National Pollutant Inventory

Emission Estimation Technique Manual

for

Lead Concentrating, Smelting and Refining

Environment Australia

First published in December 1999

EMISSION ESTIMATION TECHNIQUES
FOR
LEAD CONCENTRATING, SMELTING AND REFINING

TABLE OF CONTENTS

TABLE OF CONTENTS CONT'

LEAD CONCENTRATING, SMELTING AND REFINING

TABLE OF CONTENTS CONT'

LEAD CONCENTRATING, SMELTING, AND REFINING

LIST OF FIGURES, TABLES AND EXAMPLES

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 lead concentrating, smelting and refining.

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

- Identify which substances they are required to report as part of the NPI; and
- Estimate emissions of NPI substances to air, water and land from their facilities.

This handbook covers the concentrating, smelting and refining of lead commencing from the delivery of ore to the processing facilities, through to smelting and the production of + 99% pure lead at the refinery.

It also covers operations that produce lead concentrates only, and the smelting of lead from imported concentrates. This manual does not include extraction of ore, which is covered by the *EET Manual for Mining*.

Ancillary activities such as an acid plant, cadmium plant, selenium removal, and zinc recovery, are covered in this manual. Associated activities including power generation - combustion engines, and fuel and organic liquid storage facilities are covered briefly in this manual. These activities are covered comprehensively by separate EET manuals.

The emission of NPI substances from a processing facility's tailing storage facilities (TSFs), waste management sites, and sewerage systems are included in the reporting requirements of the NPI system, and are covered by this manual.

EET MANUAL:	Lead Concentrating, Smelting & Refining
HANDBOOK:	Lead Concentrating, Smelting & Refining
ANZSIC CODE:	2723

The scope of this manual is presented diagrammatically in Figure 1.1.

1.1 Context of this Manual

This 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 generated in this process will have varying degrees of accuracy with respect to the actual emissions from lead processing facilities. In some cases there will necessarily be a large potential error due to inherent assumptions in the various emission 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 seepage 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 a particular site characteristic related to cyanide speciation, mineralogy and pH.

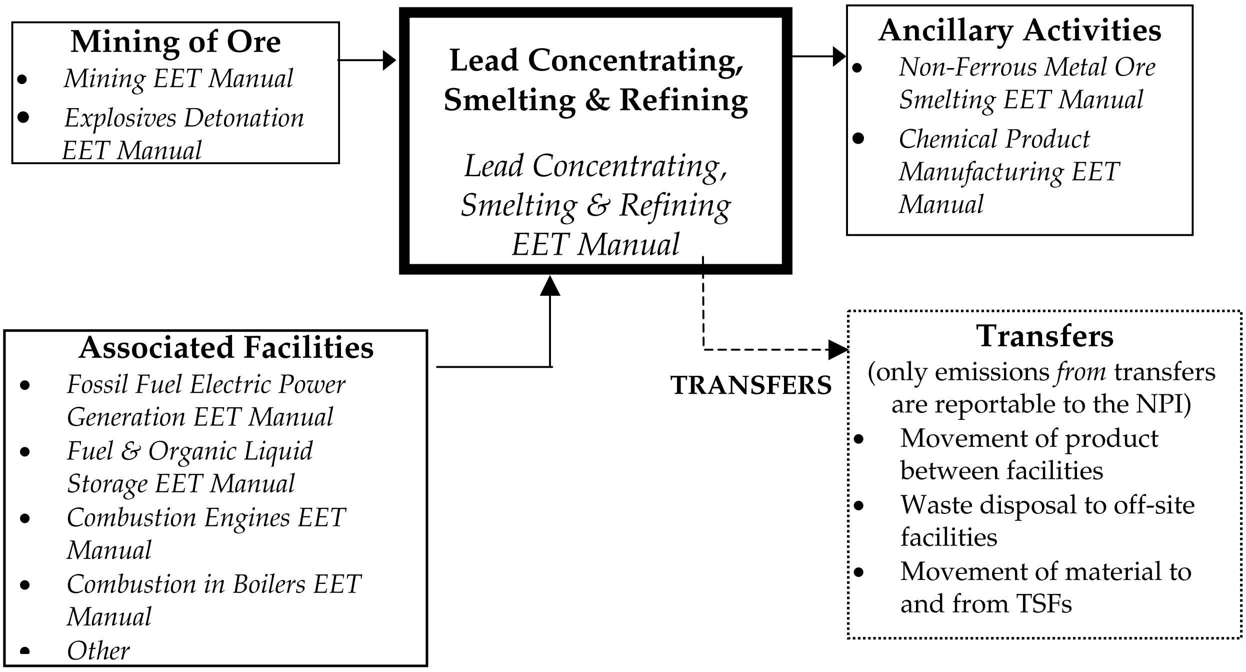


Figure 1.1 - Scope of the *Lead Concentrating, Smelting and Refining EET Manual* and its Potential Relationship With Other EET Manuals

Facilities may undertake "Ancillary Activities" such as the production of sulfuric acid or precious metal purification, either as a process input or through processing of waste streams. When estimating emissions, a facility should ensure that emissions are not "double accounted" (refer to Section 5.0). Process flowsheets should be used to minimise the potential for this. Similarly a facility needs to account for any emissions from "Associated Facilities", which may include organic and fuel storage, and energy generation equipment.

1.2 EETs Should be Considered as "Points of Reference"

The EETs and generic emission factors presented in this 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. Section 5.0 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.

1.3 Hierarchical Approach Recommended in Applying EETs

This 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. If emissions of a substance are clearly very small no matter which EET is applied, then no further assessment is required.

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.

1.4 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. However, the NPI Contextual Information and Background Information assists understanding of, for example, the relationship between factors such as natural occurrence, and substance bioavailability, and potential environmental and health impacts.

1.5 NPI Reporting Requirements

Once this manual has been published it is anticipated that each facility will begin recording emissions within three months. The substances that require reporting are included in *the NPI Guide*, Tables 1 and 2, which have been reproduced (in part) in Table 4.1 of this manual. Initially facilities need only to report on the substances in

Table 1, however in the future it is envisaged that the additional substances in Table 2 will need to be considered. At the end of each reporting year every lead concentrating, smelting and refining facility is required to report these emissions to their state Environment Protection Authority (EPA) or equivalent body. These reported levels are a summation of individual emissions from plant sectors, for example only one value for the sulfur dioxide emissions is reported (the plant total), which represents the summation of all individual emissions across the year and plant divisions. The EPA will verify that the reported levels are a reasonable estimate of the actual emissions and will forward the values to Environment Australia where they will be published on a publicly accessible internet database.

Failure to report emissions, or supplying levels which are deemed to be not of "acceptable reliability", will result in facilities and companies being named in Parliament. It is expected that peer pressure within the industry will be a key driving force behind compliance and accuracy.

1.6 Use of this Manual

This manual is structured to allow facilities to work through the issues that need to be addresses in a structured and coherent manner.

Likely emissions from facilities are discussed in Section 4.0, while Section 5.0 discusses the approach to emissions estimation and the methods available.

Sections 6.0, 7.0, and 8.0 address the possible emissions from a facility to air, water and land, and 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 estimate the emissions of a substance and how other EETs can support this EET. 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.

Section 9.0 gives examples of the application of EETs to typical emissions from lead concentrating, smelting and refining. Finally Section 10.0 identifies control measures that can be applied to reduce NPI emissions.

This manual has been prepared by National Environmental Consulting Services (NECS) for Environment Australia.

This manual has been developed for the lead concentrating, smelting and refining industry and has been based on the *Nickel Concentrating, Smelting and Refining EET Manual*.

2.0 Process Description

2.1 General

The most common lead mineral, found in the earth's crust, is galena (PbS), with cerussite ($PbCO_3$) and anglesite ($PbSO_4$) also occurring when the ore has been weathered or oxidised. The lead ore currently mined in Australia commonly contains zinc, silver and copper ore, as well as precious metals. 60% of the lead consumed in Australia is in lead/acid storage batteries, for use in motor vehicles and for backup energy supplies. In addition to this, lead sheeting is used to protect chemical plants from acids, and lead is also being employed as a barrier against noise and radiation.

Australia leads the world in economic lead resources, followed by the United States, and it is also the world leader in lead production from mining. Australia is the world's largest exporter of lead with bullion primarily exported to the United Kingdom and Korea; concentrates to Japan and Europe; and refined lead to Taiwan, Korea, Indonesia and Japan.

At the mine sites the ore minerals are liberated through crushing and grinding. The crushed ore is mixed with reagents and water to separate the valuable sulfide minerals from the gangue, so that concentrates are produced. The concentrates undergo further processing to produce lead as a pure metal. The main processing technique for primary lead refining is smelting.

Primary refined lead is only produced at Port Pirie, South Australia. This refinery processes more than three-quarters of Australia's lead concentrates. The concentrate undergoes three generic processes, sintering/smelting, refining and casting. When the concentrate is smelted the lead sulfide is reduced to lead and a layer of impurities (slag) is produced. The slag layer can be removed and the molten lead can be further purified, until lead with a purity of more than 99.9%, is achieved.

Secondary refineries, located in Sydney and Melbourne, process recycled lead, consisting primarily of lead scrap and lead/acid car batteries. More than 50% of lead consumed is from a secondary refinery. The processing of the scrap involves separating the lead from glass and plastic, then smelting and refining the metal as with a primary refinery.

Distinct processes are applied to the concentrating, smelting and refining of lead. Representative processes are discussed below and example process flowsheets are presented as a source of reference. The flowsheets are generic in nature, and are included as a guide to identifying potential sources of emissions. However, as each facility is different the emission sources identified should not be viewed as a complete list. Facilities are advised to use their own process flowsheets to assist in structuring and addressing NPI reporting requirements. When a facility does report on their emissions, it is for the facility as a whole, *not* on a section-by-section basis.

Some lead mines produce concentrate only, for smelting elsewhere, or may be fully integrates, producing final lead product from ore on-site. Thus, not all sections of this manual will be relevant to each facility. Facilities as not expected to report on substances they do not emit or produce, nor on processes that they do not undertake.

2.2 Lead Processing

2.2.1 Lead Concentrating

At the mine site the ore is drilled and blasted in large volumes, often transferred to underground rock crushers by large loaders before being hoisted to the surface in skips or driven via trucks. At the surface the ore is subjected to additional crushing and fine grinding. The first stage of separation sees the liberation of lead and other valuable sulfide minerals from the waste rock particles to form a concentrate. The lead sulfide concentrating process is presented in Figure 2.1. Concentrating is carried out in a flotation device such as a Jameson flotation cell.

Grinding

Crushed ore is ground in autogenous and ball mills to further reduce the particle size and aid in the separation of gangue. The ore is directed to a flotation circuit where lead ore is first separated while the zinc ore is suppressed. The zinc ore is then returned and floated.

Flotation

Ground lead ore and water are combined in a series of flotation cells where chemical reagents (an activator, a collector, a pH modifier and a depressant) are added and mixed, and air is then injected into the cells. The activator promotes flotation of the slower floating ferrites while the collector changes the surface tension of different minerals allowing the pyrite and lead-rich particles to attach to the air bubbles and float to the surface of the liquid forming a froth. The pH modifier aids in the production of a higher grade concentrate by discriminating between which particles attach themselves to the air bubbles, and the depressant suppresses the attachment of certain minerals to the air bubbles so that only selected compounds will float. The froth, which floats to the surface, contains the majority of the lead and iron sulfides. The tailings, which contain the waste minerals, are transferred to a scavenger cell, which separates any residual lead complexes from the tailings and recycles them to the flotation cell.

The gangue materials fall to the bottom of the flotation cells and are disposed of as tailings, often in a dam for evaporation, or they may be returned to the mine as backfilling for mined-out areas.

Although there are common reagents used in flotation cells, it is recommended that each processing facility refer to their own process flowsheet to identify which reagents are used and any possible compounds that may form.

Dewatering

Dewatering is conducted in two stages, thickening and filtration. The froth is skimmed off the top of the cell and the resulting lead sulfide rich solution is thickened. The thickened flotation concentrates are then filtered using larox filters. This process increases the grade of the ore, which may contain only 5% lead, to a concentrate assaying at more than 50% lead.

The moisture content of lead concentrate is typically 7.2%, and the concentrate is often sprayed with a dust suppressant as it leaves the mine site.

