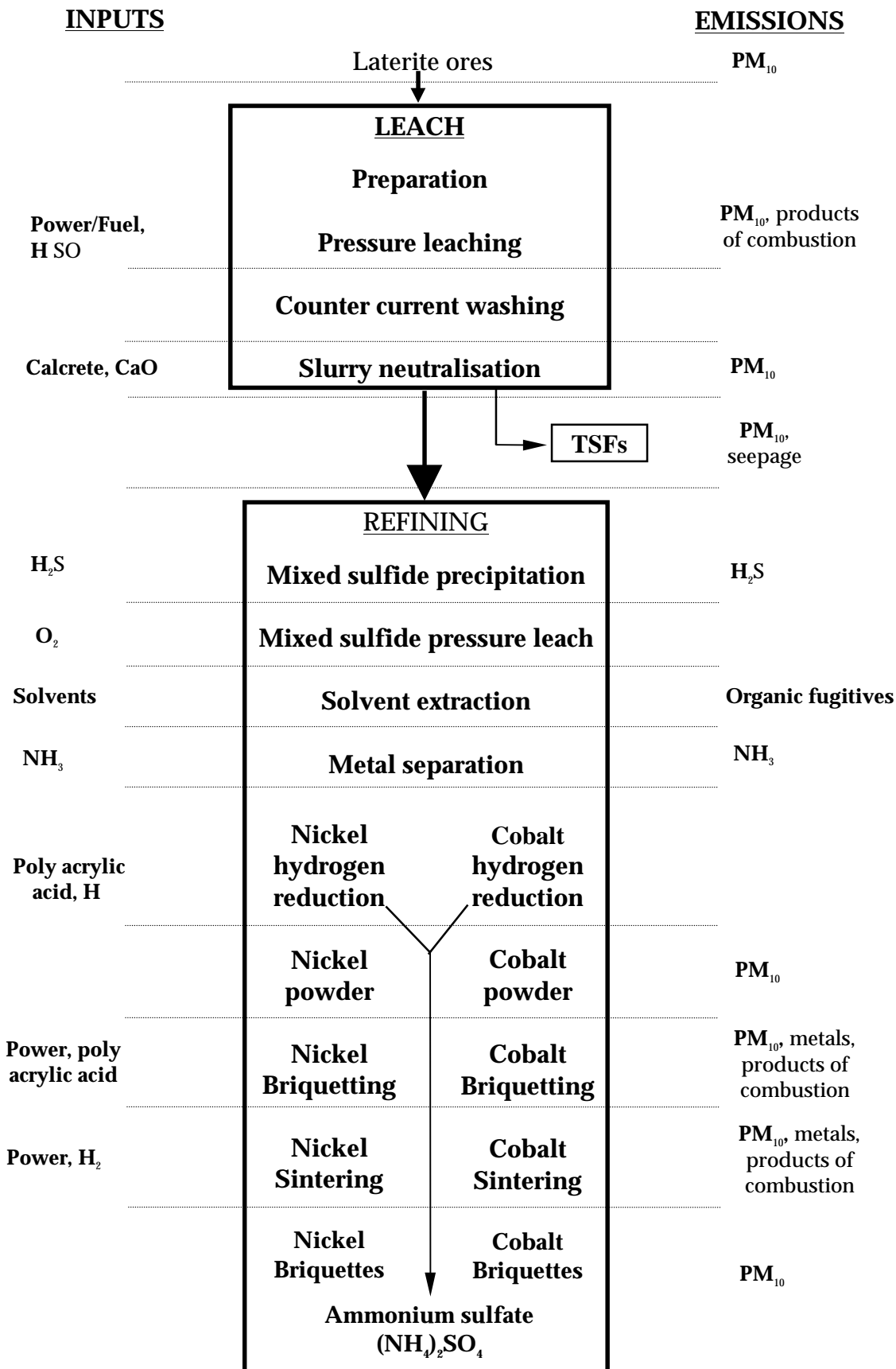
Ammonium sulfate
$(NH_4)_2SO_4$

Figure 5 - **Nickel Laterite Pressure Acid Leach Process Inputs and Emissions**

2.4　Nickel Laterite Ammonia Leach Process

The process flow diagram for the nickel laterite ammonia leach process is presented in Figure 6.

Ore Reduction and Cooling: The ground-dried ore is reduced through the addition and burning of reductant. The ore reduction process converts metal (nickel and cobalt) oxides to free metal.

Leaching and Thickening*:* The metal ions from the cooled reduced ore are then dissolved in an ammonia/ammonium carbonate solution. The solution and the metal liquor are then aerated to complete leaching and precipitate unwanted metal oxides (predominantly iron). The mixture is passed through thickeners to allow separation of the nickel/cobalt ammoniacal solution from the waste solids (tailings).

Solvent Extraction*:* The nickel/cobalt solution (product liquor) is next passed through steam stills to remove a range of impurities and recover ammonia. The solvent extraction process utilises an organic solvent, within a kerosene diluent, to extract nickel from the refined product liquor, leaving cobalt. Nickel is subsequently stripped from the nickel-loaded organic solvent, using a concentrated ammonia solution. The nickel-loaded ammonia solution is then transferred to a thickener where copper is removed as copper sulfide solids. The nickel-loaded ammonia solution is steam stripped to recover the ammonia and carbon dioxide.

Nickel Production*:* Steam stripping of nickel-loaded strip liquor produces a nickel carbonate slurry which is subsequently transferred to a thickener. The solution is filtered and the filter cake fed into a rotary kiln for calcining to nickel oxide. Nickel oxide is further treated in the furnace to produce a range of nickel and nickel oxide products.

Cobalt Production: The cobalt stream from the solvent extraction process is sulfided and thickened, before undergoing a process of atmospheric/pressure leach, solvent extraction, ion exchange before precipitation as cobalt oxide hydroxide.
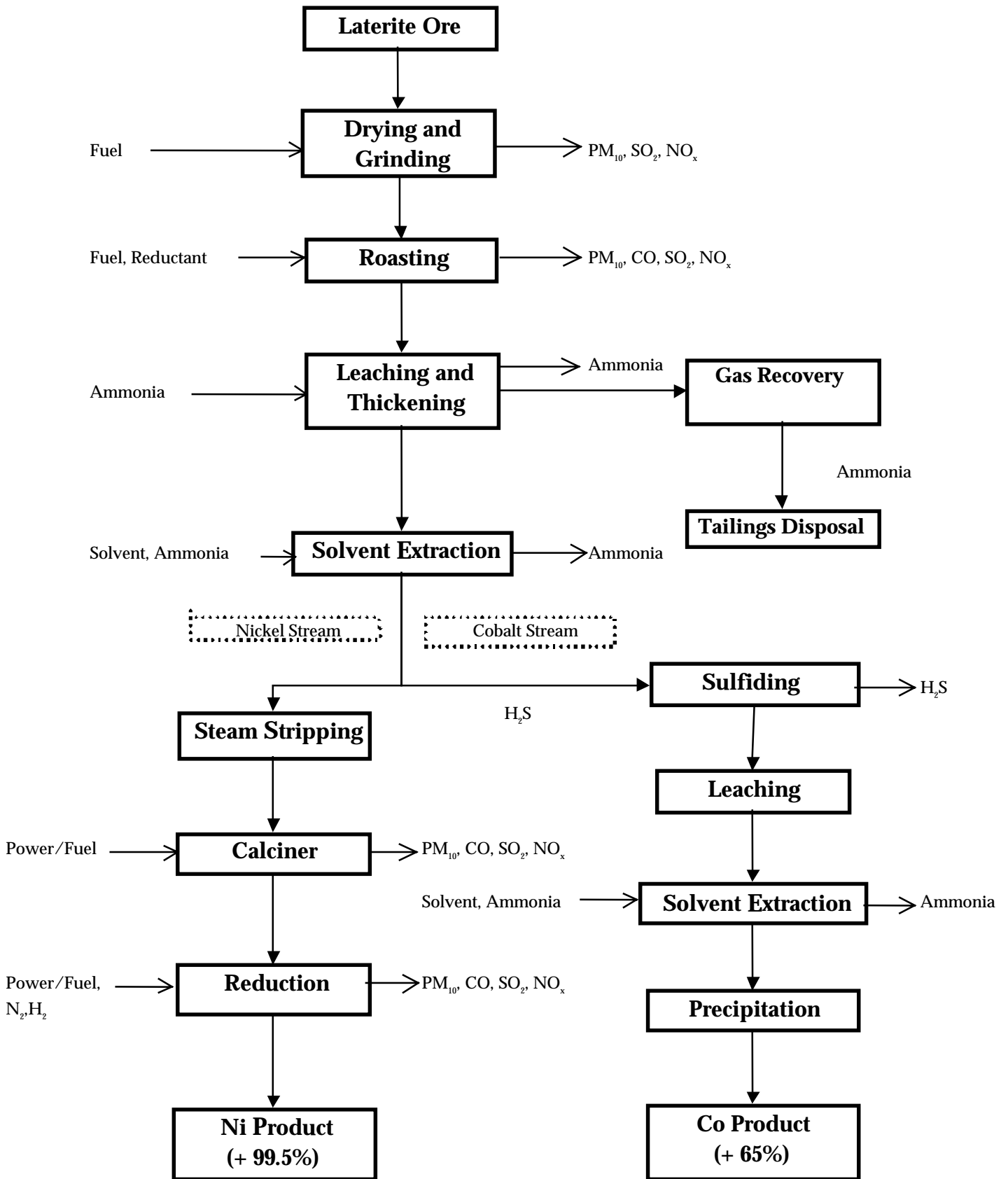
Figure 6 - **Nickel Laterite Ammonia Leach Process Inputs and Emissions**

3.0 Likely Emissions

Estimates of emissions of listed substances to air, water and land shall be reported for each substance that exceeds a defined threshold value of 'usage' or emission. The reporting list and detailed information on thresholds are contained in *The NPI Guide*.

It is the responsibility of nickel concentrating, smelting and refining facilities to determine which NPI-listed substances are triggered for reporting. Table 1 indicates those NPI-listed substances likely to be of relevance where the threshold may be triggered by the nickel concentrating, smelting and refining industry and the most appropriate method of determining whether the threshold is triggered. This table is intended as a guide to substances that may need to be reported for Nickel concentrating, smelting and refining facilities.