Figure 2.1 - Lead Flotation Circuit

CONCENTRATING LEAD ORE

INPUTS

Crushed Ore

Activator (Copper sulfate)

Collector (Ethyl xanthate Cyanamids 7016 or dithiophosphate)

Modifier lime

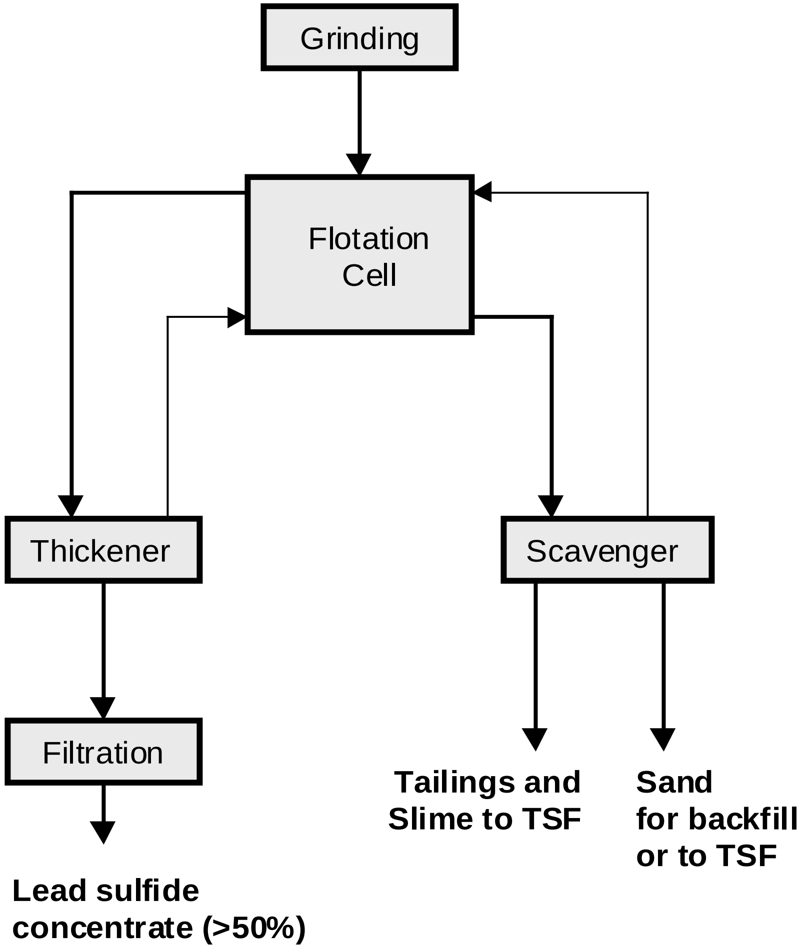
Iron depressant (Polyacrylamide, sodium cyanide)

Nitric acid

Hydrogen peroxide

Coherex binding agent

PROCESS



POTENTIAL EMISSIONS

PM_{10}
Metals

Activator Products

Carbon disulfide

PM_{10}
Cyanide
Metals

Cyanide complexes

2.2.2 Smelting Process

Sintering

To prevent the finely ground concentrate from clogging the blast furnace the concentrate is sintered. This process has two benefits, it agglomerates the particles and it also acts as an oxidising roast, to release the sulfur in the ore as sulfur dioxide and convert the minerals into oxides.

Initially the concentrate is combined with a flux. Additional input streams are also combined with the concentrate at this point (eg. Recycles). This mixture is carried along a moving grate where it is ignited in the presence of air. The oxidation of the sulfides provides enough energy to keep the reaction occurring as the grate moves. The mixture fuses together, and then the mass is crushed and screened. Any fine particles are recycled to the sinter feed and the larger particles are transferred to the blast furnace.

Smelting

One method of smelting is the Imperial Smelting Furnace (ISF) process, which is used to produce zinc and lead metal simultaneously in a blast furnace.
Figure 2.2 displays this process. The diagram of the furnace has been separated into unit sections for clarity and ease of identifying emission sources (ie. the condenser is separate to the furnace, yet in reality they are all one unit). Zinc and lead concentrates from various mines are blended and sintered to combine the fine particles into lumps and remove the sulfur as sulfur dioxide, thus oxidising the lead and zinc. The sinter reaction is:

$$PbS + 3/2\ O_2 \quad \rightarrow \quad PbO + SO_2$$

The sintered product is mixed with hot coke and smelted in a blast furnace to produce zinc vapour (gas) and molten lead according to the following reactions.

$$2C + O_2 \quad \rightarrow \quad 2CO$$

$$PbO + CO \quad \rightarrow \quad Pb_{liq} + CO_2$$

$$ZnO + CO \quad \rightarrow \quad Zn_{vap} + CO_2$$

The zinc vapour passes out of the blast furnace with the furnace gases (approximately 8% Zn) into a condenser where the stream is cooled with a spray of molten lead. The lead absorbs the zinc vapour and forms an impure molten zinc metal (98.3% Zn).

As the lead melts in the blast furnace the impurities, including silica and flux residue, form a slag which floats on top of the molten lead, thus preventing oxidation of the lead. Both the slag and the lead flow into the forehearth of the furnace where they are separated by gravity. The slag can be used as backfill underground, depending on the concentration of lead in the slag. At this stage the lead bullion may be cast and sold or transferred to another site for further processing (or processed on-site if the facilities are present).

It is important to note that other processes exist and are employed in Australia. For example, lead is also smelted in a blast furnace where the zinc reports in the slag rather than in the gas phase and is recovered though a secondary process. Similarly the recovery method for different metals (such as cadmium) also varies between facilities. For this reason it is important that facilities refer to these flowsheets only as a guide, and use there own flowsheets when reporting.

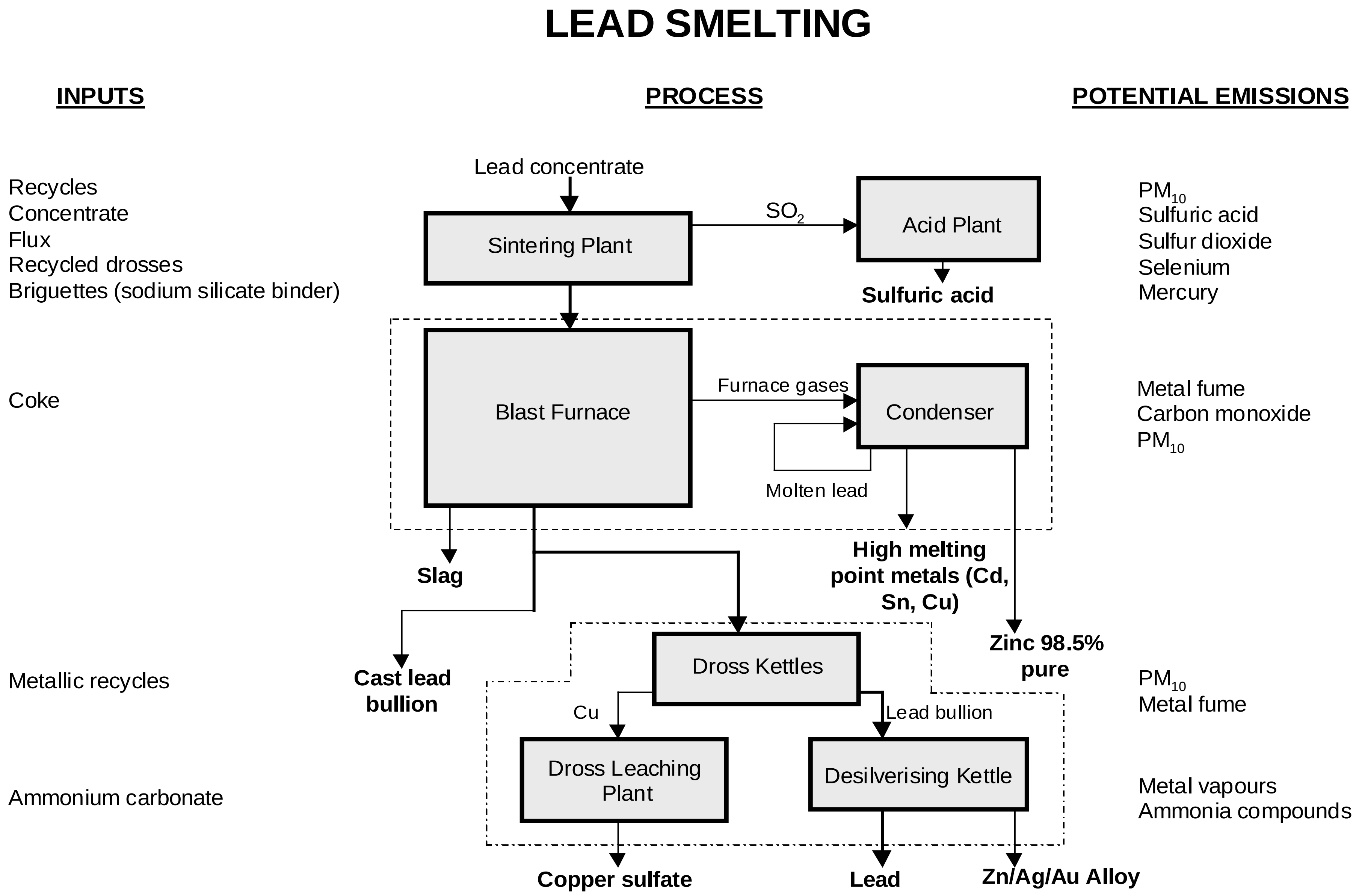
Copper Drossing

The impure ingots from the smelter are melted and the molten lead is transferred into pots for copper drossing, where the metal is gradually cooled, in stages, but kept molten. With each successive drop in temperature copper and other impurities collect in a dross layer on top of the molten lead, allowing them to be easily removed. The copper–lead dross is transferred to a leaching plant where the copper can be recovered as copper sulfate. The lead bullion is now cast into ingots for export or domestic refining at Port Pirie. As mentioned in relation to smelting, there are different methodologies employed in copper drossing depending on the bullion composition, which determines how the copper precipitates. Each different species requires a different treatment process.

Refining

The metal produced by the smelter is not pure (97% Pb). There are many methods currently utilised to refine lead, including controlled cooling, heat vaporisation and desilverising, each site should refer to their own plant's flowsheets to identify all emissions. Typically to refine the lead, the bullion is remelted and blown with air to oxidise the metallic impurities, including antimony and arsenic. These impurities form a slag layer, which is then removed. One method practiced in Australia is desilverising. The bullion flows into a desilverising kettle where it passes though molten zinc. The molten lead becomes saturated with zinc and a zinc/silver/gold alloy is formed as the metals gradually cool. This alloy is removed from the kettle, leaving pure molten lead, which can then be cast. The silver and gold is won through electrolysis of the alloy.