Table 1 - **NPI-Listed Substances Likely to Trigger Thresholds, and Proposed Methods for Determining Emissions**

SUBSTANCE	TRIGGER	METHOD **
Acrylic acid	Usage	INV
Ammonia (total)	Usage	INV
Antimony & compounds	Usage (Ore content)	D/M, G/F
Arsenic & compounds*	Usage (Ore content)	D/M, G/F
	or power usage	C
Beryllium & compounds	Usage (Ore content)	D/M, G/F
	or power usage	C
Boron & compounds	Usage (Ore content)	D/M, G/F
Cadmium & compounds*	Usage (Ore content)	D/M, G/F
	or power usage	C
Carbon disulfide	Usage (Coincidental production)	E/C
Carbon monoxide*	Fuel use	INV
Chromium (III) compounds	Usage (Ore content)	D/M, G/F
	or power usage	C
Chromium (VI) compounds*	Usage (Ore content)	D/M, G/F
	or power usage	C
Cobalt & compounds*	Usage (ore content)	D/M, G/F
Copper & compounds	Usage (Ore content)	D/M, G/F
	or power usage	C
Cyanide (inorganic) compounds*	Usage	INV
Fluoride compounds*	Usage (Ore content)	D/M, G/F
	or fuel use.	INV
Hydrochloric acid	Usage (Usage & coincidental production)	INV, E/C
	or fuel use.	INV
Hydrogen sulfide	Usage (Production on site)	INV
Lead & compounds*	Usage (Ore content & anodes)	INV, D/M, G/F
	or power usage	C

Table 1 - **NPI-Listed Substances Likely to Trigger Thresholds, and Proposed Methods for Determining Emissions cont'**

SUBSTANCE	TRIGGER	METHOD **
Magnesium oxide fume	Power usage	C
Manganese & compounds	Usage (Ore content & catalyst)	INV, D/M, G/F
Mercury & compounds*	Usage (Ore content)	D/M, G/F
	or power usage	C
Nickel & compounds	Usage (Ore content)	D/M, G/F
	or power usage	C
Nickel carbonyl*	Usage (Coincidental production)	E/C
	Power usage	C
Nickel subsulfide (matte)*	Usage (Coincidental production)	E/C
	or power usage	C
Oxides of Nitrogen*	Fuel use	INV
Particulate Matter ≤10.0 um*	Fuel use	INV
Polychlorinated dioxins and furans	Power usage	C
Polycyclic aromatic hydrocarbons (PAHs)*	Fuel use	INV
Selenium & compounds	Usage (ore content)	D/M, G/F
Sulfur dioxide*	Fuel use	INV
Sulfuric acid*	Usage (coincidental production & production on-site)	INV, E/C
Total Nitrogen*	Discharge to surface waters (sewage plants)	D/M, E/F
Total Phosphorus*	Discharge to surface waters (sewage plants)	D/M, E/F
Total Volatile Organic Compounds (VOCs)	Usage or design bulk storage or fuel use.	C, INV
Zinc and compounds	Usage (ore content)	D/M, G/F

* Substances listed in Table 1 of NPI guide.
** A number of methods can be used to determine threshold exceedence for NPI substances. The method used will be related to the substance category and available information:

- D/M : Direct Measurement ⇒ direct measurement of emissions stream (total N and P) or characterisation of the ore body.

- INV : Inventory ⇒ inventory of material usage (chemicals, fuel), with NPI content of materials identified.

- G/F : Generic Factor ⇒ generic factor applies to default concentrations to be used in the absence of facility-specific data.

- E/F : Emission Factor ⇒ emission factor to determine content in discharge stream (total N and P).

- C : Capacity ⇒ capacity applies to the storage capacity of a facility, maximum combustion rate, consumption of energy or potential maximum power consumption.

- E/C : Engineering Calculation ⇒ engineering calculations may be used for a number of substances such as sulfur dioxide.

The NPI Guide, along with Worksheets 1 and 2 (at the front of this Handbook), are available to assist facilities in determining substances that exceed reporting triggers.

You should note that while the reporting threshold for a substance may not be triggered during one reporting period, it may be triggered in another reporting period. As such, it is important to review NPI reporting requirements each reporting period.

3.1   Reporting Thresholds

Thresholds have been set for five categories, although a substance may exceed thresholds in more than one category (for example, copper may trigger reporting through its use and/or the facility's fuel usage). These are detailed below in simple terms. The NPI reporting list and detailed information on thresholds are contained in *The NPI Guide.*

3.1.1   Category 1

Category 1 substances trigger reporting through the 'use' of 10 tonnes or more per year of that substance.

'Use' has a very broad definition within the NPI and includes coincidental production and handling. Within the nickel industry, trace metals within ore may trigger reporting thresholds, as may the coincidental production of carbon disulfide from the breakdown of xanthates and the NPI substance content of process chemicals used at facilities.

Ore handled at nickel concentrating, smelting and refining facilities may contain a sufficient concentration of NPI metals & compounds to trigger the Category 1 reporting threshold of 10 tonnes per annum.

Ore will need to be characterised for all NPI metals & compounds to determine the contribution of ore metal 'use' to the total facility 'use' of metals and compounds.

Direct measurement by representative sampling is the most accurate means of characterising ore and hence determining 'usage' of trace metals as the metals content of ore will vary between and within facilities. In the absence of facility-specific assays, generic ore assays may be used as the basis for reporting of metals 'usage'. These generic assays are presented in Appendix A.

Where substances are 'used' as a result of coincidental production, such as carbon disulfide from the decay of xanthates, engineering calculations may be appropriate to determine the amount that is 'used' based on the chemical reaction rates.

Reference to facility inventories will facilitate the calculation of the mass of NPI substances 'used' through their presence in process chemicals. This approach will require recording of the volumes of process chemicals used in a reporting period and determination of the concentration of NPI substances in those chemicals. This data may be available from material safety data sheets (MSDS) or directly from suppliers.

3.1.2   Category 1a

This category considers total volatile organic compounds (VOC) only and the threshold is triggered through either the mass of VOCs used annually or the total VOC storage capacity of the facility.

The reporting threshold for a category 1a substance is exceeded in a reporting period if the activities involve the use of 25 tonnes or more of the substance in that period.   The reporting threshold for a category 1a substance is only exceeded for bulk storage facilities if their design capacity also exceeds 25 kilotonnes.

VOC emission estimation from tanks is addressed by the *EET Manual for Fuel and Organic Liquid Storage.*

3.1.3   Category 2a

Category 2a encompasses products of combustion.

Reporting thresholds are triggered if a facility:
- burns 400 tonnes or more of fuel or waste in a year; or
- burns 1 tonne or more of fuel or waste in an hour at any time during the reporting year.

Exceedence of threshold triggers may be determined through reference to masses of fuel used from facility inventories, or maximum fuel combustion rates.

3.1.4   Category 2b

Category 2b encompasses products of combustion.

Reporting thresholds are triggered where a facility:
- burns 2,000 tonnes or more of fuel or waste in a year;
- consumes 60,000 megawatt hours or more of energy in a year; or
- the maximum potential power consumption of the facility at any time in the year is rated at 20 megawatts or more.

3.1.5   Category 3

Category 3 substances are nitrogen and phosphorus. These are reportable if emissions to water (excluding groundwater) exceed the following scheduled amounts:
- 15 tonnes per year of total nitrogen; and
- 3 tonnes per year of total phosphorus.

Direct measurement (through representative sampling) of the total nitrogen and phosphorus content of surface water discharges is likely to be the most appropriate means of determining whether reporting thresholds are triggered.

4.0 Emission Estimation

Estimates of emissions of 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.

Those techniques available for estimating emissions of NPI substances from nickel concentrating, smelting and refining activities are detailed in Table 2.

The estimation techniques detailed provide a range of options for facilities. These EETs may be supplemented by other techniques to develop facility-specific EETs or to confirm the accuracy of alternate EETs.

While particular estimation methods are generally more suited to some applications, the estimation method selected will be dependent upon a number of factors, such as:

- cost of estimation techniques;
- ease of measurement or monitoring;
- availability of suitable emission factors;
- level of accuracy desired;
- nature of the substance; and
- existing monitoring and data availability.

It should be appreciated that while the NPI requires reporting of metals and compounds, such as lead and compounds, emissions relate only to the amount of metal emitted.

For example if $CuSO_4$ were emitted to the environment, only the Cu component would be reportable. While $CuSO_4$ has a molecular weight of 159 the Cu component has a molecular weight of only 63. Reporting of the total $CuSO_4$ emissions would therefore lead to an emissions estimate of two-and-a-half times greater than that required.

When estimating emissions it may be simpler to determine the percentage content of NPI substances within distinct emission streams and report that percentage of the total emission.

Wherever practicable, facilities should ensure that only the reportable component of an emission is reported. In some circumstances this may be very difficult to achieve and in these cases a liberal estimate should be made.

For example, the NPI requires that inorganic cyanide compounds only are reported. The form in which cyanide is emitted should be factored into emissions estimation where practicable, although this may be very difficult to achieve where extensive cyanide complexes are emitted. Where this is the case total cyanide emissions should be reported.

The NPI addresses the total loading, of those forms of a substance required by the NPI, to the environment and does not distinguish between bioavailable and non-bioavailable forms of a substance (except for total nitrogen and phosphorus emissions).

For example, for metals such as cadmium and compounds, the total loading of cadmium to the environment must be reported not just the available forms of cadmium.

In reporting emissions it is important to note that while the reporting threshold for a substance may be triggered this does not mean that the emissions will be significant. For example most trace metals in the processed ore are likely to be disposed of to the TSFs. However only emissions <u>from</u> TSFs must be reported within the NPI process.

The NPI has a commitment of not requiring any additional monitoring by facilities in order to estimate their emissions. While monitoring is an EET available to facilities, a range of EETs that do not require direct monitoring is available. However, in the absence of monitoring data, a lower level of accuracy can be expected.

Appendix B details sources of data that may already be available to facilities. This data may be used to assist in NPI reporting requirements.

A combination of these methods may be employed to estimate emissions to the environment from particular process areas, such as emissions from TSFs.

The nickel concentrating, smelting and refining industry also requires a range of raw material inputs, which at some facilities are produced on site. Likewise some facilities may produce additional products through their emissions treatment processes. These are referred to in this Manual as 'Ancillary Activities' and may include:

- hydrogen production;
- sulfuric acid production;
- ammonium sulfate production; and
- hydrogen sulfide production.

Where EET Manuals have been produced to assist in NPI reporting of these 'Ancillary Activities', they should be referred to in order to ensure that all substance usage and emissions are fully accounted for. EET Manuals include *Ammonium Sulfate and Inorganic Chemicals Manufacture.* Where manuals are not available, the use and emission of substances should be accounted for as part of the facilities estimation methods detailed in this handbook.

In all cases, when estimating emissions a facility should ensure that emissions are not 'double accounted' between different processes.

Table 2 details the NPI substance, the stage in the process where it is used and emitted, and indicates appropriate emission estimation techniques. While emission factors (E/F) are identified as potential EETs for substances, emission factors may not currently be available for all substances. It is anticipated that emission factors will be developed for these substances in the future.

The *NPI Guide* provides guidance on the most appropriate approach to the estimation of emissions for particular categories of substances.