Figure 2.2 - Primary Smelting of Lead



2.3 Secondary Lead Processing

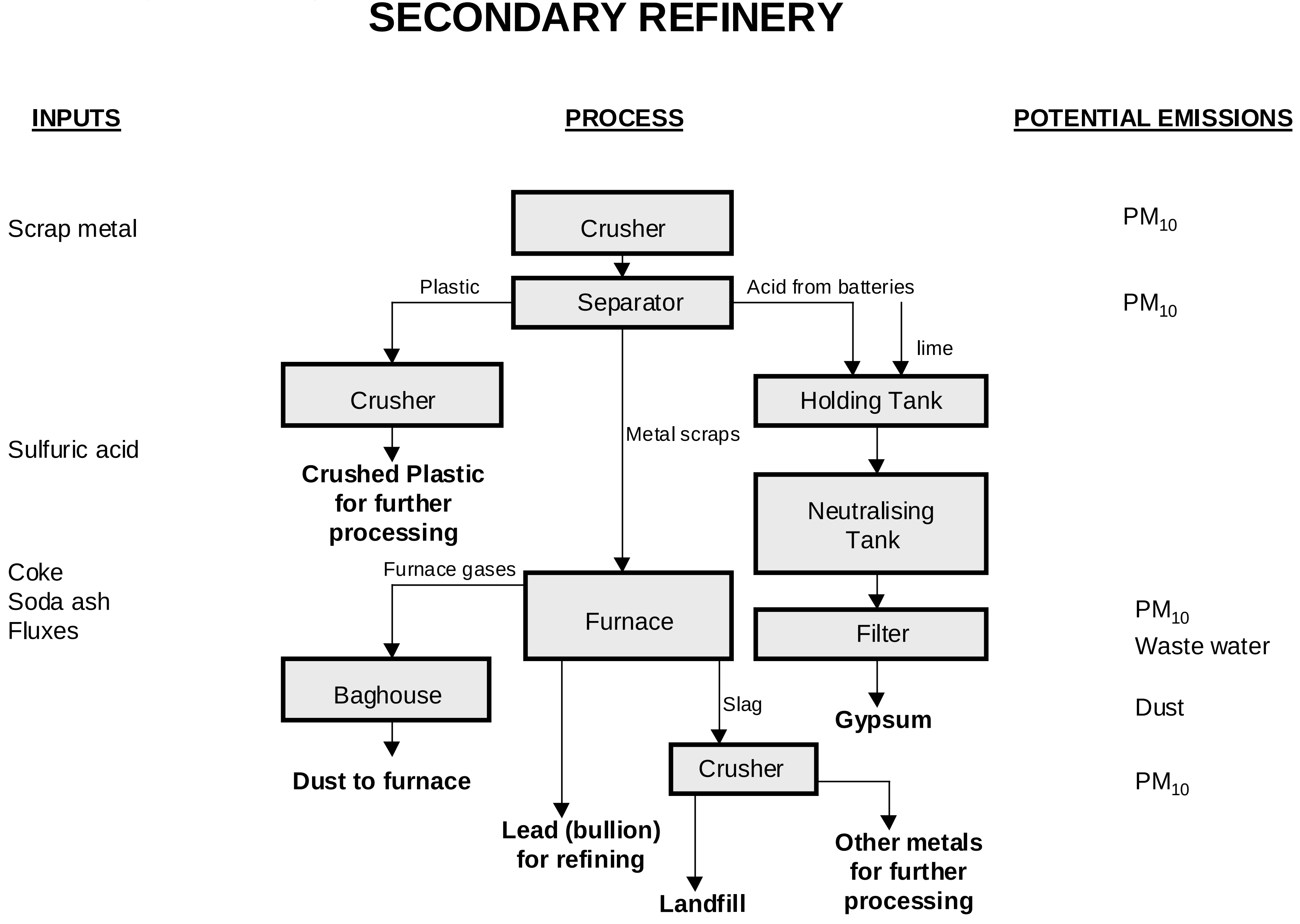
More than 50% of lead consumed in Australia is recycled. The secondary refineries are located in Sydney and Melbourne, with a feed which consists of scrap lead batteries (85% of feed), drosses and residues from lead manufacturers, lead sheeting and pipes, lead paint and chemicals, and lead dust.
Figure 2.3 demonstrates a typical flowsheet for the refining of lead scrap, it is recommended that each facility refer to their own process flowsheets to allow complete identification of emissions.

The processing of lead scrap is based on three operations, scrap pretreatment, lead smelting and lead refining. The pretreatment operation aims to remove the majority of the non-metal materials that do not contain any lead. The scrap is crushed and separated. The plastic undergoes further crushing and it can then be processed at a plastic-recycling centre for use as "black plastic" in products such as septic tanks, rubbish bins or flowerpots. Similarly other scrap can be processed on-site, if the facilities are available, or passed onto other processing centres. Any scrap that does contain lead is fed into a furnace (typically either a rotary or reverberatory furnace) where it is smelted.

The lead, tapped from the furnace, is refined to remove any metals from non-metals, as described in Section 2.2 on primary smelters. The slag and the molten lead are separated at tapping, and the lead is either cast into ingots or further refined to produce pure lead.

Another by product of recycling lead-acid batteries is gypsum. The acid is separated from the processing stream during pretreatment. From there it is transferred to a holding tank then is processed in the effluent treatment plant (ETP), where the acid (typically sulfuric acid) is neutralised with lime, resulting in the formation of gypsum and wastewater. The gypsum is disposed of with the slag from the furnace and the wastewater can be used on-site or discharged to the sewer.

Figure 2.3 - Secondary Lead Refining



3.0 Ancillary Activities and Associated Facilities

3.1 Ancillary Activities

A number of by-products from lead smelting and refining can be produced through ancillary activities. The sulfur dioxide gas released during the sintering process can be used to produce sulfuric acid, while zinc vapour and copper sulfate can be recovered from the smelting process. Finally, cadmium, gold and silver, as well as small amount of other metals are recovered in the refinery. Secondary refineries produce gypsum, landfill, and many metals that were components of lead alloys.

Lead smelters and refineries may have a number of associated activities. These activities can also produce NPI reportable emissions. Such activities may include fuel and organic liquid storage and power generation.

3.1.1 Acid Plant

A significant environmental problem faced when smelting and refining lead from sulfide ore is the formation of sulfur dioxide gas during the sintering process. There are two methods of removing the gas, either through direct venting or the production of sulfuric acid. Under current guidelines the production of sulfuric acid is encouraged, owing to the adverse environmental effects of sulfur dioxide gas. The hot gases, emitted from the sinter plant, will contain dust. To remove this dust the gas is typically initially cleaned, which can be conducted using hot gas precipitators followed by a sequence of wet scrubbers. Final cleaning may be conducted using electrostatic mist precipitators, however the sequence and choice of unit operations varies between facilities.

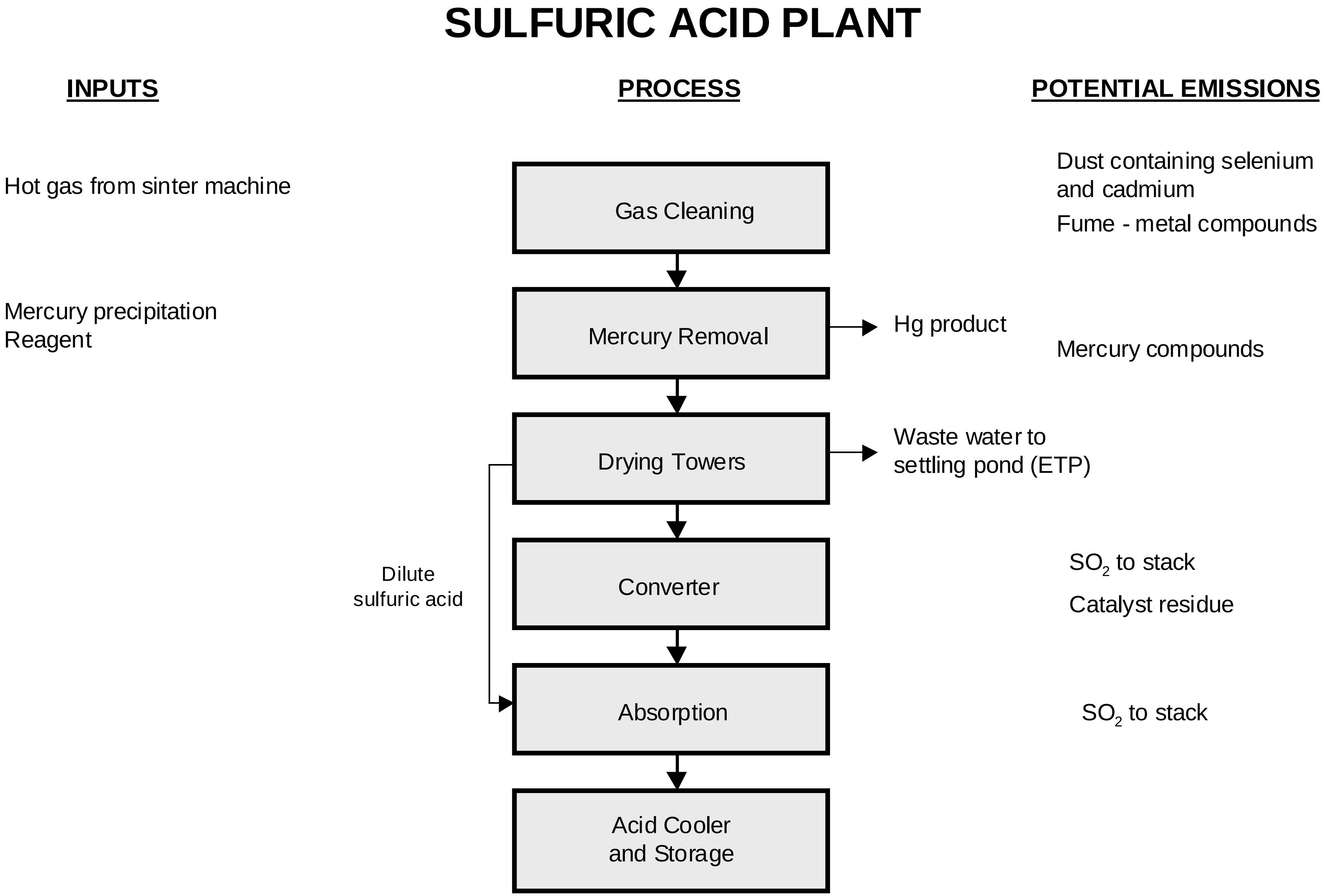
After cleaning, the gas is dried to remove water then passed to the converter (or series of converters with intermediate heat recovery) where the sulfur dioxide is catalytically converted to sulfur trioxide. The sulfur trioxide is dissolved in an absorber to form sulfuric acid (refer to Figure 3.1). This sulfuric acid may be used within the plant or may be sold. As the flowsheets incorporated into this manual are generic it is important for facilities to refer to their own process flowsheets.

The sulfuric acid process comprising the drying towers, converters, heat exchangers and absorption towers is often referred to as the contact acid process, and the resultant acid (approximately 98% sulfuric acid) is often referred to as contact acid.

3.1.2 Selenium Removal Process

Several of the lead concentrates refined in Australia contain selenium, which accumulates in the electrostatic mist precipitator dust. Selenium is removed as dust and fume from the hot gas precipitators. The dust is heated with strong sulfuric acid and the selenium is extracted as selenium dioxide fume. This fume is then scrubbed with water to produce selenious acid, and crude selenium is recovered by precipitation.

Figure 3.1 - Sulfuric Acid Plant



3.1.3 Zinc Recovery

When lead is smelted, depending on the process, zinc either reports as zinc oxide which is reduced to pure zinc and flows out of the furnace with the hot gasses as a vapour, or is contained in the slag tapped from the blast furnace.

If an ISF is employed then the zinc is a vapour. These gases are passed through to a condenser followed by a series of filters, to remove any dust. Within the condenser the zinc vapour is sprayed with molten lead, resulting in the temperature of the stream decreasing and the zinc becoming absorbed within the lead, to form molten lead containing 2.3% zinc. The metal is passed though a series of cooling channels where the zinc comes out of the solution and can be removed. It is now 98.5% pure and can be further refined or may be cast into ingots.

In the case of large lead smelters the majority of the zinc is contained within the slag. It is recovered through a process of slag fuming, leaching and electrolysis. The zinc may then be cast.

3.1.4 Cadmium Plant

Cadmium is a minor constituent in most sinter feed materials. If the sinter gas is processed through an acid plant some of the cadmium is volatilised and can be collected from the hot gas precipitators, wash towers, and electrostatic mist precipitators. The fume is leached, washed and passed through ion exchange columns for cadmium removal and trommelled to recover cadmium. The crude cadmium from this operation is melted, partially refined, cast and then remelted with cadmium/zinc alloy in the refinery and distilled in a small refluxing column.

3.2 Associated Facilities

There is a number of other activities that need to be considered when calculating the NPI emissions of substances for the site.

3.2.1 Fuel and Organic Liquid Storage

Storage for fuel and organic substances can occur at lead processing sites. They are used to hold substances such as LPG, diesel, petrol and oil for combustion purposes. Kerosene-type organics may also be stored for solvent extraction operations, as well as small quantities of organics used in the concentration process and for other operations.

Please refer to the *EET Manual for Fuel and Organic Liquid Storage* for further information.

3.2.2 Fossil Fuel Electric Generation

Fossil fuel electric power generation plants are delineated into steam plants, gas turbines, co-generation and internal combustion engines. In relation to the lead processing industry it is likely that the only fossil fuel electric power generation system used would be the internal combustion engines.

Internal combustion engines using petrol, natural gas, distillate and LPG coupled to generators are commonly used to provide electricity to remote sites and stand-by (emergency) facilities.

Please refer to the *EET Manual for Fossil Fuel Electric Power Generation* for further information.

3.2.3 Combustion Engines

As mentioned previously, a frequent application of large stationary diesel engines is electricity generation in remote areas and as a stand-by service. Mines and processing facilities that have these engines need to consider their emissions during NPI calculations.

Please refer to the *EET Manual for Combustion Engines* for further information.

3.3 Maintenance Activities

Maintenance activities may require degreasing of metal components that lead to emissions to air and water. Components of all wash-down water streams need to be considered when calculating emissions to water and land, as this effluent may contain metals, sulfuric acid and descaling chemicals. Each lead processing site is required to investigate all the chemicals used as part of maintenance activities to ensure that NPI reporting requirements are met.

4.0 Possible 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 Section 4.1 and the *NPI Guide*.

It is the responsibility of lead concentrating, smelting and refining facilities to determine which NPI substances are triggered for reporting. Table 4.1 indicates those NPI substances likely to be of relevance where the threshold may be triggered by the lead 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 lead concentrating, smelting and refining facilities. A thorough inventory for each facility will provide a more accurate and concise list.

The corresponding suggested methodology is only a guide, each facility will need to examine their current monitoring systems to identify which method is the most appropriate.

Table 4.1 - NPI-Listed Substances Likely to Trigger Reporting, and Proposed Methods for Determining Threshold Exceedance

SUBSTANCE	TRIGGER	CATEGORY	METHOD
Ammonia (total)	Usage	1	INV
Antimony & compounds	Usage (Ore content)	1	DM, GF
Arsenic & compounds*	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Beryllium & compounds	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Boron & compounds	Usage (Ore content)	1	DM, GF
Cadmium & compounds*	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Carbon disulfide	Usage (Coincidental production)	1	DM, EC
Carbon monoxide*	Usage (Coincidental production)	1	DM, EC
	Fuel use	2a	DM, INV
Chromium (III) compounds	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Chromium (VI) compounds*	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Cobalt & compounds*	Usage (Ore content)	1	DM, GF
Copper & compounds	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Cyanide (inorganic) compounds*	Usage	1	INV

Table 4.1 - NPI-Listed Substances Likely to Trigger Reporting, and Proposed Methods for Determining Threshold Exceedance cont'

SUBSTANCE	TRIGGER	CATEGORY	METHOD
Fluoride compounds*	Usage (Ore content)	1	DM, GF
	or fuel use	2a	INV
Hydrochloric acid	Usage (Usage & coincidental production)	1	INV, EC, DM
	or fuel use	2a	INV
Hydrogen sulfide	Usage (Production on-site)	1	DM, EC
Lead & compounds*	Usage (Ore content & anodes)	1	INV, DM, GF
	or power usage	2b	C
Magnesium oxide fume	Power usage	2b	C
Manganese & compounds	Usage (Ore content & catalyst)	1	DM, GF
Mercury & compounds*	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Nickel & compounds	Usage (Ore content)	1	DM, GF
	or power usage	2b	C
Nickel carbonyl	Usage (Coincidental production)	1	EC, DM
	or power usage	2b	C
Nickel subsulfide (matte)	Usage (Coincidental production)	1	EC, DM
	or power usage	2b	C
Oxides of nitrogen*	Fuel use	2a	DM, EC
Particulate matter ≤10μm*	Fuel use	2a	DM, EF
Polychlorinated dioxins & furans	Power usage	2b	C
Polycyclic aromatic hydrocarbons	Fuel Use	2b	DM, INV
Selenium & compounds	Usage (ore content)	1	DM, GF
Sulfur dioxide*	Fuel use	1	DM, EC
	or power usage	2b	DM, EC
Sulfuric acid*	Usage (coincidental production)	1	INV, EC
Total nitrogen*	Discharge to surface waters	3	DM, EF
Total phosphorus*	Discharge to surface waters	3	DM, EF
Total Volatile Organic Compounds	Use or design bulk storage	1a	C, INV
	or fuel use	2a	C, INV
Zinc & compounds	Usage (ore content)	1	DM, GF

* Substances included in Table 1 of the *NPI Guide.*

** A number of methods may be used to determine threshold exceedance for NPI substances. The method used will be related to the substance category and available information. Suggested methods that may be used to calculate the emissions can be found in Tables 5.1 and 5.2.

DM: Direct Measurement → Direct measurement of NPI reportable emissions in the stream (total N and P) or characterisation of the ore body;

INV: Inventory → Inventory or material usage (chemicals, fuel), with NPI content of materials identified;

GF: Generic Factor → Generic factor applies to default concentrations to be used in the absence of facility-specific data;

EF: Emission Factor → Emission factor to determine content in discharge stream (eg. 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; and

EC: Engineering Calculation → Engineering calculations may be used for a number of substances such as sulfur dioxide.

NPI worksheets are available to assist facilities in determining substances that exceed reporting triggers. These worksheets are included in Appendix B of the *NPI Guide*.

It is important to 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.

4.1 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*.

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

Within the lead industry, trace metals within concentrate (or ore for concentrating facilities) may trigger reporting thresholds, as may the coincidental production carbon disulfide from the decay of xanthates and the NPI substance content of process chemicals used at facilities.

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

Direct measurement, by representative sampling, is the most accurate means of characterising ore/concentrate and hence determining "usage" of trace metals, as the metal content of ore/concentrate 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 the *EET Manual for Mining*.

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 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.

Table 4.2 below presents the concentrations within the ore that will trigger the reporting threshold for Category 1 NPI substances.

Table 4.2 - NPI Triggers as Related to Metal Concentration in Ore

Metal conc. in ore (ppm)	Amount of ore treated (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

Total volatile organic compounds (VOCs) are considered under Category 1a. For more information on the emission estimation of VOCs, please refer to the *EET Manual for Fuel and Organic Liquid Storage.*

You should refer to the *EET Manuals for Combustion Engines* and *Combustion in Boilers* when estimating emissions of substances that are products of combustion (ie. Category 2a and 2b substances).

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.

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

4.2 Reporting Requirements

Each facility is required to complete Worksheet 3 - Section B of the *NPI Guide* for each substance triggered. This form requires the facility to specify the quantity of the substance emitted (in kilograms per year) and distinguish the quantity emitted to air, water and land. The worksheet also requires that the emission estimation technique be recorded.

Facilities have the option of differentiating between point source emissions and fugitive emissions, as well as including a predicted release quantity for the next reporting year.

For a more detailed discussion on reporting thresholds and requirements facilities should refer to the *NPI Guide*.

5.0 Emission Estimation

5.1 Emission Estimation Techniques

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

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility.

The four types described in the *NPI Guide* are:

- Sampling or direct measurement;
- Mass balance;
- Fuel analysis or other engineering calculations; and
- Emission factors.

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

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

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.

Those techniques available for estimating emissions of NPI substances from lead concentrating, smelting and refining activities are detailed in Table 5.1, while techniques available for estimating emissions from ancillary activities and associated facilities at lead concentrating, smelting and refining sites are detailed in Table 5.2.

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 on a number of factors, such as:

- Cost of estimation techniques;
- Ease of measurement or monitoring;
- Level or accuracy desired;
- Nature of the substance; and
- Existing monitoring and data availability.

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 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 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.

It should be appreciated that while the NPI requires reporting of metals and compounds, such as copper 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 about two and a half times greater than the actual emissions figure.

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.

For example, the NPI requires that inorganic cyanide compounds only be reported. The form in which cyanide is emitted should be factored into emission estimations 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.

For example, when considering metals such as cadmium and compounds, the total loading of cadmium to the environment must be reported, not just the bioavailable 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 necessarily of the same magnitude. For example, most trace metals in the processed ore are likely to be disposed of to the TSFs. However, only emissions from 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 are available. However, in the absence of monitoring data, a lower level of accuracy can be expected.

Appendix A details sources of data that may already be available to facilities. These 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 lead concentrating, smelting and refining industry also requires a range of raw material inputs that may be produced on-site at some facilities. Likewise some facilities may produce additional products through their emissions treatment processes, dependent on the geochemistry of the ore. These are referred to in this manual as “Ancillary Activities” and may include:

- Zinc production;
- Copper production;
- Sulfuric acid production;
- Cadmium production;
- Selenium production; and
- Mercury production.

Where EET manuals have been produced to assist 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. For example, when sulfuric acid is used in the production of fertilisers the appropriate EET manual should be referred to in order to identify all emissions. Where manuals are not available, the use and emission of substances should be accounted for as part of the facility’s estimation methods detailed in this manual.

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

Tables 5.1 and 5.2 detail the NPI substance, the stage in the process where it is used and emitted, and indicates appropriate emission estimation techniques. While emission factors (EF) are identified as potential EETs for substances, emission factors may be currently not available for all substances. It is anticipated that emission factors will be developed for these substances in the future.

The emission estimation techniques listed in Tables 5.1 and 5.2 are to be regarded as a guide only, and each facility will need to investigate what sources of data they currently have (refer to Appendix A of this document for potential data sources) and how they can be applied. Similarly, the emission pathway (ie. to air, water, or land) listed for each substance is the commonly expected pathway. However, it is possible that some facilities may release some substances via an alternate pathway, which must be included when reporting emissions. Thus each facility needs to refer to their individual flowsheets to identify what their emissions are and how they are released.

Tables 5.1 and 5.2 have divided the facility into plant sections to aid in identifying where possible emissions may occur. However, when a facility reports their emissions the amount will be reported for the facility as a whole, for example a lead smelter will report only one value for SO_2, which is the summation of all the individual and fugitive SO_2 emissions across the entire facility.

Table 5.1 - Techniques Available for Estimating Emissions of NPI Substances from Lead Concentrating, Smelting and Refining Activities

Substances	Concentrating			Smelting			Emissions From	
	Grinding	Flotation	Thickening & Filtering	Sintering	ISF Blast Furnace	Refinery	Slag landfill	TSFs
Ammonia					A MB			W,L MB
Antimony	A MB			A MB	A MB	A MB	A MB	W,L MB
Arsenic	A MB			A DM	A DM	A DM	A MB	W,L DM
Beryllium & compounds	A MB			A DM	A DM	A DM	A MB	W,L MB
Boron & compounds	A MB			A DM	A DM	A DM	A MB	W,L MB
Cadmium & compounds	A MB			A DM	A DM	A DM	A MB	W,L DM
Carbon disulfide		A EC						W,L MB
Carbon monoxide				A DM	A DM	A DM		
Chromium (III) & compounds	A MB			A MB	A MB	A MB	A MB	W,L MB
Chromium (VI) & compounds	A MB			A MB	A MB	A MB	A MB	W,L MB
Cobalt & compounds	A MB			A MB	A MB	A MB	A MB	W,L MB

Table 5.1 - Techniques Available for Estimating Emissions of NPI Substances from Lead Concentrating, Smelting and Refining Activities cont'

Substances	Concentrating			Smelting			Emissions From	
	Grinding	Flotation	Thickening & Filtering	Sintering	ISF Blast Furnace	Refinery	Slag landfill	TSFs
Copper & compounds	A MB			A MB	A MB	A MB	A MB	W,L MB
Cyanide	A MB			A MB	A MB	A MB	A MB	W,L MB
Fluoride compounds								W,L MB
Hydrochloric acid		W EC		A DM	A DM	A DM		W,L MB
Hydrogen sulfide				A DM				
Lead & compounds	A MB			A DM	A DM	A DM	A MB	W,L DM
Manganese Oxide Fume				A DM	A DM	A DM	A DM	
Manganese & compounds	A MB			A MB	A MB	A MB	A MB	W,L MB
Mercury & compounds	A MB			A DM	A DM	A DM	A MB	W,L DM
Nickel & compounds	A MB			A DM	A DM	A DM	A DM	W,L DM
Nickel carbonyl								
Nickel Subsulfide	A MB			A MB	A MB	A MB	A MB	W,L MB

Table 5.1 - Techniques Available for Estimating Emissions of NPI Substances from Lead Concentrating, Smelting and Refining Activities cont'

Substances	Concentrating			Smelting			Emissions From	
	Grinding	Flotation	Thickening & Filtering	Sintering	ISF Blast Furnace	Refinery	Slag landfill	TSFs
Organo-tin compounds								W,L MB
Oxides of Nitrogen				A EC	A EC	A EC		
Particulate matter ≤10µm	A EF	A EF		A EF	A EF	A EF		
Polychlorinated dioxins & furans				A DM	A DM	A DM		A DM
Selenium & compounds	A MB			A DM	A DM	A DM	A MB	W,L DM
Sulfur dioxide				A DM	A DM			
Sulfuric acid								W DM
Total Nitrogen								W EC
Total Phosphorus								W,L EC
Zinc & compounds	A MB			A DM	A DM	A DM	A MB	W,L DM