Table 2 - Relevant NPI-Listed Substances for the Nickel Processing Industry, and Associated Emission Estimation Methods

| SUBSTANCE | POWER GENERATION | CONCENTRATING | | | SMELTING | | REFINING -Sulfides | | | | LATERITE PROCESS | | TSFs |
		CRUSHING & MILLING	FLOTATION	THICKENING & DRYING	FURNACE & CONVERTER	GRANULATOR	CRUSHING & MILLING	LEACHING	THICKENING	LIQUOR STRIPPING	LEACH	REFINE	OR SEWAGE
D/M: Direct Measurement , M/B: Mass Balance, E/F: Emission Factors, E/C: Engineering Calculations, M: Modelling **A: Emission to Air, W: Emission to Water, L: Emissions to Land, including Groundwater**													
Acrylic acid										**A** M/B		**A** M/B	
Ammonia (total)										**A** D/M , M/B , E/C	**A** D/M, M/B	**A** D/M, M/B	
Antimony & compounds		**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Arsenic & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Beryllium & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Boron & compounds		**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Cadmium & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Carbon disulfide			**A** D/M, M/B, E/C								**A** D/M, M/B, E/C		
Carbon monoxide	**A** E/F												
Chromium (III) compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Chromium (VI) compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Cobalt & compounds		**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B

Table 2 - **Relevant NPI-Listed Substances for the Nickel Processing Industry, and Associated Emission Estimation Methods cont'**

SUBSTANCE	POWER GENERATION	CONCENTRATING			SMELTING		REFINING -Sulfides				LATERITE PROCESS		TSFs OR SEWAGE
		CRUSHING & MILLING	FLOTATION	THICKENING & DRYING	FURNACE & CONVERTER	GRANULATOR	CRUSHING & MILLING	LEACHING	THICKENING	LIQUOR STRIPPING	LEACH	REFINE	
D/M: Direct Measurement , M/B: Mass Balance, E/F: Emission Factors, E/C: Engineering Calculations, M: Modelling A: Emission to Air, W: Emission to Water, L: Emissions to Land, including Groundwater													
Copper & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Cyanide (inorganic) compounds			**A** D/M, M/B, M, E/C									**A** D/M, M/B, M, E/C	**A, W, L** D/M, M/B, M, E/C
Fluoride compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Hydrochloric acid	**A** E/F, M/B				**A** D/M, M/B	**A** D/M, M/B	**A** D/M, M/B						**W, L** D/M, M/B
Hydrogen sulfide									**A** D/M, M/B		**A** D/M, M/B	**A** D/M, M/B	
Lead & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Magnesium oxide fume	**A** E/F, M/B												
Manganese & compounds		**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Mercury & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Nickel & compounds	**A** E/F	**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Nickel carbonyl													

Table 2 - Relevant NPI-Listed Substances for the Nickel Processing Industry, and Associated Emission Estimation Methods cont'

| Substance | Power Generation | Concentrating | | | Smelting | | Refining -Sulfides | | | | Laterite Process | | TSFs |
		Crushing & Milling	Flotation	Thickening & Drying	Furnace & Converter	Granulator	Crushing & Milling	Leaching	Thickening	Liquor Stripping	Leach	Refine	or Sewage
D/M: Direct Measurement , M/B: Mass Balance, E/F: Emission Factors, E/C: Engineering Calculations, M: Modelling **A: Emission to Air, W: Emission to Water, L: Emissions to Land, including Groundwater**												
Nickel subsulfide	**A** E/F, E/C				**A** D/M, M/B	**A** D/M, M/B	**A** D/M, M/B						
Oxides of Nitrogen	**A** E/F, M/B												
Particulate Matter ≤10.0 um	**A** E/F, D/M												
Polychlorinated dioxins and furans	**A** E/F, E/C												
Polycyclic aromatic hydrocarbons	**A** E/F, E/C												
Selenium & compounds		**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B
Sulfur dioxide	**A** E/F												
Sulfuric acid					**A** D/M, M/B, E/C		**A** D/M, M/B, E/C				**A** D/M, M/B, E/C		
Total Nitrogen													**W** D/M
Total Phosphorus													**W** D/M
Total Volatile Organic Compounds	**A** E/F, E/C												
Zinc and compounds		**A** M/B			**A** M/B	**A** M/B	**A** M/B				**A** M/B		**W, L** M/B

4.1 Elements of the Environment

4.1.1 Emissions to Air

Significant emissions to air within the nickel concentrating, smelting and refining industry will be related to:

- stack emissions from smelters;
- the stockpiling, movement and comminution of ore;
- the operation of process plants including solvent extraction heap leaches; and
- the operation of tailing storage facilities (TSFs).

Emissions to air are estimated from their point of creation rather than at the facility boundary. Emissions estimation takes no account of the fate of emitted substances, such as the speed of their subsequent decay within the atmosphere.

Air emissions may be categorised as:

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

Emission factor EETs are the usual method for determining losses through fugitive emissions.

Point source emissions
These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere. An air emissions control device such as a carbon adsorption unit, scrubber, baghouse, or afterburner may 'treat' stack emissions prior to their release, reducing their total loading to the atmosphere.

4.1.2 Emissions to Water

Emissions of substances to water can be categorised as discharges to:
- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

Groundwater is not considered as a 'water body' within the context of NPI reporting. Groundwater is included within emissions to land.

Significant emissions to water within the nickel concentrating, smelting and refining industry will be related to:
- runoff and erosion from the facility area (refer to the *EET Manual for Mining*);
- the discharge of treated process waters (eg. treated TSF decant water);
- the discharge of sewage and domestic wastewaters; and
- spills to surface waters.

The most accurate technique for estimating emissions to the environment via wastewater is likely to be direct measurement. However, facilities may use other EETs for the purposes of reporting within the NPI.

4.1.3 Emissions to Land

Emissions of substances to land on-site may include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids, and the use of chemicals to control various elements of the environment where these emissions contain listed substances. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries, such as TSFs; and
- unintentional leaks and spills.

In relation to the nickel concentrating, smelting and refining industry, discharges to land such as purpose built TSFs, solid waste dumps and waste rock dumps are classed as transfers. However, emissions from these facilities to the environment are included within the scope of the NPI and will generally be addressed as either emissions to groundwater (land) or to air.

5.0   Mass Balance

Mass balance provides an estimate of emissions where known quantities of substances are supplied to a process, and the process fate of the substance is both known and quantifiable.

It is essential that the mass balance calculation addresses all losses and fates of a substance and utilises the best available data.

As a result of inherent errors in the estimation of inputs to and losses from a facility or process, and the fates of those substances, the effectiveness of a mass balance approach in estimating minor emissions may be questionable and may contain broad error bands.

5.1   Water Balance

Tailings Storage Facilities (TSFs) represent a significant potential emission source of some NPI substances. A comprehensive water balance will assist in the identification and quantification of emission pathways, allowing the emission pathways of soluble and volatile substances to be more accurately identified and estimated (Source: BPEMIM, Cyanide Management, 1995).
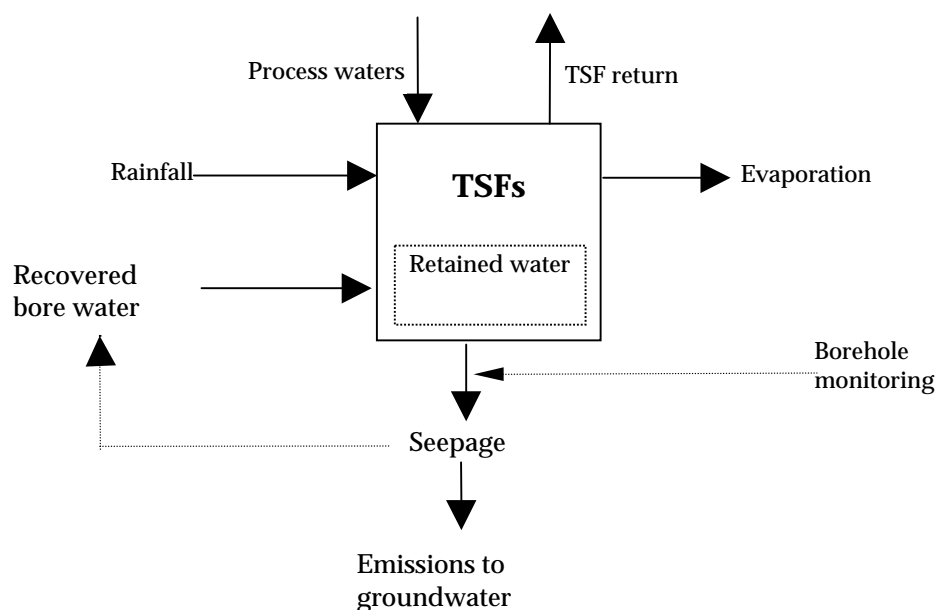
Figure 7 - **TSF Water Balance**

A comprehensive water balance, when used in conjunction with EETs, will facilitate the estimation of emissions of soluble NPI substances (eg. metals) from TSFs.

For example, the difference between known water inputs and losses (including rainfall and evaporation) in the water balance can normally be assumed to represent seepage. Emissions of soluble NPI substances may be estimated through direct measurement of monitored boreholes and relating this data to the known hydraulic conductivity of the soils.

However, it is noted that estimates of the inputs/outputs of some water balances may have significant associated error bands. Work recently undertaken by MERIWA demonstrates the errors that may be associated with the calculation of evaporative losses from the surface of TSFs. This is well illustrated by the following example from MERIWA Project Report M241, 1998;

> **For a TSF of 100 ha, an evaporative loss of 100 mm is equivalent to a total volume of 100,000m^3.**
>
> **Evaporative losses are influenced by a wide variety of factors. Increasing salinity may reduce evaporation by as much as 60 - 95% of the potential evaporative rate. As such estimating to an accuracy of 100 mm may require extensive study and characterisation and any errors in calculating these losses may result in significant inaccuracies.**

5.2   Metals

Metals may be emitted:

- through seepage from TSFs and heap/dump leach pads;
- as dust; and
- as a result of TSF overflow.

The mass balance approach may be utilised to estimate emissions of metals in a manner similar to that used to estimate the emission of cyanide through seepage (refer to Section 5.5)

The mass of reportable NPI metals lost to the environment through seepage may be estimated using:

- estimates of seepage rate; and
- the concentration of NPI metals in TSFs return water or dump / heap leach liquors

While these seepage rates will be facility-specific, generic seepage rates of between **0 - 10 %** has been quoted within the industry (Mt Keith Nickel 1996, ANCOLD, per. comms.).

Metals concentrations should be assumed as being equal to that in the **TSFs return water** unless facility-specific data suggests otherwise.

$$M = \frac{[V*S]*C_m}{100}$$

where

M	=	mass of metal emitted through seepage, kg
V	=	volume of water and/or slurry to TSF, m^3
C$_m$	=	concentration of metal, kg/m^3

Where data on the permeability of TSF construction material is known Darcy's Law may be applied to calculate hydraulic loadings to the environment. Darcy's Law is most applicable where an impermeable membrane has not been installed as part of the TSF design. Where an impermeable membrane has been installed but seepage is known to be occurring, Darcy's Law may be applied where facilities can estimate the surface area of the liner where its integrity has been compromised.

$$Seepage = [K * A * S_y * (dh/dl)] \ m^3/d$$

Where:
K = vertical permeability of TSF floor material, m/day
A = surface area of TSF cell floor, m^2
S_y = specific yield of tailings material, %
dh = thickness of tailings in the cell, m
dl = hydraulic head above floor of the cell, m

Specific yield is the amount of water potentially released by the tailings material. For example where the saturated moisture content of the tailings is known to be 10% the specific yield may be half of the saturated moisture content and would be expressed as 5%.

The seepage would be applied to the equation below to estimate emissions:

Mass of metal emitted through seepage (kg)	=	Volume of calculated seepage (m^3/d)	*	Number of days TSF operated (d)	*	Concentration of metal (kg / m^3)

In the absence of facility-specific data the following data should be used in calculating seepage;

- 10 % seepage rate;
- metals concentration equal to that in TSFs return water; and
- no bore water recovery.

Borehole recovery may be factored into the estimation technique where metal concentrations and volumes of recovered bore water are known.

Mass of metal emitted through seepage with bore recovery (kg)	=	Mass of metal emitted through seepage (kg)	-	Concentration of metal in recovered bore water (kg / m^3)	*	Volume of recovered bore water (m^3)

Alternative metals EETs include Direct Measurement & Modelling

5.3   Chemical Usage

The emission of chemicals from facilities from some sources (either as a result of normal operations, spillages or incidents) may be estimated through mass balance.

Process and domestic chemicals used within the facility may be emitted to the environment. The full inventory of these chemicals used within a reporting period may be assumed either to be emitted to the environment, or to be transferred to an alternative disposal, recycling or reuse facility.

In order to estimate the fate of chemicals, and their component NPI substances, the following approach should be taken:

- Mass of NPI substances within chemicals determined (including coincidental production);
- Inventory (or hazardous substances registers) of chemical usage maintained; and
- Fate of chemical determined -
    ⇒ is chemical emitted to the environment or transferred?
    ⇒ is chemical treated prior to emission from the facility?
    ⇒ is chemical emitted to air, water or land?
    ⇒ does chemical undergo partitioning into other forms?
    ⇒ what are the fates of partitioned substances?

This approach may be applied to chemical usage in areas such as:

- chemical storage areas;
- laboratories;
- workshops;
- kitchens;
- domestic; and
- washdown areas.

> *Alternative chemicals usage EETs include Direct Measurement*

5.4   Converter and Smelter Emissions

Emissions (eg. sulfur dioxide and metals) from converter and smelter operations may be estimated through the use of mass balance. However, some direct sampling may be desirable to improve components of the mass balance, eg. sulfur/metals content of process inputs and outputs.

It is important that the fates of component substances are considered within the mass balance and that all assumptions are stated. For example, it may be assumed that all sulfur is converted to sulfur dioxide during combustion, and ash content analyses may suggest that a percentage of some metals are emitted.

The mass balance approach allows fugitive and other emissions to the environment to be estimated.

5.4.1 Emissions Estimation for Converter and Smelter Operations

In a similar manner in which emissions from combustion are estimated, emissions from converter and smelter operations may be estimated using a mass balance.
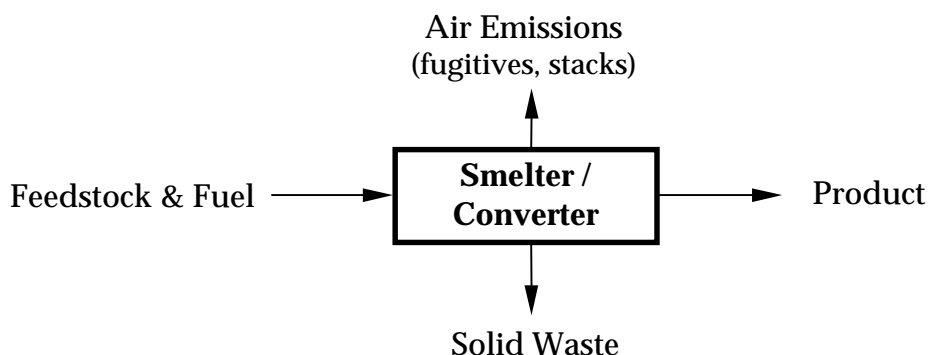
Figure 8 - **Mass Balance Approach for Converter and Smelter Operations**

Air emissions may be estimated where substance concentration of the feedstock, fuel, product, and solid wastes, have been effectively characterised.

$$\text{Emission of substance} \atop \text{kg/hr} = \text{Rate of Feedstock Addition} \atop \text{kg/hr} * \frac{\text{wt \%}}{100} * \frac{MW_p}{EW_f}$$

where:

wt %	=	weight percent of substance in feedstock
MW_p	=	molecular weight of substance emitted (kg/kg-mole)
EW_f	=	elemental weight of substance in feedstock (kg/kg-mole)

Sulfur dioxide (SO_2) emissions from converter and smelter operations may be estimated through the use of mass balance. However, direct monitoring will be required for some aspects of the mass balance, such as sulfur content of process inputs and outputs.

The approach detailed below allows for fugitive and other emissions to the environment to be accounted for, and the verification of on-line monitoring and mass balance findings.

Where data is not available estimates may be used and any shortfalls assumed to be losses to the environment.

While there are many variables in the mass balance, the errors inherent to the mass balance approach may be minimised through continued development and refinement of the mass balance equation.

Flux

Concentrate (A1)   Fuel (A3)

```
                  ┌─────────────┐
                  │ Smelter and │────────→ Flash furnace slag (B)
          ┌───────│  Converter  │
          │       │   Process   │────────→ Waste gases
          ↓       └─────────────┘            - flash furnace
  ┌──────────────┐     │                     - converter
  │  Acid Plant  │     │                           (C)
  └──────────────┘     │
     │        │        ↓
     ↓        ↓    Final Matte Product
   H₂SO₄    Acid      - flash furnace
  product    Plant    - converter
    (E)      Gases         (F)
```
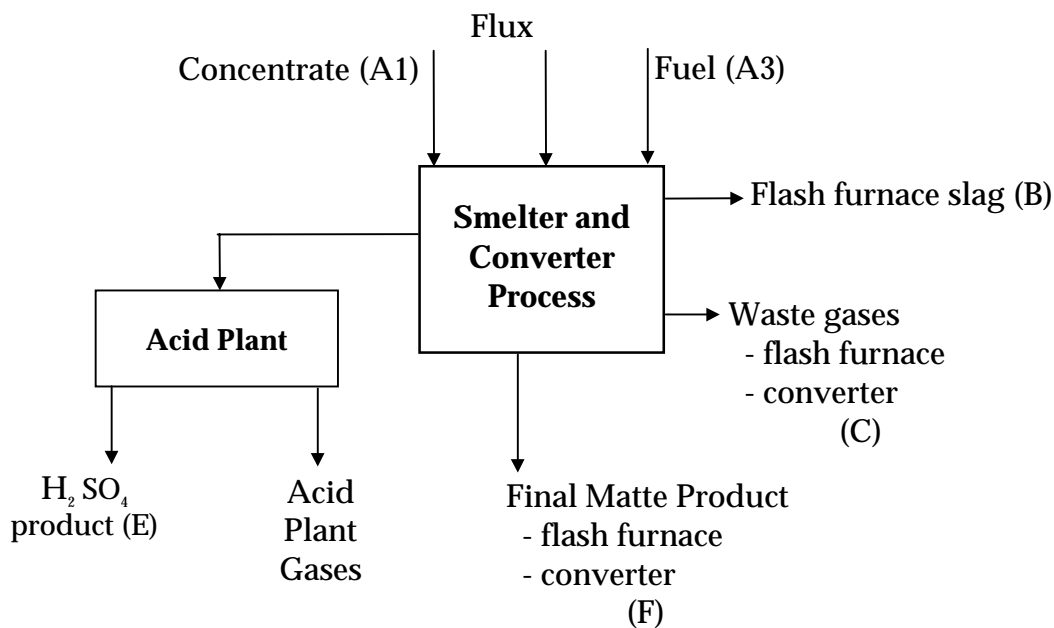
Where: Inputs = Estimated outputs + Assumed outputs
ie.   A 1+ A2 + A3 = (B+ C + D) + (E + F)+ Fugitives

Figure 9 - **Mass Balance of Sulfur Dioxide Emissions from Smelter and Converter
        Operations**

Example 1 - **Sulfur Dioxide Emission**

*This example considers sulfur dioxide losses from the converter and smelter. The
approach is largely based on mass balance using direct measurement data.*

Sulfur dioxide emissions from the smelter and converter may be estimated using a simple
mass balance as detailed below. The greater the level of accuracy applied to the process
inputs and outputs, the more accurate the estimate of emissions will be.

```
                       Air Emissions
                      (fugitives, stacks)
                             ↑
                       ┌──────────┐
Feedstock & Fuel ─────→│ Smelter / │────→ Product
                       │ Converter │
                       └──────────┘
                             ↓
                        Solid Waste
```
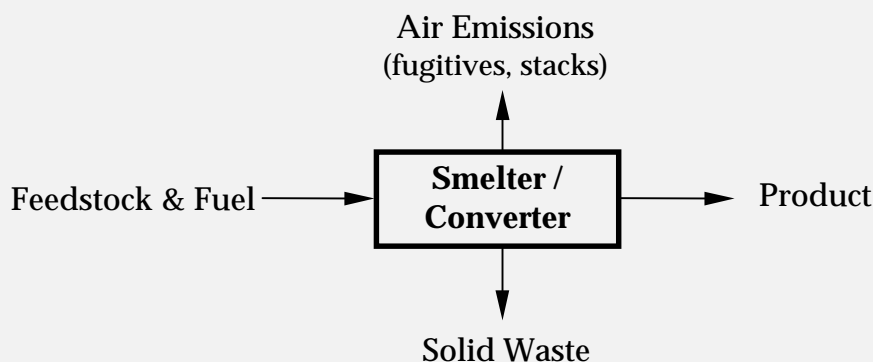
The weight percent of sulfur (as elemental S) in the fuel and feedstock (concentrate and
flux) is used to estimate the total inputs to the process.

Example 1 - **Sulfur Dioxide Emission cont'**

Outputs are based on representative sampling product (matte) and waste (slag). In the example presented, stack emissions are estimated through representative sampling, allowing the fugitive emissions to be estimated. However the NPI requires reporting of emissions to air and as such direct measurement of stack emissions is not required to effectively estimate emissions using mass balance approach.

Flux
(A2) - 1,430 tonnes

Concentrate
(A1) - 165,950

Fuel
(A3) - 190 tonnes

Fugitives

Smelter and Converter Process

Flash furnace slag
(B) - 3,520 tonnes

Acid Plant

Waste gases
- flash furnace (C1) - 14,150 tonnes
- converter (C2) - 13,000 tonnes

$H_2 SO_4$ product
(E) - 110,000 tonnes

Acid Plant Gases
(D) - 130 tonnes

Final Matte Product
- flash furnace (F1) - 460 tonnes
- converter (F2) - 25,400
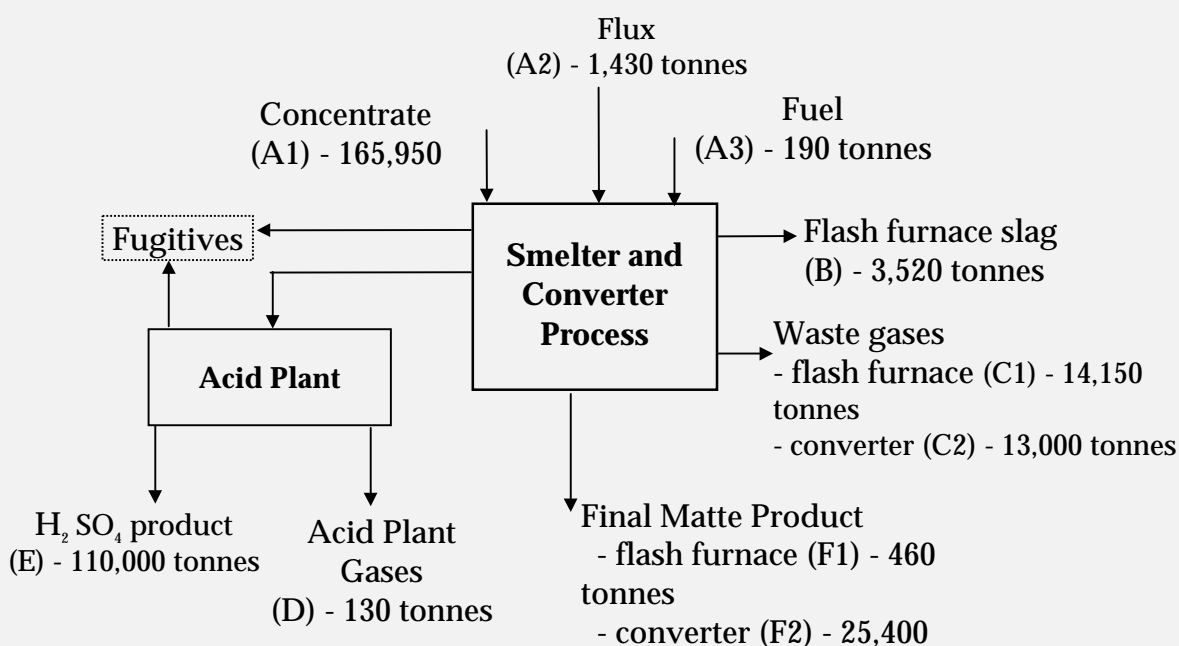
Inputs = Estimated Outputs + Assumed Outputs