Notes :

DM	Direct Measurement	A	Emission to Air
MB	Mass Balance	W	Emission to Water
EC	Engineering Calculations	L	Emission to Land
EF	Emission Factor		

Table 5.2 - Techniques Available for Estimating Emissions of NPI Substances from Ancillary Activities and Associated Activities Related to Lead Processing

Substance	Acid Plant	Cadmium Plant	Selenium Plant	Mercury Plant	Fossil Fuel Electric Generation	Fuel & Organic Liquid Storage	Combustion Engines	Waste Water Treatment Plant
Ammonia	A DM							
Antimony		A MB	A MB		A MB		A MB	W DM, MB
Arsenic		A MB	A MB		A MB		A MB	W DM, MB
Beryllium & compounds	A MB	W DM	A MB		A MB			
Boron & compounds	A MB	W DM	A MB		A MB			
Cadmium & compounds	A MB	W DM	A MB					W DM, MB
Carbon monoxide					A MB		A MB	
Chromium (III) & compounds					A MB		A MB	W DM, MB
Chromium (VI) & compounds					A MB		A MB	W DM, MB
Cobalt & compounds	A MB	W DM	A MB		A MB			W DM, MB
Copper & compounds		A MB	A MB		A MB			W DM, MB

Table 5.2 - Techniques Available for Estimating Emissions of NPI Substances from Ancillary Activities and Associated Activities Related to Lead Processing cont'

Substance	Acid Plant	Cadmium Plant	Selenium Plant	Mercury Plant	Fossil Fuel Electric Generation	Fuel & Organic Liquid Storage	Combustion Engines	Waste Water Treatment Plant
Cyanide								
Fluoride								W DM, MB
Hydrogen Sulfide				A EF				
Lead & compounds			A,W MB DM		A MB		A MB	W DM, MB
Manganese & compounds			A MB		A MB		A MB	W DM, MB
Mercury & compounds	A MB		A/W MB DM	W,L EF DM	A MB		A MB	W DM, MB
Nickel & Compounds								W DM, MB
Nickel carbonyl								
Nickel subsulfide								
Organo-tin compounds								
Oxides of nitrogen					A MB		A MB	
Particulate matter ≤10µm			A MB		A MB		A MB	

Table 5.2 - Techniques Available for Estimating Emissions of NPI Substances from Ancillary Activities and Associated Activities Related to Lead Processing cont'

Substance	Acid Plant	Cadmium Plant	Selenium Plant	Mercury Plant	Fossil Fuel Electric Generation	Fuel & Organic Liquid Storage	Combustion Engines	Waste Water Treatment Plant
Polycyclic aromatic hydrocarbons					A DM	A DM	A DM	
Selenium & compounds			A,W DM		A MB		A MB	W DM, MB
Sulfur dioxide	A DM				A MB		A MB	
Sulfuric acid	A,W MB	A,W MB	A,W MB	A,W MB				
Total nitrogen								
Total phosphorus								W DM, EF
Total VOCs					A EF	A EF	A EF	W DM, EF
Zinc & compounds		A,W MB DM	A,W MB DM		A MB		A MB	W DM, MB

Notes:				
	DM	Direct Measurement	A	Emission to Air
	MB	Mass Balance	W	Emission to Water
	EC	Engineering Calculations	L	Emission to Land
	EF	Emission Factor		

5.1.1 Direct Measurement

While not a requirement of the NPI, 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:

- More accurately estimate their emissions of particular NPI substances;
- Develop site-specific emission factors;
- Verify estimates from alternative EETs; or
- Provide supporting data for other EETs.

Source measurement 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 measurement program should be decided in order to avoid unnecessary ongoing monitoring.

Facilities may have existing source monitoring commitments and data that 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 source 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 mass of the final emission stream.

Equation 5.1

$$E_i = C_i * V * [273 / (273 + T)]$$

where:

E_i	=	hourly emissions of pollutant i	(kg/hr)
C_i	=	concentration of pollutant i	(kg/m^3)
V	=	stack gas volumetric flow rate	(m^3/hr)
T	=	gas temperature	(°C)
273	=	273 K (0°C)	

Where direct measurement is undertaken, it is essential that sampling and source 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 relevant standards.

5.1.2 Engineering Calculations

Engineering calculations may be used to estimate emissions from processes subject to rigid controls, such as where a substance is formed coincidentally, such as carbon disulfide, where the substance breaks down very quickly in the atmosphere, or where its fate is well understood from process chemistry and operations.

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 may 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 (such as vapour pressure) of the substance and mathematical relationships (such as ideal gas law).

Modelling, an advanced form of an engineering calculation, may be utilised to determine the fate of substances emitted to the environment, including emissions to air and groundwater.

For cyanide and dissolved metal 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 significant influences may be included within the model itself.

5.1.3 Mass Balance

Mass balances provide 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 calculations address 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.

Chemical Usage

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

Process and domestic type 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 to be emitted to the environment or 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-type activities; and
- Washdown areas.

Effluent Streams

If a facility uses a listed mineral acid or base, with this acid or base being effectively neutralised in use or during wastewater treatment (to a pH of 6 to 8, as required by most State and Territory effluent standards), even though a threshold is triggered a “zero” emission may be reported. If the acid or base is itself transformed into another listed substance, however, the quantity of this substance coincidentally produced must be determined to assess if a threshold value has been reached. For example, sulfuric acid, which is itself a listed substance, often yields hydrogen sulfide in effluent streams, and requires reporting where co-incidental production exceeds 10 tonnes.

Wastewater treatment may precipitate the reportable chemical in a sludge. Facilities are often required to obtain data on the concentration of metals or other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge multiplied by the concentrations of the substance in the sludge. Although listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with determining other process losses or may require reporting if the sludge is disposed of on-site.

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

5.1.4 Emission Factors

Background

An emission factor (EF) is a tool that is used to estimate emissions to the environment, and may be either formulae or value that are derived from similar operations. They 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, such as in furnaces and for fuel usage, generally.

In this manual, an EF relates to the quantity of substances emitted from a source to some common activity associated with those emissions. Emission factors are obtained from United States (US), European and Australian sources. They are usually expressed as the weight of the substance emitted multiplied by the unit weight, volume, distance or duration of the activity emitting the substance, such as the mass of PM_{10} and TSP produced per tonne of ore handled.

Emission factors are used to estimate a facility's emissions by the following equation:

Equation 5.2

$$E_i = A * EF_i * [1 - CE_i/100]$$

where:

E_i = hourly emissions of pollutant i (kg/hr)
A = activity rate (t/hr)
EF_i = uncontrolled emission factor for 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 substance 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.

5.2 Acceptable Reliability and Uncertainty

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

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

5.2.1 Direct Measurement

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

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

5.2.2 Mass Balance

Calculating emissions using a mass balance appears to be a straightforward approach to emission estimation. However, it is likely that few Australian lead facilities consistently track material usage and waste generation with the overall accuracy needed for application of this method. Inaccuracies associated with individual material tracking, or other activities inherent in each material handling stage, can result in large deviations for total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only ± 5 percent in any one step of the operation can significantly skew emission estimations.

5.2.3 Engineering Calculations

Theoretical and complex equations, or models, can be used for estimating emissions. Though the accuracy of such models are debatable.

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

5.2.4 Emission Factors

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 (US EPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in the reference section of this document. The emission factor ratings will not form part of the public NPI database.

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

The EFR system is as follows:

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

Estimating your 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 have a rating of "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.

5.3 NPI Reporting Steps

Step 1

Identify all substances and materials used and/or produced through production processes on your site each year.

Step 2

Determine what substances identified in Step 1 are also listed on Appendix A *NPI Guide* Table 1: NPI Substances. Substances that are likely to be used at lead processing and associated facilities are listed in Table 4.1.

The substances that match are required to be reported to the NPI, if the threshold for reporting is met.

Step 3

Determine quantities used on-site for those substances identified in Step 2, as well as the amount of energy and fuel consumed

Step 4

Compare the quantities used for the substances against the thresholds.

If your facility triggers a threshold for a substance or substances, you are required to report emissions of that substance to the NPI.

Step 5

Calculate the emissions for each substance from both fugitive and point sources. Refer to Tables 5.1 and 5.2, which present recommended techniques available for estimating emissions from various sources.

Refer to Sections 6.0, 7.0 and 8.0 of this manual, which provide examples of the various ways to calculate emissions to air, water and land.

6.0 Emissions To Air

6.1 Background

Significant emissions to air within the lead 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; and
- The operation of TSFs.

Emissions to air are estimated from their point of creation rather than at the facility boundary. Emissions estimation does not take into account the fate of emitted substances, such as the speed of their subsequent decay within the atmosphere.

Air emissions may be categorised as:

- Fugitive emissions; and
- Point source emissions

Fugitive Emissions

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

Emission factor EETs are the usual method for determining losses through fugitive emissions, however in the absence of suitable emission factors alternate EET's will need to be applied. These may include engineering calculations, such as modelling PM_{10} from stockpiles, or a facility developed EET. As discussed previously in Section 5.0, you may estimate your emissions by using the EETs presented in this manual and your data will be included in the NPI database as being of "acceptable reliability". Or if your relevant environmental authority has approved the use of emission estimation techniques that are *not* outlined in this manual your data will also be displayed as being of "acceptable reliability".

Point Source Emissions

These emissions are exhausted into a vent (excluding roof vents) or stack and emitted through a single point source into the atmosphere. An air emissions control device such as a carbon adsorption unit, scrubber, fabric filter, or afterburner may "treat" stack emissions prior to their release, reducing their total loading to the atmosphere.

6.2 Smelter Emissions

Emissions from primary lead smelters are principally particulate matter and oxides of sulfur. Emissions are generated primarily from the smelting furnaces. Fugitive emissions are generated during material handling operations. Zinc and lead oxides or sulfides are the significant constituents of the particulate matter, but other metals such as arsenic, antimony, cadmium, and mercury may also be present, along with metallic sulfates.

Significant emissions of SO_2 occur from various processes associated with primary lead smelting. Recovery of this SO_2 for production of sulfuric acid is good environmental practice, and may be economically beneficial. Fuel combustion products also contribute to emissions from smelting furnaces.

The remaining smelter operations process material containing very little sulfur, resulting in insignificant SO_2 emissions.

6.2.1 Direct Measurement

Direct measurement (or source measurement) is one of the more accurate methods of estimating air emissions from smelters. Source measurement programs for air emissions such as SO_2 or airborne metal particulates are often part of the licensing requirements for the smelter complex. A discussion on the application of this technique to SO_2 emissions can be found in Section 9.1.

6.2.2 Mass Balance

Emissions (such as sulfur dioxide and metals) from smelter and refining operations may be estimated through the use of a mass balance. However, some direct sampling may be desirable to improve components of the mass balance eg. sulfur/metal 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 slag 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 (though with varying accuracy). Figure 6.1 shows a typical “box” approach to mass balances.

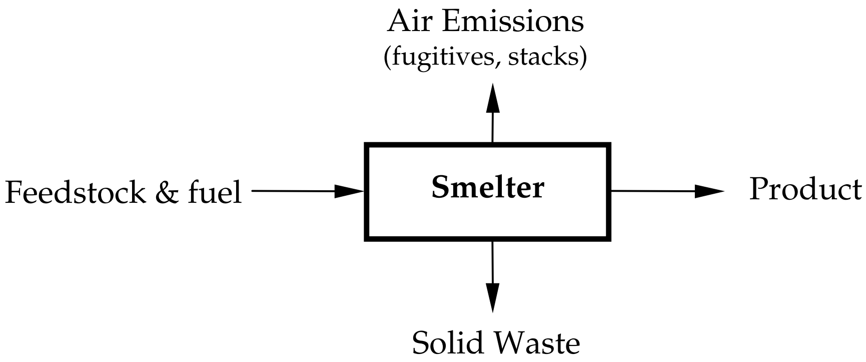


Figure 6.1 - Emissions Estimation for Smelter Operations

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

Sulfur dioxide (SO_2) emissions from 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, as displayed through the addition of more variables in Figure 6.2.

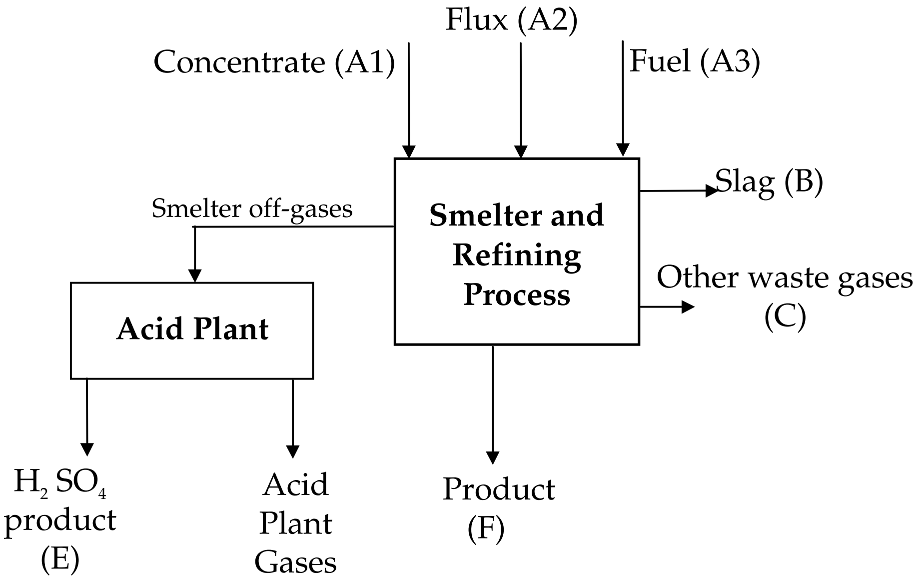


Figure 6.2 - Refined Mass Balance Model

Where:	Inputs	=	Estimated outputs	+	Assumed outputs
For example:	A1 + A2 + A3	=	(B + C + D) + (E + F)	+	Fugitives

6.3 Dust and PM_{10}

6.3.1 Direct Measurement

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 of fugitive emissions 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.

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

6.3.2 Emission Factors

Processing Areas

The *EET Manual for Mining* provides emission factors for PM_{10} and TSP sources within the processing area. It should be noted that TSP is *not* a reporting requirement under the NPI, but may be used to estimate metal content of emitted dust.

Metal emissions can be estimated as a fraction of the TSP emissions, based on available assay data. Where assay data and facility-specific information are not available for metals in dust emissions, the concentrations in Table B2 of the *EET Manual for Mining* should be used as a default to estimate metal emissions.

Tailing Storage Facilities (TSFs)

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).

Retaining a wet surface on TSFs will prevent dust generation (BPEMIM, Tailings Containment, 1995), while TSFs with a low salt content (and 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 information 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.

Smelting Facility

Particulate emission factors were extracted from the US EPA AP-42 document (1999).

Controlled and uncontrolled particulate emission factors for points within a lead smelting facility are presented in Table 6.1 and Table 6.2.

These emission factors should be applied carefully. Emission factors for sintering operations are derived from data from a single facility no longer operating. Others are estimated based on similar operations in the steel, lead, and copper industries (US EPA, 1999).

Table 6.1 - Emission Factors for Lead Processing Air Emissions

Process	PM_{10}[a]	Lead	SO_2	Emission Factor Rating
Ore crushing[b]	0.018	0.001	NA	E
Ore screening[c]	0.005	0.001	NA	E
Tetrahedrite drier[d] Controlled - baghouse	0.013	0.0003	NA	E
Sinter Machine (weak gas)[e] Controlled - baghouse	0.052	0.009	275	E
Sinter building fugitives[f] Uncontrolled	0.058	0.016	NA	E
Sinter Storage[g]	NA	NA	NA	E
Blast furnace[h], dross kettles, reverberatory furnace Controlled - baghouse	0.43	0.034	23	E
Speiss pit[k]	NA	NA	NA	E

[a] Filterable and condensable particulate ≤10µm mean diameter
[b] Entire ore crushing building at one facility, including transfer points: kg/t of ore, except lead which is kg/t of lead in ore.
[c] Tests at one facility: kg/tonne of ore
[d] kg/t dried: tested at one facility.
[e] kg/t sinter produced, tests at one facility. The sinter machine is controlled by ESPs and scrubbers.
[f] From 1971 tests on two facilities.
[g] kg/t throughput; including charge car loading, from tests at one facility.
[h] kg/t of bullion, includes dross kettles from tests at one facility.
[k] kg/t granulated from tests at one facility.

(US EPA, AP-42 Table 12.6-1, 1999)

Table 6.2 - Volume Source Emission Factors from 1990 Tests

Volume Source	Lead (kg/t) [A]	PM_{10} (kg/t)[B]
Crushing Mill	0.0006	0.0042
Blast Furnace Charge Building	0.00024	0.0028
Blast Furnace Feed Floor	0.00020	0.0001
Blast Furnace Tapping Platform	0.0027	0.0028

[A] Units are kg Pb/t of ore

[B] Units are kg PM_{10}/t of ore

(*US EPA Background Report AP-42. Section 12.6 Primary Lead, Smelting and Refining)*

Secondary Lead Processing Facilities

Table 6.3 and Table 6.4 contain emission factors for secondary lead processing facilities from the US EPA AP-42 Chapter 12.11.

Table 6.3 - Emission Factors for Secondary Lead Processing [a]

Process	Particulate[b]				Lead[b]				SO_2	
	Uncontrolled	Emission Factor Rating	Controlled	Emission Factor Rating	Uncontrolled	Emission Factor Rating	Controlled	Emission Factor Rating	Uncontrolled	Emission Factor Rating
Sweating[c] (kg/t charge)	16-35	E	ND	NA	4-8[d]	E	ND	NA	ND	ND
Reverberatory smelting	162	C	0.50	C	32[e]	D	ND	NA	40	C
Blast smelting-cupola[f]	153	C	1.12	C	52[g]	D	0.15[h]	C	27	C
Kettle refining	0.02[j]	C	ND	NA	0.006[j]	D	ND	NA	ND	NA
Kettle Oxidation	≤ 20[k]	E	ND	NA	ND	NA	ND	NA	ND	NA
Casting	0.02[j]	C	ND	NA	0.007[j]	C	ND	NA	ND	NA

[a] Emission Factor units expressed as kg of pollutant/t metal produced. ND = no data; NA = not applicable

[b] Particulate and lead emission factors are based on quantity of lead product produced, except as noted.

[c] Estimated from sweating furnace emissions from non-lead secondary non-ferrous processing industries.

[d] Based on assumption that uncontrolled reverberatory furnace flue emissions are 23% lead.

[e] Uncontrolled reverberatory furnace flue emissions are 23% lead. Blast furnace emissions have lead content of 34% based on single uncontrolled plant test.

[f] Blast furnace emissions are combined flue gases and associated ventilation hood streams (charging and tapping).

[g] Blast furnace emissions have lead content of 26%, based on single controlled plant test.

[h] Based on quantity of material charged to furnaces.

[j] Lead content of kettle refining emissions is 40% and of casting emissions is 36%.

[k] Essentially all product lead oxide is entrained in an air stream and subsequently recovered by baghouse with average collection efficiency >99%. Factor represents emissions of lead oxide that escape a baghouse used to collect the lead oxide product. Represents approximate upper limit for emissions.

(US EPA, AP-42 Table 12.11-1, 1999)

Table 6.4 - Fugitive Emission Factors for Secondary Lead Processing[a]
(Emission Factor Rating: E)

Operation	Particulate	Lead
Sweating	0.8-1.8[b]	0.2-0.9[c]
Smelting	4.3-12.1	0.1-0.3
Kettle refining	0.001	0.0003
Casting	0.001	0.0004

[a] Based on amount of lead produced except for sweating which is based on quantity of material charged to furnace. Fugitive emissions estimated to be 5% of uncontrolled stack emissions.
[b] Sweating furnace emissions estimated from non-lead secondary nonferrous processing industries.
[c] Assumes 23% lead content of uncontrolled blast furnace flue emissions.
(US EPA, AP-42 Table 12.11-3, 1999)

6.4 Metals in Dust

6.4.1 Direct Measurement

PM_{10} and TSP emissions may contain a metal fraction. This metal fraction may be estimated from available ore assays, however the proportion of PM_{10} and TSP samples by direct analysis will allow more accurate estimation of the facility's emissions of these metals. Periodic analysis of dust samples will allow the proportion of dust to be determined with a further level of accuracy.

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.

6.4.2 Emission Factors

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

These emissions may be estimated using an emission factor approach from:

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

The metal 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). However, greater accuracy may be obtained by direct analysis of PM_{10} and TSP filter samples in order to determine the speciation of the dust.

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

6.5 Emissions From Ancillary Activities and Associated Facilities

Associated facilities at zinc smelters and refineries can also produce NPI reportable emissions. Please refer to the EET Manuals mentioned below for further guidance on estimating emissions from these ancillary activities.

6.5.1 Emission Estimation for Fuel

Fuel analysis is an example of an engineering calculation and can be used to predict SO_2, metals, and other emissions based on the application of conservation laws, if fuel rate is measured. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes elements such as sulfur that may be converted into other compounds during the combustion process.

SO_2 emissions from combustion can be calculated based on the concentration of sulfur in fuel. Equation 6.1 can be used in fuel analysis emission calculations.

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.

Equation 6.1

$$E_{kpy,SO2} = Q_f * C_i/100 * \frac{MW_{SO_2}}{EW_S} * OpHrs$$

where:

$E_{kpy,SO2}$	=	amount of SO_2 emitted	(kg/yr)
Q_f	=	fuel use	(kg/hr)
C_i	=	pollutant concentration of fuel	weight percent %
MW_{SO_2}	=	molecular weight of SO_2 (= 64)	(kg/kg-mole)
EW_S	=	elemental weight of S (= 32)	(kg/kg-mole)
OpHrs	=	operating hours	(hr/yr)

Example 6.1 illustrates the use of Equation 6.1.

Example 6.1 - Using Fuel Analysis Data

$E_{kpy,SO2}$ may be calculated using Equation 6.1 and given the following:

Q_f = 20 900 kg/hr
Weight percent sulfur in fuel = 1.17%
Operating hours = 1500 hr/yr

$$E_{kpy,SO2} = Q_f * C_i/100 * \frac{MW_{SO_2}}{EW_S} * OpHrs$$

$$= 20\,900 * \frac{1.17}{100} * \left(\frac{64}{32}\right) * 1500$$

$$= 733\,590 \text{ kg/yr}$$

Therefore, under these operating conditions the amount of SO_2 emitted to the air is 733 590 kg per year.

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

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

6.5.2 Air Emissions from Fuel and Organic Liquid Storage

Estimation of emissions from storage vessels containing fuel and organic liquids is required by the NPI. Please refer to the *EET Manual for Fuel and Organic Liquid Storage* for further information.

6.5.3 Air Emissions from Fossil Fuel Electric Power Generation

The *EET Manual for Fossil Fuel Electric Power Generation* describes the procedures and recommended approaches for estimating emissions from facilities engaged in fossil fuel electric power generation. The manual considers combustion and non-combustion sources of emissions to air, water and land.

A fossil fuel electricity generation plant is delineated into five (5) categories - the only category applicable to the lead processing sites is the internal combustion engine, commonly used for small remote sites or stand-by (emergency) generation. Therefore, emission estimations will relate to internal combustion (stationary) engines.

6.5.4 Emissions from Internal Combustion (Stationary) Engines

The *EET Manual for Combustion Engines* contains emission factors and emission estimation techniques that can be used as guidance on estimating emissions from internal combustion engines.

6.5.5 Maintenance Activities - Emission Factors for Solvent Degreasing

Solvent degreasing within the lead processing industry is related to maintenance activities. Table 6.5 contains emission factors for solvent emissions.

Table 6.5 - Emission Factors for Solvent Emissions

Solvent Used	Use	Emission Factor[1] (kg/kg solvent used)	Emission Factor Rating
Dichloromethane			
Uncontrolled	Vapour Degreasing	0.930	E
Controlled	Cold Cleaners	0.890	E
Tetrachloroethylene			
Uncontrolled	Vapour Degreasing	0.890	E
Controlled	Cold Cleaners	0.850	E
Trichloroethylene			
Uncontrolled	Vapour Degreasing	0.910	E
Controlled	Cold Cleaners	0.870	E

[1] *Emission Estimation Technique Manual for Ferrous Foundries* (National Pollutant Inventory, 1998).