A1 + A2 + A3 = (B + E + F1 + F2) + (D + C1 + C2) + Fugitives
167,570 = (139,380) + (27,280) + Fugitives
Fugitives = 167,570 - 166,660
Fugitives = 910 tonnes

Sulfur dioxide emissions from converter smelter for reporting period

Sulfur Dioxide Emissions to Air: **28,190,000 kg**
Sulfur Dioxide Emissions to Land: **NIL**
Sulfur Dioxide Emissions to Water: **NIL**

Alternative converter/smelter EETs include Direct Measurement

5.4.2 Emissions Estimation for Fuel

Fuel analysis can be used to predict SO_2, metals, and other emissions resulting from combustion.

The basic equation used in fuel analysis emission calculations is the following:

$$\text{Emission of Substance (kg/hr)} = \text{Rate of Fuel Usage (kg/hr)} * \frac{\text{wt \%}}{100} * \frac{MW_p}{EW_f}$$

where:

wt %	=	weight percent of the element in the fuel.
MW_p	=	molecular weight of substance emitted (kg/kg-mole)
EW_f	=	elemental weight of substance in fuel (kg/kg-mole)

SO_2 emissions from combustion can be calculated based on the concentration of sulfur in the fuel.

This approach assumes complete (100%) conversion of sulfur to SO_2. Therefore, for every kilogram of sulfur (EW = 32) burned, two kilograms of SO_2 (MW = 64) are emitted.

$$\text{Emission of } SO_2 \text{ (kg/hr)} = \text{Fuel Usage (kg/hr)} * \frac{\text{wt \% S}}{100} * \frac{MW_{SO2}}{EW_S}$$

Where: wt % S = weight percent of sulfur (as elemental S) in the fuel.

The emissions are estimated as kg/hr and as such should be multiplied by the hours of operation in order to determine the total emission load.

Guidance on emissions from fuel combustion may also be found in the following NPI EET Manuals:

- *Fossil Fuel Electric Power Generation*;
- *Combustion Engines*; and
- *Combustion in Boilers.*

5.5   Cyanide Balance

Cyanide is used in small quantities at a limited number of facilities for arsenic suppression within the nickel concentrating, smelting and refining industry. It is likely that most facilities will not trigger the reporting threshold for cyanide.

The NPI requires that inorganic cyanide compounds are reported where the threshold is triggered. As such when estimating emissions of cyanide to the environment it is important that **total cyanide** is reported where the CN^- mass is not known.

Cyanide fates within the process and TSFs are extremely complex. Evaporation, reduction, oxidation, precipitation, adsorption, desorption, exchange reactions are just a

few of many possible simultaneous events. Ultimately, all cyanide is either emitted to the environment, decomposed or complexed within the TSFs.

A mass balance approach may be employed to develop a flow diagram of cyanide additions and losses to the process. It is likely, however, that the mass balance approach will be supported by other EETs, (eg. direct measurement and modelling), in order to increase the accuracy of estimated emissions.

5.5.1   Cyanide Emissions from Storage and Mixing Areas

Cyanide emissions from storage and mixing areas will mainly be due to spillage losses and may be estimated through effective record keeping of all spills and inventories of supplies.

Losses to ground and water may be differentiated through effective record keeping of all spills, and the fate of spilled material (washed to treatment process, absorbed and disposed of to licensed site etc).

5.5.2   Cyanide Emissions from the Ore Processing Area
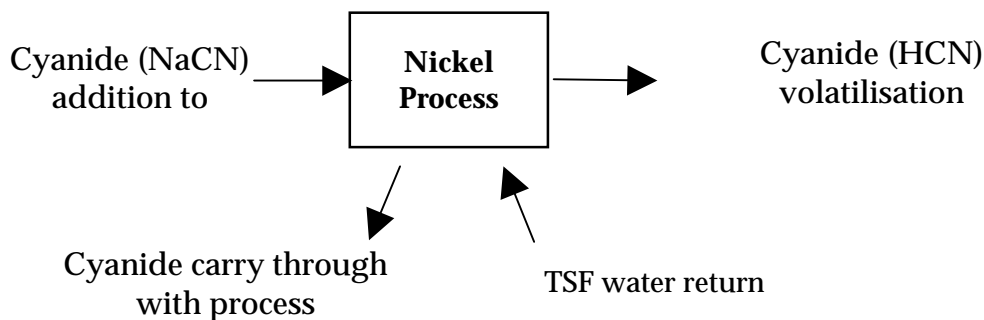
Figure 10 - **Mass Balance of Cyanide Emissions from the Ore Processing Area**

A mass balance approach may be used to estimate the emissions of cyanide through the volatilisation (and other losses such as carry over with product).

$$\begin{array}{c} \text{Mass of cyanide lost} \\ \text{through volatilisation} \\ \\ \text{(kg)} \end{array} = \left[\begin{array}{cc} \text{Mass of} & + \text{ Mass of cyanide} \\ \text{cyanide added} & \text{in TSF return} \\ \text{to process} & \text{water} \\ \text{(kg)} & \text{(kg)} \end{array} \right] - \begin{array}{c} \text{Mass of cyanide} \\ \text{carried to TSF} \\ \\ \text{(kg)} \end{array}$$

5.5.3 Cyanide Emissions from TSFs
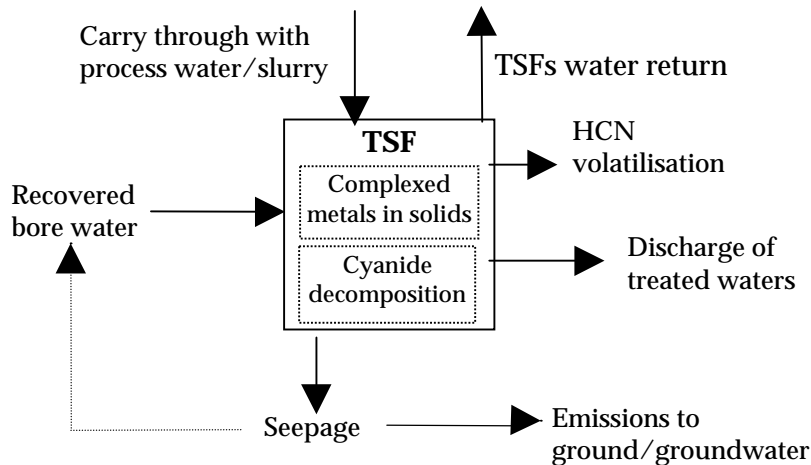
Figure 11 - **Mass Balance of Cyanide Emissions from TSFs**

Cyanide may be emitted to the environment via the following pathways:

Seepage

The mass of cyanide lost to the environment through groundwater seepage may be estimated using:

• seepage rates; and
• the concentration of total cyanide in TSFs return water.

While these seepage rates will be facility-specific, generic seepage rates of between **0 - 10 %** have been quoted within the industry (Mt Keith Nickel 1996, ANCOLD per. comms.). The 10% figure can be used as a point of reference for reporting purposes. Alternatively the seepage load calculated using Darcy's Law may be applied.

Cyanide concentrations in seepage may be assumed as being equal to that in the <u>TSFs return water</u> (total cyanide) unless facility-specific data suggests otherwise.

Mass of cyanide emitted through seepage (kg)	=	**(Volume of water and/or slurry to TSF) (m^3)**	*	**Seepage rate (%)**	*	**Concentration of cyanide (kg / m^3)**

In the absence of facility-specific data the following parameters may be used in calculating seepage;

• 10 % seepage rate;
• total cyanide concentrations equal to that in TSFs return water; and
• no bore water recovery

Borehole recovery may be factored into the estimation technique where cyanide concentration, and volumes of recovered bore water are known.

Volatilisation

In natural degradation most 'free' cyanide is lost through volatilisation (BPEMIM, Cyanide Management, 1998). The cyanide is volatilised as HCN, which ultimately breaks down to form ammonia and carbon dioxide

At present there is no reliable method for estimating emissions of cyanide from TSFs using a mass balance. The emissions factors for volatilisation from TSFs presented in Section 6.7.2 may be used to estimate these emissions.

> *Alternative cyanide EETs include Emission Factors,*
> *Modelling & Direct Measurement*

6.0   Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. Emission factors are a useful tool for estimating emissions where the relationship between the emission and the "use" of substances is well defined. Emission factors are widely used in estimating emissions from combustion sources, (eg. furnaces and fuel usage).

Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted, such as the mass of PM_{10} and TSP produced per tonne of ore handled.

Emission factors are used to estimate emissions by the general equation:

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

where :

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

Some emission factors may involve the use of more complex equations and require differentiation of substances fates.   Estimation of cyanide fates is an example of a substance that may require the use of more complex EETs.

Emission factors are derived from direct measurement of actual emission loads from a range of similar plants or equipment. While emission factors have an empirical basis they are based on standard equipment and operating practices. As such, the site-specific characteristics of facilities will introduce inaccuracies to the use of emission factors, and with the increasing use of improved technologies and control methods, emission factors may become dated.

Emission factors may be verified at individual facilities by carrying out direct monitoring of emission sources and developing site-specific variations to the standard factors to reflect on-site operational processes and practices.

6.1   Carbon Disulfide

In the nickel industry carbon disulfide is formed through the breakdown of xanthates which are added at the flotation stage of ore processing.

Xanthate breakdown is influenced by a number of factors.   Within the nickel concentrating, smelting and refining industry the most significant of these factors are:

- pH (below pH 7 the xanthate decomposition rate increases dramatically); and
- temperature (10°C rise in temperature may cause a threefold increase in decomposition rates).

[Source: WMC Report Ref 692 634, 1992]

The stoichiometry of xanthate decomposition, and hence CS_2 formation, will also vary according to the pH.

- Hydrolytic decomposition (alkali conditions) of the xanthate ion results in a stoichiometry of 1:0.5 (xanthate to CS_2).

- Hydrolysis decomposition (acidic conditions) of the xanthate ion results in a stoichiometry of 1:1 (xanthate to CS_2).

[Source: WMC Report Ref 692 634, 1992]

The decomposition stoichiometry will vary with the form of xanthate used at particular facilities. Facilities should verify the stoichiometry(s) to be applied based on their use of xanthate types.

The nickel concentrating, smelting and refining area will generally be of an alkaline pH. However at some facilities this may be very difficult to achieve. TSFs are also likely to be alkaline, although the geochemistry of the ore being handled may result in TSFs becoming acid.