7.0 Emissions to Water

7.1 Background

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. A discharge to groundwater is included as an emission to land.

Significant emissions to water within the lead concentrating, smelting and refining industry, including the ancillary activities and associated facilities, will be related to:

- Run-off and erosion from the concentrating and processing areas (refer to the *EET Manual for Mining*);
- The discharge of treated process waters (such as treated TSF decant water and from an effluent treatment plant);
- The discharge of sewage and domestic wastewaters; and
- Spills to surface waters.

The most accurate techniques 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.

7.1.1 Run-off and Erosion

Run-off and sediment eroded from a site may contain metals. The efficiency of the existing stormwater management program will determine the amount of sediment in run-off. Actual emissions will be highly dependent on the weather conditions over the reporting period and a function of the size of the catchment. At some facilities, run-off is collected, treated and reused in the processing plant, thus it is now classified as a *transfer* rather than an *emission*.

Direct Measurement

Site-specific information on water quality and flow rates can be used to characterise emissions. Water quality is likely to be routinely monitored and flow rates from specific catchments may be known from monitoring or from estimations based on calibrated models or engineering calculations eg. Australian Rainfall and Run-off.

Mass Balance

Emissions of metals to water may be estimated through the use of a mass balance. This technique requires the quantification of total materials into and out of the process with the difference being accounted for in terms of releases to air, water and land or as transfers.

7.1.2 Discharge of Treated Process Waters

The majority of smelters have effluent treatment plants (ETP) to treat process water and sometimes, when necessary, stormwater run-off. The treatment involves the manipulation of pH levels by the addition of chemicals such as sodium hydroxide to enable the precipitation of heavy metals in the solution in the form of metal hydroxides. The precipitated metals are then recycled to the smelting process or can be sold. The resulting effluent is then discharged off-site, generally in accordance with licence requirements.

Direct Measurement

If monitoring of metal levels and the flow rate is required as part of the licence conditions for discharge, then the metals emitted from the site are known.

Mass Balance

This technique can be used in conjunction with direct monitoring to estimate emissions to water.

7.1.3 Discharge of Sewage and Domestic Wastewaters

Direct Measurement

Total nitrogen and total phosphorus loadings may be estimated by 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 is fully considered.

Emission Estimation

The example presented below is based on generic emission factors and provides indicative facility population levels likely to result in exceedence of Category 3 thresholds.

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 (Table 7.1). This data has been applied to the NPI reporting thresholds to provide an indicative facility population that will result in exceedence of the reporting thresholds.

Table 7.1 - West Australian Water Corporation Wastewater Treatment Design Criteria for Total Nitrogen and Phosphorus

	kg per person per day	Indicative Facility Population
Total nitrogen	0.011	>3500
Total phosphorus	0.0025	>3000

Assumes:
- Annual dry weather flow of 200 litres(L) per person per day
- Total nitrogen concentration of 55 mg/L (range of 40-70)
- Total phosphorus concentration of 12.5 mg/L (range of 10-15)
- 365 days per year of nitrogen and phosphorous loading

Estimation of total nitrogen and total phosphorus emissions may be made using the equation shown below:

Equation 7.1

$$M_{NorP} = \overline{M}_{NorP} * N_{pers} * N_{days} * \frac{1-E}{100}$$

where:

M_{NorP}	=	mass of total Nitrogen or Phosphorus emitted	(kg)
$\overline{M}_{NorP}$	=	average loading of Nitrogen or Phosphorus per person per day	(kg/p/d)
N_{pers}	=	average number of personnel on-site	
N_{days}	=	number of days of loading to the sewage treatment system	
E	=	efficiency of sewage treatment system	

7.1.4 Spills to Surface Water

If spills occur, it is unlikely that the amount discharged is accurately known. In this case an estimate of the volume of the substance discharged may be able to be made and previous data on the concentration of the pollutant in the discharge can then be used to derive an approximation of the amount of pollutant emitted.

8.0 Emissions to Land

8.1 Background

Emissions of substances to land on-site may result from 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 (such as fertilisers and pesticides). These emission sources can be broadly categorised as:

- Surface impoundments of liquids and slurries, such as TSFs;
- Storage of, or transfer to waste storage facility, of slag or jarosite; and
- Unintentional leaks and spills.

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

8.2 Groundwater Modelling - Fates and 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.

It is important to note that estimates of emissions to groundwater are based on annual rates of infiltration into the groundwater system, NOT the estimated discharge *off-site* via groundwater.

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

The leachability of materials may be used to estimate the rate of leaching into groundwater and thus further leachability testing may be required.

8.3 TSF Seepage

8.3.1 Direct Measurement

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

Borehole 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.

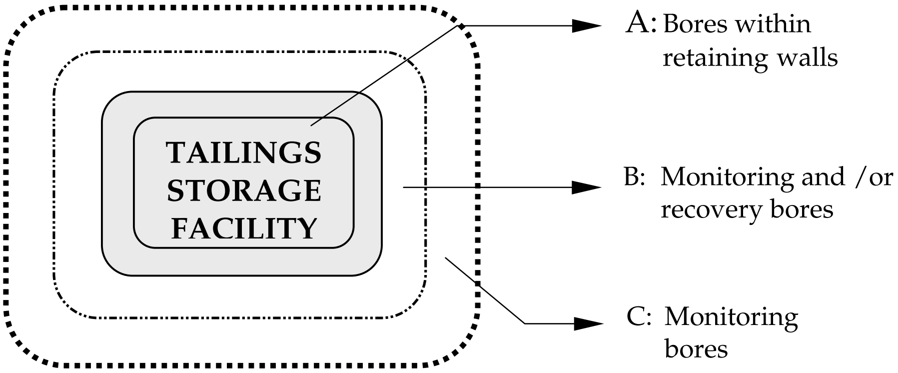


Figure 8.1 - Bore Hole Arrangement for TSFs

Figure 8.1 displays a typical arrangement for bore hole placement, it should be noted that alternative recovery systems (such as trenches) may also be used. 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 as 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".

Equation 8.1

$$Y_{TSF} = A_{infl} * K_{hyd} * \Psi_{hyd}$$

where:

Y_{TSF}	=	TSF hydraulic loading	(m^3/day)
A_{inf}	=	cross sectional area of zone of influence	(m^2)
K_{hyd}	=	hydraulic conductivity	(m/day)
Ψ_{hyd}	=	hydraulic gradient	

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

Equation 8.2

$$Y_{emit} = Y_{TSF} - V_{H20}$$

where:

Y_{emit}	=	emitted hydraulic loading	(m^3/day)
Y_{TSF}	=	TSF hydraulic loading	(m^3/day)
V_{H20}	=	volume of recovered water	(m^3/day)

The emission of NPI substances is then estimated.

Equation 8.3

$$M = C_B * Y_{emit} * T$$

where:

M	=	mass of substance emitted	(kg)
C_B	=	concentration of substance in bores 'B'	(kg/m^3)
Y_{emit}	=	emitted hydraulic loading	(m^3/day)
T	=	period	(days)

8.3.2 Modelling

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 emissions of dissolved substances such as cyanide and metals.

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

8.3.3 Mass Balance

Water Balance

Tailings Storage Facilities (TSFs) represent a significant potential emission source of some NPI substances. A comprehensive water balance, refer to Figure 8.2, 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).

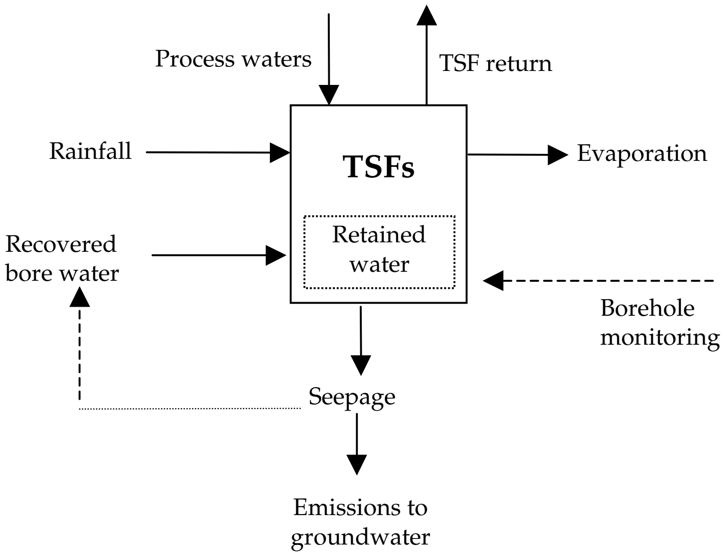


Figure 8.2 - TSF Water Balance

A comprehensive water balance, when used in conjunction with EETs, will facilitate the estimation of emissions of soluble NPI substances (such as 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.

It is noted, however, 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 M241m 1998;

> *For a TSF of 100 ha, an evaporative loss of 100 mm is equivalent to a total volume of 100 000* m^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.*

Metals in Water

Metals may be emitted:

- Through seepage from TSFs;
- 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.

While these seepage rates will be facility-specific, generic seepage rates of between **0 - 10%** of return waters have been quoted within the nickel industry (Mt Keith Nickel 1996, ANCOLD, pers. comm.) and can be applied to the lead industry.

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

- Estimates of seepage rate;
- The concentration of NPI metals in TSFs return water; and
- The retention of NPI metals by the TSF or pad liner or under liner. If this is known, assume retention is zero.

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

Equation 8.4

$$M_M = C_M * V_{slurry} * V/100$$

where:

M_M = mass of metal emitted through seepage (kg)
C_M = concentration of metal (kg/m^3)
V_{slurry} = volume of water/slurry throughput to TSF per year (m^3)
V = seepage rate (%)

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 to facilities that can estimate the surface area of the liner where its integrity has been compromised.

Equation 8.5

$$V_{seepage} = \left[K * A * S_y * \left(\frac{dh}{dl} \right) \right]$$

where:

$V_{seepage}$ = volume of calculated seepage (m^3/day)
K = vertical permeability of TSF floor material (m/day)
A = surface area of TSF cell floor (m^2)
S_y = specific yield of tailings materials (%)
dh = thickness of tailings in the cell (m)
dl = hydraulic head above floor of the cell (m)

Specific yield (S_y) 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:

Equation 8.6

$$E_M = V_{seepage} * N_{days} * C_M$$

where:

E_M = emission of the metal (kg)
$V_{seepage}$ = as above (m^3/day)
N_{days} = number of days TSF operated (days)
C_M = 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 of return waters;
- Metals concentration equal to that in TSFs return water; and
- No bore water recovery.

Metals may be retained in the TSF or pad liner or under-liner. If test data on metals retention is available, a more accurate estimate may be obtained. If no data are available, assume retention is zero.

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

Equation 8.7

$$M_{M\text{-}seepage} = M_{M\text{-}bore} - C_{M\text{-}bore} * V_{bore\text{-}water}$$

where:

$M_{M\text{-}sepage}$ = mass of metal emitted through seepage (kg)
$M_{M\text{-}bore}$ = mass of metal emitted through recovered bore water (kg)
$C_{M\text{-}bore}$ = concentration of metal in bore water (kg/m^3)
$V_{bore\text{-}water}$ = volume of recovered bore water (m^3)

9.0 Examples of Applying EETS

9.1 Sulfur Dioxide

9.1.1 Background

As there are considerable quantities of sulfur in lead sulfide ores (Section 2.1), significant sulfur dioxide (SO_2) emissions occur at various processes associated with lead smelting. Recovery of this SO_2 is good environmental practice and may be economically beneficial. Typically the hot gases are captured and piped to an acid plant for the manufacture of sulfuric acid.

The use of a sulfuric acid plant to treat lead smelter effluent gas streams requires that particulate-free gas streams with a steady SO_2 concentration of at least three percent are maintained.

The remaining smelter operations process material containing very little sulfur, resulting in insignificant SO_2 emissions.

Sulfur dioxide not released through a vent or stack is classified as a fugitive emission.

The *EET Manual for Nickel Concentrating, Smelting & Refining (Nickel EET Manual)* provides detailed examples of how the emission estimation techniques can be applied to SO_2 emissions, and the discussion below is based on this. The following techniques can be used to estimate the amount of SO_2 emitted.