Available data suggests a wide range of xanthate decomposition rates under varying conditions. Additionally, limited carry over of xanthate may take place with the product and some carry over to TSFs (approx. 2% [Society of Mining Engineers, 1976]) may also occur.

However, as the first point of reference, it can be assumed that 100% degradation of xanthate occurs within the processing area.

On this assumption CS$_2$ emission may be estimated using the equation:

Alkali Conditions (>7) :
Emissions of CS$_2$ (kg)   =   0.5 * Mass Xanthate (kg)* MW$_{CS2}$/MW$_{xanthate}$
Acidic Conditions (<7) :
Emissions of CS$_2$ (kg)   =   1.0 * Mass Xanthate (kg)* MW$_{CS2}$/MW$_{xanthate}$

Example 2 - Carbon Disulfide Emission

A facility uses 150kg of Sodium Ethyl Xanthate (SEX). For each mole of SEX used, 0.5 moles of CS$_2$ are produced (alkali conditions).

Molecular Weight$_{CS2}$ (MW$_{CS2}$) = 76g
Molecular Weight$_{CS2}$ (MW$_{SEX}$) = 144g

Emission of CS$_2$ (kg)   = 0.5 * Mass Xanthate (kg)* MW$_{CS2}$ /MW$_{xanthate}$
                                 = 0.5 * 150 * 76/144 kg
                                 = 40 kg

Alternative CS$_2$ EETs include Direct Measurement

6.2   Dust: PM$_{10}$ and Total Suspended Particulates (TSP)

Table 3 provides emission factors for PM$_{10}$ and TSP sources within the processing area. The PM$_{10}$/TSP ratio allows the PM$_{10}$ emission factor to be verified at the facility level where TSP monitoring is undertaken.

You should note that TSP is not a reporting requirement under the NPI and is used to estimate metals content of emitted dust only. Also, while PM$_{10}$ reporting is triggered by fuel usage, all sources of PM$_{10}$ emissions must be estimated if the reporting threshold is triggered.

Emission factors for high and low moisture content ores are presented and are for uncontrolled emissions.

Metal emissions can be estimated as a fraction of the TSP emissions, based on available assay data. Where assay data and facility-specific information is not available for metals in dust emissions, the concentrations in Appendix A should be used as a default to estimate metal emissions.

Dust emissions from TSFs should only be calculated from those TSFs with the potential to result in dust emissions. A range of factors influence the dust generation from TSFs, including:

- moisture content;
- salt concentration;
- vegetation cover and organic matter (lichens, moss etc);
- surface structure (structural & textural cracks & inhomogenity);
- traffic (mechanical and animals); and
- weathering.
[Source: Carras, 1998]

Table 3 - **Emission Factors for Dust Generation**

Operation/Activity	TSP Emission Factor	PM$_{10}$ Emission Factor	PM$_{10}$/TSP Ratio	TSP Emission Factor	PM$_{10}$ Emission Factor	PM$_{10}$/TSP Ratio	Units	Emission Factor Rating
	High Moisture content ores			Low moisture content ores				
Primary crushing	0.01	0.004	0.4	0.2	0.02	0.1	kg/t	C
Secondary crushing	0.03	0.012	0.4	0.6	NDA		kg/t	D
Tertiary crushing	0.03	0.01	0.33	1.4	0.08	0.06	kg/t	E
Wet grinding (milling)	0	0		0	0		kg/t	
Handling transferring and conveying	0.005	0.002	0.4	0.06	0.03	0.5	kg/t	C
Loading stockpiles *	0.004	0.0017	0.42	0.004	0.0017	0.42	kg/t	U
Unloading from stockpiles *	0.03	0.013	0.42	0.03	0.013	0.42	kg/t	U
Loading to trains *	0.0004	0.00017	0.42	0.0004	0.00017	0.42	kg/t	U
Miscellaneous transfer points *	0.009	0.0038	0.42	0.009	0.0038	0.42	kg/t	U
Wind erosion (including stockpiles & TSFs) *	0.4	0.2	0.50	0.4	0.2	0.50	kg/ha/h	U

(Source: *EET Manual for Mining* [USEPA, 1995])   * High and low moisture content emission factors assumed as equal

Note:

1. NDA - No data available
2. Generally a high-moisture ore is taken to be one which either naturally, or as a result of additional moisture at the primary crusher (usually), has a moisture content of more than 4% by weight.
3. Estimated Control Efficiencies For Various Control Measures:
   - 30% for windbreaks
   - 50% water sprays to keep ore wet
   - 65% for hooding with cyclones
   - 75% for hooding with scrubbers
   - 83% for hooding with fabric filters
   - 100% enclosed or underground
4. Controls are multiplicative. For example, water sprays used in conjunction with wind breaks give an emission which is [(1 - (50/100)) * (1 - (30/100)) = 0.35] of the uncontrolled emission (ie. 50% of 70% of the total uncontrolled emissions)

Retaining a wet surface on TSFs will prevent dust generation (BPEMIM, Tailings Containment, 1995), while TSFs with a low salt content, (and a low moisture content), have a greater potential for dust generation than TSFs with a high salt content. Revegetation of decommissioned TSFs will minimise their potential for dust generation.

The potential for TSFs to generate dust should be assessed on a facility basis. The assessment should be based on known factors that influence dust generation and observational/monitored results.

In the absence of facility-specific dust generation factors the following assumptions may be made:

- zero dust generation from TSFs where hyper saline water used in process;
- zero dust generation from 'wet' area of TSFs; and
- zero dust generation from vegetated TSFs.

Alternative dust EETs include Direct Measurement

6.3 Metals in Dust

PM_{10} and TSP may contain a metal fraction, which will represent part of the facility's metals emissions.

The speciation of dust, both PM_{10} and TSP, using an emission factors approach may be achieved using:

- Metals content of ore (generic or facility-specific); and
- Dust generation estimates (either through emission factors, modelling or direct monitoring).

The metals fraction for all processing dust sources may be assumed to be the same as that for unprocessed ore, in the absence of more suitable data. Fractions may be sourced from facility-specific assays of generic ore types (Appendix A).

The metals (and cyanide) content of TSF dust emissions should be based on representative sampling of the TSFs surface matrix.

Alternative metals content of dust EETs include Direct Measurement

6.4 Sewage

The reporting threshold for Category 3 substances is unlikely to be exceeded at most facilities, however, it is the responsibility of each facility to determine whether they exceed the reporting threshold.

Based on the West Australian Water Corporation wastewater treatment design criteria, the per person per day loading of total nitrogen and phosphorus has been calculated. The data in Table 4 below has been applied to the NPI reporting thresholds to provide an indicative facility population that will result in exceedence of the reporting thresholds.

Table 4 - **Indicative Pollution Figures for Wastewater NPI Threshold Tripping**

	kg per person per day	Indicative facility population
Total Nitrogen	0.011	3736
Total Phosphorus	0.0025	3288

Derived from West Australian Water Corporation wastewater treatment design criteria.

Assumes: Annual dry weather flow of 200 litres per person per day

               Total nitrogen concentration of 55 mg/L (range of 40 – 70 mg/L)

               Total phosphorus concentration of 12.5 mg/L (range of 10 – 15 mg/L)

               365 days per year of N and P loading

Using standard sewage loading data for Total Nitrogen and Total Phosphorus, an estimation of Total Nitrogen and Total Phosphorus emissions may be made using the equation shown below:

$$M = [A_l * A_n * N_d] * E_s/100$$

where

M	=	mass of total N or P emitted, kg/yr
A_l	=	average loading of N or P per person per day, kg/p/d
A_n	=	average number of personnel on-site, p
N_d	=	number of days of loading to the sewage system, d/yr
E_s	=	efficiency of sewage treatment system[1], %

[1] The efficiency of the sewage treatment system is defined as the ratio of the effluent Total N or P divided by the influent Total N or P. The value is specific for a given treatment plant and can be determined by sampling the influent and effluent streams.

> *Alternative total nitrogen & phosphorus EETs include Direct Measurement*

6.5   Combustion Emissions

The use of emission factors for estimating emissions from combustion has been extensively studied and may be used to provide a relatively accurate estimate of substance emission.

Reference may be made to the following EET Manuals for combustion emission factors:

- *Fossil Fuel Electric Power Generation;*
- *Combustion in Boilers; and*
- *Combustion Engines.*

6.6   Nickel

Nickel emission factors from smelting operations presented below. However, these emission factors are based on limited data and should be used with caution as a facility's <u>true emissions</u> may be significantly different to its <u>estimated emissions</u> where these factors are applied.

Table 5 - **Nickel Emission Factors from Primary Smelting Operations**

Source	Emissions Control Device	Emission Factor (kg/tonne of nickel produced)
Rotary Dryers	Cyclone/scrubber	0.21
Crusher House	Fabric filter	0.026
Day Bin	Fabric filter	0.0007
Calciners	Electrostatic precipitator	0.23
Skip Hoists	Fabric filter	0.028
Ore Smelter	Fabric filter	0.0037
Refining furnace	Fabric filter	0.0065
OVERALL FOR PLANT	----	1.2

[Source: USEPA, 1984]

6.7   Cyanide

6.7.1   Cyanide Emissions from the Ore Processing Area

Based on research carried out by CSIRO it is estimated that **1%** of total cyanide is lost through volatilisation as HCN within the processing <u>area of gold operations.</u> (Heath et al, 1998).

This estimate is assumed to be applicable to the nickel processing industry for the purposes of this manual.

Cyanide emissions should be reported as mass of CN rather than HCN and can be converted using the stoichiometry detailed below.

$$\text{Mass of CN emitted (kg)} = \text{Mass of HCN (kg)} * MW_{CN}/WM_{HCN}$$

$$\text{Mass of CN emitted (kg)} = \text{Mass of HCN (kg)} * 0.96$$

6.7.2   Cyanide Emissions from the TSFs

It has been estimated that volatilisation of HCN accounts for 90% of the natural degradation of cyanide from TSFs <u>within the gold industry</u> (Ellis, 1997; Simovic, 1984) and is assumed to be the case for the nickel processing industry for the requirements of this manual.

Volatilisation is, however, extremely pH dependent as a result of the HCN/CN^- flux. A range of other factors also influences the rate of volatilisation although pH is the most significant factor.

This percentage degradation is however dependent on pH conditions. Where **'free' cyanide** concentration and pH of the TSF return water are known the percentage degradation may be estimated based on the conditions detailed below;

Table 6 - **Effect of pH on the Volatilisation of Cyanide**

pH	Percentage of natural degradation due to volatilisation ($V_\%$)
6	90 %
7	90 %
8	80 %
9	60 %
10	20 %
11	0 %
12	0 %

(Based on Ellis, 1997, Simovic, 1984)

This data is applied using the equation below:

$$\begin{array}{c} \text{HCN} \\ \text{volatilisation} \\ \text{from TSFs} \\ \text{(kg)} \end{array} = \left[\begin{array}{ccc} \text{Free cyanide} & * & \text{Volume of water} \\ \text{concentration in} & & \text{and/or slurry to} \\ \text{TSF return water} & & \text{TSF} \\ \text{(kg / m}^3\text{)} & & \text{(m}^3\text{)} \end{array} \right] * \; V_\% /100$$

Alternative cyanide EETs include Mass Balance, Modelling and Direct Measurement

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7.0   Modelling

Modelling may be utilised to determine the fate of substances emitted to the environment, including emissions to air and groundwater.

This EET may be of particular use for estimation of emissions of substances such as PM_{10}, cyanide and dissolved metals and their emission through TSFs seepage.

For cyanide and dissolved metals emissions from TSFs, modelling would be likely to have at least two components:

- the fate of the substance within the TSF; and
- the fate and transport of substances within groundwater.

Models may be very simple, based on minimal data and making broad based assumptions, or complex with factors for weather influences, chemical speciation and site-specific factors.

The complexity of a model will influence the accuracy of any emission estimations made using this method.   Wherever possible, however, models should be verified by direct measurement under a range of conditions.   With effective model verification, models may be factored to allow for site-specific influences, and other significant influences may be included within the model itself.

7.1   Groundwater Modelling - Fates & Trajectories

Groundwater movement may be modelled to allow prediction of groundwater fates and that of any associated dissolved substances.   Additionally, modelling will allow the temporal prediction of groundwater movement allowing the potential for the breakdown of substances within the groundwater or their in-situ adsorption to be estimated.

Groundwater models may be based on limited data such as calculated groundwater flow rates and direction, or contain in-depth data such as the geology and hydrogeology of the area. The complexity of models should be stated when used to estimate emissions in order to ensure that the error bands associated with the reported data are fully appreciated.

The fate of dissolved metals resulting from TSF seepage would be suited to this approach.

7.2   Seepage from TSFs

Seepage from TSFs is generally accounted for as part of the design criteria and should not be viewed as a failure of the containment system.

Modelling of seepage from TSFs is recognised as an appropriate means of designing and operating TSFs. Models may be used to estimate emission of dissolved substances such as cyanide and metals.

There are many commercially available models available.   Models include PC-SEEP, a two-dimensional unsaturated/saturated groundwater flow model (Mt Keith Nickel, 1996).

8.0   Engineering Calculations

Engineering calculations may be used to estimate emissions from processes subject to rigid controls, such as where a substance is formed coincidentally, (eg. carbon disulfide), or where the substance breaks down very quickly in the atmosphere (eg. nickel carbonyl).

These processes may be designed to operate at a given efficiency and while variations will occur it may be valid to assume a given performance efficiency under normal operating conditions.

Engineering calculations also utilise standard physical and chemical laws and constants to allow the estimation of particular emissions. These may include equilibrium constants, thermodynamic properties of processes, chemical reactions, pressure constants and physical laws such as Boyle's Law.

Engineering calculations are based on known performance standards of particular processes and equipment, physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

9.0 Direct Measurement or Source Monitoring

While not a requirement of the NPI, additional direct measurement (or source monitoring) is one of the more accurate methods of estimating emissions of substances from processes and facilities.

Facilities may decide to undertake direct measurement in order to:

- estimate their emissions of particular NPI substances;
- verify estimates from alternative EETs; and
- provide supporting data for other EETs.

Where direct measurement is undertaken it is essential to ensure background levels are fully considered. Some areas will have significant background levels of NPI substances either as a consequence of adjacent activities (eg. TSP and PM_{10}) and as a consequence of the natural background levels (eg. metals in particular geological formations).

Monitoring programs should be designed to be representative of the parameters being considered, taking standard and non-standard conditions into account. Additionally the immediate and long-term aim of the monitoring program should be decided in order to avoid unnecessary ongoing monitoring.

Facilities may have existing monitoring commitments and data, which can be applied to the reporting requirements of the NPI. Potential sources of existing data are discussed in Appendix B.

Facilities may also have the analytical expertise on site to enable the monitoring and analysis of NPI substances to be undertaken in a more cost-effective manner.

Direct measurement data may be used to calculate actual loads to the environment by multiplying the concentration of the NPI substances in the final emission stream, by the volume of the final emission stream.

$$\begin{matrix} \textbf{mass} & = & \textbf{substance} & * & \textbf{volume of} \\ \textbf{emitted} & & \textbf{concentration} & & \textbf{total emission} \\ \textbf{(kg)} & & \textbf{(kg / m}^3\textbf{)} & & \textbf{(m}^3\textbf{)} \end{matrix}$$

Where direct measurement is undertaken it is essential that sampling and monitoring procedures are established. The procedures should ensure that all sampling and analyses are undertaken in a standard manner and in compliance with Australian, or other, standards.

9.1 Total Nitrogen and Total Phosphorus

Total nitrogen and total phosphorus loadings may be estimated using direct measurement based on:

- wastewater flows; and
- representative concentrations of total nitrogen and phosphorus in wastewater flows.

Direct measurement is applied to 'end of pipe' emissions ensuring that the facility-specific efficiency of wastewater treatment plants are fully considered.

Alternative total nitrogen and phosphorus EETs include Emission Factors

9.2   Dust & PM$_{10}$

PM$_{10}$ emissions are estimated from their point of creation. As such, the presence of a buffer zone will not influence the estimated emissions.

Direct measurement may be designed to monitor overall site emissions or emissions from particular processes. In all cases it will be important to ensure background levels are considered and factored into emission estimations.

Alternative PM$_{10}$, and TSP, EETs include Emission Factors and Modelling

9.3   Metals in Dust

PM$_{10}$ and TSP emissions will contain a metal fraction. Speciation of PM$_{10}$ and TSP levels will be necessary to allow estimation of the facility's emissions of these metals.

Periodic analysis of dust samples will allow the speciation of dust with a greater level of accuracy.

The degree of dust speciation required will be determined by the range of substances for which the reporting threshold has been triggered. It is important to note that reporting of metals may be triggered by a number of categories but all triggered substances must be estimated from all sources for reporting purposes.

Alternative metal EETs include Emission Factors

9.4   TSF Seepage

Seepage from TSFs may be estimated through the use of a system of monitoring bore holes.

Bore hole layout and depths will be dependent on facility-specific conditions, such as hydrogeology, depth to groundwater and groundwater flow direction. However in order to achieve an accurate estimation of emissions, such as cyanide and metals, boreholes should:

- intercept known preferential flow paths; and
- be located at a range of distances from the TSFs.
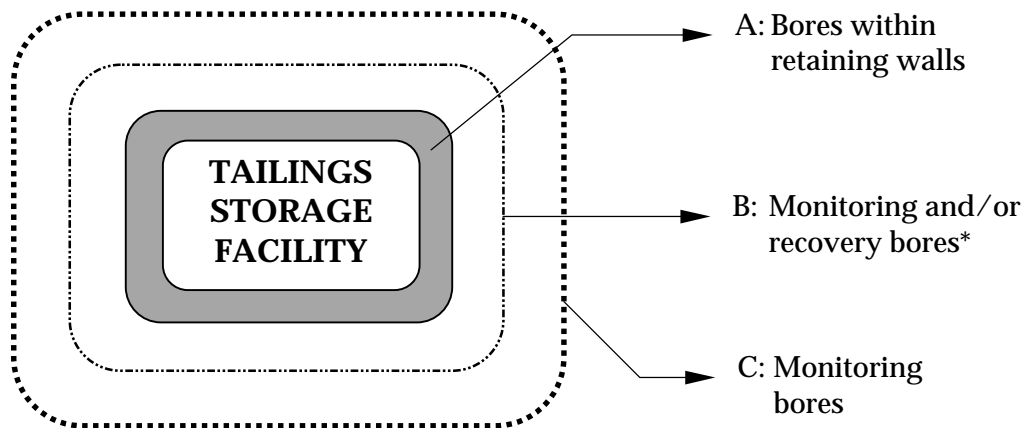
*   Alternative recovery systems, such as trenches, may also be used.

Figure 12 - **TSF Bore Hole Monitoring Approach**

NPI substances detected (above background levels) at bores 'B' (monitoring and/or recovery) will not be considered as emissions to the environment if recovered water is treated, for example pumping back to the TSF. The substances contained in the volume of water not recovered will be considered emissions to the environment.

NPI substances detected (above background levels) at bores 'C' (monitoring) will be considered as emissions to the environment.

The mass of NPI substances emitted will be estimated by multiplying the detected concentration at bores 'B' by the known hydraulic loading beyond bores 'B' (from the zone of influence and hydraulic conductivity of the soil) and the monitoring interval.

The hydraulic loading around the TSF is estimated using the equation below. The equation may be used to estimate the hydraulic loading from all 'faces' of the TSF (north, south, east, and west) as a single entity or in distinct areas where the hydraulic gradient is known to differ significantly.

The hydraulic gradient is based on the hydraulic head produced by the TSF and the physical gradient between bores 'A' and 'B'.

$$\begin{matrix} \textbf{TSF} \\ \textbf{Hydraulic Loading} \\ \textbf{(m}^3\textbf{/day)} \end{matrix} = \begin{matrix} \textbf{Cross sectional area} \\ \textbf{of zone of influence} \\ \textbf{(m}^2\textbf{)} \end{matrix} * \begin{matrix} \textbf{Hydraulic} \\ \textbf{conductivity} \\ \textbf{(m/day)} \end{matrix} * \begin{matrix} \textbf{Hydraulic} \\ \textbf{gradient} \end{matrix}$$

The Emitted Hydraulic Loading is estimated by subtracting the volume of recovered water from the TSF Hydraulic Loading.

$$\begin{matrix} \textbf{Emitted Hydraulic} \\ \textbf{Loading} \\ \textbf{(m}^3\textbf{/day)} \end{matrix} = \begin{matrix} \textbf{TSF} \\ \textbf{Hydraulic Loading} \\ \textbf{(m}^3\textbf{/day)} \end{matrix} - \begin{matrix} \textbf{Volume of} \\ \textbf{recovered water} \\ \textbf{(m}^3\textbf{/day)} \end{matrix}$$

The emission of NPI substances is then estimated

Mass of substance emitted	=	**Concentration of substance in bores 'B'**	*	**Emitted Hydraulic Loading**	*	**Period**
(kg)		**(kg / m^3)**		**(m^3 / day)**		**(Days)**

Alternative seepage from TSFs EETs include Emission Factors, Modelling & Mass Balance

9.5   Cyanide

In monitoring for cyanide it is essential to:

- clearly define the purpose of the monitoring;
- define the form of cyanide which is to be monitored (free, total, WAD, complexed);
- develop an appropriate sampling regime (including replicates and blanks); and
- ensure samples are effectively preserved and treated appropriately.

(Source: BPEMIM, Cyanide Management; Minerals Council of Australia, 1996)

A flow diagram detailing the fate of cyanide within the facility, and its form at all fate pathways, should be developed to ensure that:

- monitored data is appropriate; and
- cyanide stoichiometry is valid.

In-depth guidance in the development of a cyanide monitoring program should be sourced from the references above, process technicians and specialist laboratories.

Cyanides comprise a large class of organic and inorganic chemical compounds that contain a chemical group comprising a nitrogen atom triply bonded to a carbon atom.

Of this class of chemicals only the inorganic cyanides are relevant to the mining industry (NPI reporting is for inorganic cyanide compounds). Free cyanide (CN$^-$) should be estimated and reported for the requirements of the NPI.

Alternative cyanide EETs include Mass Balance, Emission Factors and Modelling

10.0   Emission Factor Rating

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks.   They are based on rating systems developed by the United States Environmental Protection Agency (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found Section 12.0 of this Manual.   The emission factor ratings <u>will not</u> form part of the public NPI database.

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

The EFR system is as follows:

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

Estimating the facility's emissions based on emission factors only, and without taking into account any control measures, may have an uncertainty as high as 100%.

Where emission factor ratings have not been included, these emission factors should be assumed to be 'U', or unrated factors. This rating reflects the limited amount of research and data upon which the factors have been based, and/or the confidence associated with the factor itself.

11.0 Definitions

Reference should be made to the National Pollution Inventory and *The NPI Guide* for definition of terms used within the NPI system.

Boundary	Boundary is defined in varying ways depending on the emission type. For emissions to air boundary is the point of creation (such as the surface of a liquid during evaporation, or the wheels of a vehicle for dust generation). For emissions to land and water, boundary is the point at which a substance is no longer contained (such as a spill to ground from a process vessel, or a discharge to surface waters from a treatment works).
Direct Measurement	Technique used to estimate emissions to the environment through the sampling and analysis of emission streams.
Emission	Any release of substances to the environment whether it is in a pure form or contained in other matter. Emissions may be solid, liquid or gaseous.
Emission Factor	A number or equation that may be applied to raw data from a facility to estimate emissions from that facility without the need for emissions sampling and analysis. This technique is most often used to estimate gaseous emissions to the environment.
Fugitive Emissions	Emissions not released from a vent or stack.
Inventory	Means of recording usage and stores of all materials, and product, held on a facility or utilised by a process.
Mass Balance Technique	Estimation of emissions to the environment through equalisation of inputs and outputs to a particular process or facility.
Power Generation	Production of power for the operation of facilities and use in processes.

12.0 References

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The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage and from your local environmental protection agency (see the front of the NPI Guide for details);

- Combustion in Boilers;
- Combustion Engines;
- Fuel & Organic Liquid Storage;
- Fossil Fuel Electric Power Generation; and
- Sewage & Wastewater Treatment.

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Appendix A - **Generic Ore Assays**

Table A1: Generic Ore Assays

Element	Symbol	Basalt	Granite	Coal	Soil	Earth's Crust	Marine Clays	Marine Carbonates	Shale	Limestone	Sandstone	Sediment
Antimony	Sb	0.69	0.2	3.5	1	0.2	1	0.05	1.5	0.3	0.05	1.2
Arsenic	As	1.5	1.5	6.5	6	1.5	13	1	13	1	1	7.7
Beryllium	Be	0.3	5	1	0.3	2.6	2.6		3	<1	<1	2
Boron	B	8	12	70	20	10	230	55	130	20	30	100
Cadmium	Cd	0.13	0.09	0.2	0.35	0.11	0.21	0.23	0.22	0.028	0.05	0.17
Chromium	Cr	200	4	20	70	100	90	11	90	11	35	72
Cobalt	Co	35	1	5.4	8	20	74	7	19	0.1	0.3	14
Copper	Cu	90	13	15	30	50	25	30	39	5.5	30	33
Fluorine	F	510	1400	-	200	950	730	550	800	220	180	640
Lead	Pb	3	24	30	35	14	80	17	23	5.7	10	19
Manganese	Mn	1500	400	41	1000	950	6700	1000	850	620	460	770
Mercury	Hg	0.12	0.08	0.23	0.06	0.05	0.08	0.46	0.18	0.16	0.29	0.19
Nickel	Ni	150	0.5	15	50	80	225	30	68	7	9	52
Selenium	Se	0.05	0.05	2.9	7	0.05	0.17	0.17	0.5	0.03	<0.01	0.42
Zinc	Zn	150	240	31	90	190	150	20	160	20	220	150

(Source: *EET Manual for Mining*)

1. All figures in mg/kg (or g/tonne).
2. Extracted and adapted from Bowen, H.J.M. 1979. *Environmental Chemistry of the Elements*, Academic Press and generally checked against Berkman, D.A. 1989 *Field Geologists Manual*, The Australasian Institute of Mining and Metallurgy.
3. The figures listed above are average or median concentrations of the particular element within the rock or material specified.
4. The NPI requires the reporting of emissions of the elements listed in this Table and their compounds. As noted in the body of the handbook, it is recognised that trace metal analyses are not routinely undertaken for mining operations. In these situations, it is likely that the trace metal concentrations would be average to below average. Thus, where data on particular elements is not available, the average concentrations listed above for the particular material type should be used. In most cases, it would be expected that a low reliability would be attached to the emission estimate.
5. Further to Note 3, trace metal concentrations will be significantly greater than average where the reportable metal occurs at the site. For example, at a silver, lead and zinc mine, the concentrations of lead, zinc and probably cadmium in waste rocks, TSFs and soils will be significantly greater than the average concentrations listed in the above Table. It is expected that where it is necessary to use an assumed trace metal concentration to estimate emissions from a site, the facility will nominate a credible figure that can be justified to the administering authority. The reliability attached to the estimate will generally depend on the data sets available from which the estimate has been calculated.

The table below presents the concentrations within the ore that will trigger the reporting threshold for Category 1 NPI substances.

Metal conc. in ore (ppm)	Annual tonnage (millions of tonnes)
0.1	100
0.2	50
0.3	33.3
0.4	25
0.5	20
0.6	16.7
0.7	14.3
0.8	12.5
0.9	11.1
1	10
10	1
100	0.1

Appendix B - **Existing Data**

Existing Data

The emission estimation methods proposed in this manual require best available data. This data may be available within a corporation or facility in a range of forms and sharing this data between facilities will aid reporting and allow for a greater level of accuracy in the estimation of emissions.

This data may be used to:

- directly estimate emissions;
- provide guidance on the most appropriate estimation methods to be used; and
- provide guidance on where direct monitoring may be most beneficially carried out.

It is not intended that facilities disclose proprietary or sensitive information, rather that this information is used in-house to assist in the NPI reporting process.

Data sources may include the following.

Existing Data & Research

Research projects of interest to industry are often sponsored, such as university PhD's and final year projects. These may be very directed areas of research, such as slag content and leachability or hydrogeological contamination, and may not be widely available within a facility or may be held at a corporate level.

Some mine sites currently address their dust emissions as three distinct components:

- the monitoring of ambient dust levels:
- the assessment of dust sources; and
- the implementation of dust control strategies.

Data of this type may be applied to emission estimation methods to increase their accuracy either directly through the development of emission factors or indirectly by identifying additional process within mass balances.

Mines may also have carried out discrete monitoring studies to determine the health or environmental impacts of particular substances. While these studies may have shown that minimal health or environmental risk is posed and hence ongoing monitoring is not required, it may also be used to allow more accurate estimation of NPI substances.

Many mines will have access to geotechnical data and groundwater data for the mine site from exploration work carried out in the past. This data may provide information on groundwater flows, the location of palaeochannels and other geological formations, and provide useful data for deciding the location and depths of any monitoring boreholes.

Process Monitoring

Elements of the process may be monitored regularly in order to optimise recovery of the product. This data may be applied to emission estimation methods such as mass balance, serving as a verification of the mass balance to that stage of the process and raw data.

Monitored areas may include:

* ore;
* concentrate; and
* TSFs water input and return.

Monitoring may also be undertaken for health and safety requirements and may include:

* ammonia;
* cyanide;
* acids; and
* carbon monoxide.

Licenses & Reporting

Mine sites may be required to carry out monitoring which can be applied to the requirements of the NPI. This data may include the following parameters:

* sulfur dioxide;
* sulfuric acid fumes;
* arsenic (As);
* dust and particulates;
* metals; selenium, antimony. beryllium, cadmium. lead, mercury, chromium, manganese, cobalt, copper, nickel, zinc;
* chemical spills, including cyanide; and
* dangerous goods licensing.

Facilities may monitor TSFs and storage ponds at regular intervals to ascertain reuse potential and treatment methods such as neutralisation. Where seepage from ponds and TSFs is suspected monitoring of bore holes may also be undertaken. Parameters may be expressed as soluble or total, and may include:

* pH;
* conductivity and TDS;
* standing water level; and
* metals.

This data may be used:

* directly where NPI substances are being monitored and reported;
* indirectly such as dust monitoring where speciation of the dust component may be required; and
* relationally where the ratio of a monitored parameter can be related to the emissions of an NPI substance.

Approvals Data

Nickel mines may have Consultative Environmental Reviews (CERs), Public Environmental Reviews (PERs), Notifications of Intent (NOIs) or other approval documents that contain a range of facility characterisation and operational efficiency data. This may be applied to emission estimation methods to provide greater accuracy in reported data.

For example from March 1993 all proposal submitted to WA DoME require a detailed summary and list of commitments. The range of information must be reported under the guidelines (NOI Guidelines, 1993) including:

- properties of TSFs;
- TSF construction parameters;
- decant or under drainage systems;
- liner type; and
- monitoring.

Regulatory Data

Regulatory and government departments may hold extensive data relating to individual facilities, state and territories, or national and international sources. This data may be accessed to provide a more extensive database of available information with which to develop facility or corporate emission estimation strategies.

Suppliers

Suppliers should be able to provide in depth data regarding the fates of supplied chemicals within the process.

A good example of this would be xanthates which breakdown to form carbon disulfide. Suppliers may be able to provide data relating to the proportional breakdown of xanthates, environmental stability, and potential for carry through in the nickel process and to TSFs.

Inventory

A facility inventory may be used to identify all inputs to the nickel process and the usage rates in relation to ore treated and product achieved. The inventory should be used as a tool to assist in the estimating and reporting process and will not need to be submitted with estimated emissions.

In addition to its use within the NPI framework a facility inventory may also be used to determine material usage across the site assisting in:

- financial planning;
- resource planning;
- waste minimisation; and
- environmental reporting.

It is likely that most facilities will have an inventory of some type and reference to this may enhance the accuracy of emission estimation and be applied to all emission estimation methodologies.

An *example* of an existing facility inventory is presented below.

INPUTS	Units	Jan	Feb	Mar	...	Dec	TOTAL
Tonnes of ore treated	tonnes						
Nickel production	kg						
Sodium Cyanide	tonnes						
Quicklime (78% CaO)	tonnes						
(88% CaO)	tonnes						
Oxygen	m3						
Carbon	tonnes						
Flocculant	tonnes						
Antiscalent	tonnes						
Diesel	litres						
Grinding balls	tonnes						
Electricity	kWh						
LP Gas	tonnes						
Caustic soda	tonnes						
Hydrochloric acid	tonnes						
Potable Water	kl						
Bore Water Total	kl						
Decant Water from TSFs	kl						
TSF dewatering system	kl						
TSF decant return	kl						
TSF underdrainage	kl						

Appendix C - Transfers

Transfers

Transfers are the movement of NPI waste substances from the facility. For the nickel industry these may include:

- discharges of waste to sewer;
- all material to managed landfill or waste treatment sites outside of the facility; and
- all material leaving the facility to be reused, recycled, recovered, treated reprocessed or destroyed.

The reporting of transfers is not a requirement of the NPI at this stage. However the concept of transfers is being trialed and may become a requirement of the NPI following the 1999 review. If transfers are to be estimated the appropriate EETs detailed in this manual may be used.

Examples of transfers of relevance to the nickel industry, if included in the NPI, may include:

- Management of arsenic waste through its disposal at intractable waste sites.
- Off-site disposal of wastewater and sludge from treatment processes will represent a transfer.
- Off-site disposal of solid wastes will represent a transfer.