9.1.2 Direct Measurement

Direct measurement (or source monitoring) is one of the most accurate methods of estimating emissions of SO_2. Usually, SO_2 emissions are measured at the stack exit points. The gas is emitted from the sinter machine and the main furnace, as well as from subsequent furnace areas. All these areas also contribute to fugitive emissions.

Most smelters have stack-monitoring programs designed to meet environmental licence conditions. These conditions generally specify an amount of SO_2 that is not to be exceeded. Ambient SO_2 is also measured to meet environment and health-related goals.

Elements of the processing of lead are also regularly monitored in order to optimise the recovery of the product eg. the efficiency of the gas collection and treatment system to ensure that the maximum amount of gas is directed to the acid plant to make sulfuric acid.

Direct measurement data can be used to calculate actual amounts emitted to the environment, by multiplying the concentration of SO_2 in the final emission stream (stack emission) by the mass of the emission stream, as in Equation 9.1.

Equation 9.1

$$M_{SO2} = C_{SO2} * V_{SO2} * \left(\frac{273}{273 + T}\right)$$

where:

E_{SO_2} = emission of sulfur dioxide (kg/hr)
C_{SO_2} = concentration of SO_2 (kg/m^3)
V_{SO_2} = stack gas volumetric flow rate (m^3/hr)
T = temperature (°C)

Direct measurement is generally undertaken according to standard sampling and monitoring procedures in compliance with the environmental conditions specified in the licence. If direct measurement is to be undertaken outside this regulatory system, then sampling and monitoring should be undertaken in accordance with Australian standards.

9.1.3 Mass Balance

This technique provides an estimate of emissions where known quantities of a substance are supplied to a process and the process fate of the substance is both known and quantifiable.

It is imperative that the mass balance calculations address all losses and fates of a substance and utilises best available data. This approach allows fugitive and other emissions to the environment to be estimated.

Sulfur dioxide emissions from smelter operations may be estimated through the use of a mass balance. However, the greater the level of accuracy applied to the process inputs and outputs, the more accurate the estimate of emission will be. In Figure 9.1 below, the diagram shows a simplified approach to SO_2 emissions from sinter/smelter operations.

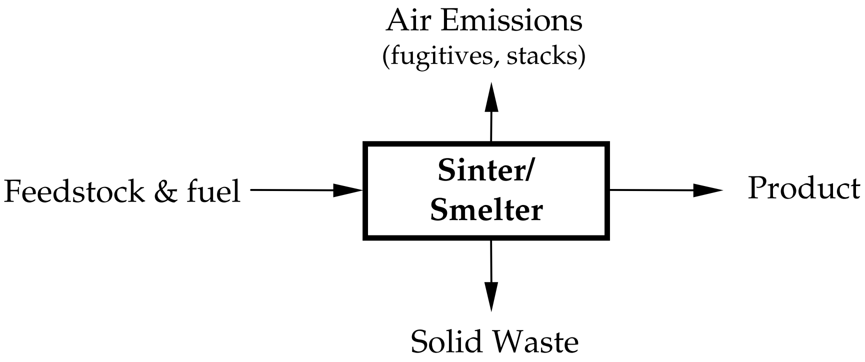


Figure 9.1 - Estimating SO_2 Emissions

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. Outputs are based on representative sampling product and waste (slag).

Example 9.1 - Mass Balance Technique for Estimating SO_2

In the example presented (refer to Figure 9.2), stack emissions are estimated through representative sampling, allowing the fugitive emissions to be estimated. However, direct measurement of stack emissions is not required to effectively estimate emissions using a mass balance approach.

In this example, SO_2 emissions are calculated based on the sulfur content of the input and output streams. The quantity of SO_2 that may be produced from each stream is calculated by multiplying the concentration of sulfur by 2 (= $MW_{SO2}/EW_S = 64/32$). For example, the flux stream contains 715 tonnes of sulfur, which will produce 1430 tonnes of SO_2.

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 in this approach may be minimised through continued development and refinement of the mass balance equation.

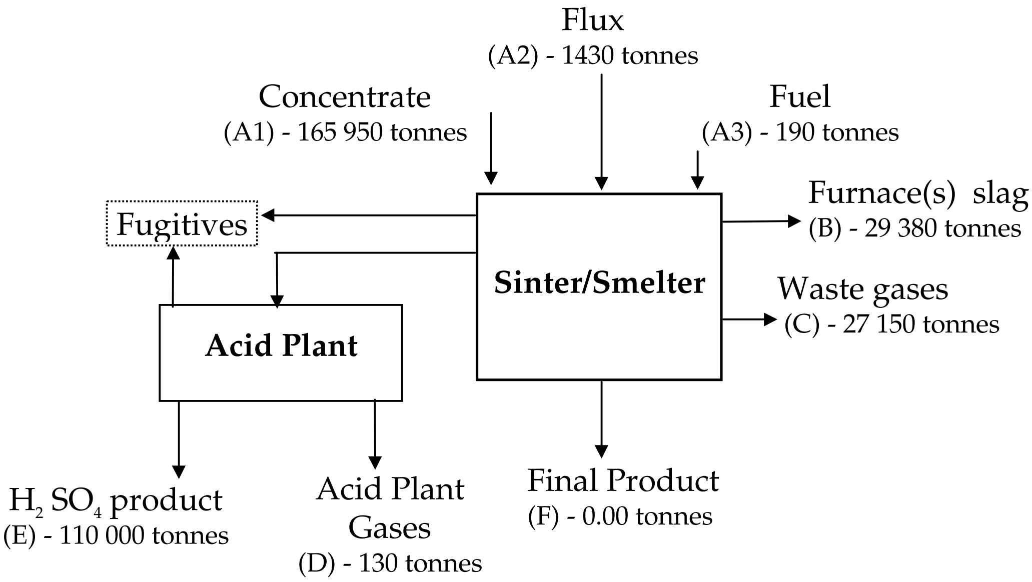


Figure 9.2 - Mass Balance SO_2 Calculations for Example 9.1

Inputs	=	Estimated Outputs + Assumed Outputs
A1 + A2 + A3	=	(B + E + F) + (D + C) + Fugitives
167 570	=	(139 380) + (27 280) + Fugitives
Fugitives	=	167 570 - 166 660
Fugitives	=	910 tonnes of SO_2

9.1.4 Emission Factors

It is unlikely that any lead processing facilities in Australia would need to use emission factors for estimating sulfur dioxide emissions, because most sites are required to monitor sulfur dioxide under licence conditions and can use direct measurement or at least a mass balance.

The US EPA publishes emission factors for various industries in the document known as AP-42, which is periodically updated and is available on the Internet. The AP-42 chapter on lead smelting contained no emission factors for fugitive sulfur dioxide as at August 1999.

9.2 Cyanide

9.2.1 Mass Balance

Sodium cyanide may be used in lead concentrating as an iron depressant. It is likely that most lead concentrating, smelting and refining facilities will 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, and exchange reactions are just a few of many possible simultaneous events. All cyanide is ultimately decomposed or forms complexes within the TSFs. Cyanide can be emitted to air, water and land, and this example includes all three emission media as the mass balance approach accounts for all input and output sources.

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 other EETs, such as direct measurement and modelling will support the mass balance approach, in order to increase the accuracy of estimated emissions.

9.2.2 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 licenced site etc.).

9.2.3 Cyanide Emissions from the Processing Area

A mass balance approach (based on Figure 9.3) may be used to estimate the emissions of cyanide through the volatilisation (and other losses such as carry over with product).

Equation 9.2

$$MV_{CN} = M_{CN} + M_{CNreturn} - M_{CNTSF} - M_{CNneut} - M_{CNseep}$$

where:

MV_{CN}	=	mass of cyanide lost through volatilisation	(kg)
M_{CN}	=	mass of cyanide added to the process	(kg)
$M_{CNreturn}$	=	mass of cyanide in TSF return water	(kg)
M_{CNTSF}	=	mass of cyanide carried to TSF	(kg)
M_{CNneut}	=	mass of cyanide neutralised prior to TSF	(kg)
M_{CNseep}	=	mass of cyanide loss in seepage from TSF	(kg)

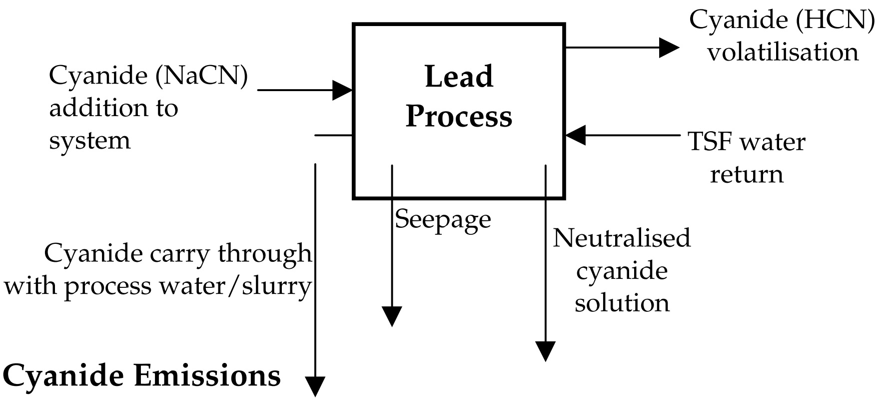


Figure 9.3 - Cyanide Emissions

9.2.4 Cyanide Emissions from TSFs

Figure 9.4 illustrates the mass balance approach to cyanide emissions from TSFs.

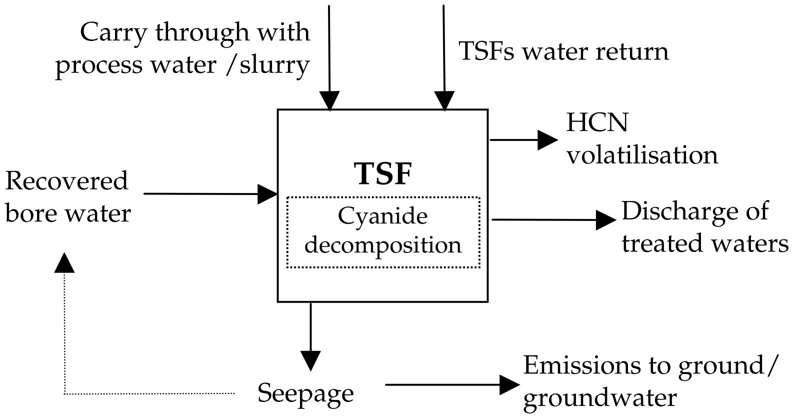


Figure 9.4 - Mass Balance Approach to Cyanide Emissions from TSFs

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

- Seepage; and
- Volatilisation

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 in monitoring bores.

While these seepage rates will be facility-specific, generic seepage rates of between **0 - 10%** of return waters have been quoted within the industry (Mt Keith Nickel 1996, ANCOLD pers. comm. Previously referenced in the *Nickel EET Manual*). The 10% figure can be used as a point of reference for reporting purposes. Alternatively the seepage load calculated using Darcy's Law can be applied (refer to Section 8.3 for more detail on the application of Darcy's Law).

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

Equation 9.3

$$M_{CNS} = V_{slurry} * V/100 * C_{CN}$$

where:

M_{CNS}	=	mass of cyanide emitted through seepage	(kg)
V_{slurry}	=	volume of water/slurry throughput to TSF per year	(m^3)
V	=	seepage rate	(%)
C_{CN}	=	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 in monitoring bores; 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 emission factors for volatilisation from TSFs presented below may be used to estimate these emissions.

9.2.5 Emission Factors

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 area of gold operations (Heath *et al*, 1998). This estimate is assumed to be applicable to the lead processing industry for the purposes of this manual.

Emissions should be reported as mass of CN^- using the stoichiometry detailed in Equation 9.4.

Equation 9.4

$$M_{CN^-} = M_{HCN} * 0.54$$

where:

M_{CN^-} = mass of CN^- emitted (kg)
M_{HCN} = mass of HCN (as kg of NaCN emitted)
0.54 = the stoichiometry

Cyanide Emissions from TSFs

It has been estimated that volatilisation of HCN accounts for 90% of the natural degradation of cyanide from TSFs within the gold industry (Ellis, 1997; Simovic, 1984) and is assumed to be the case for the lead 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 influence the rate of volatilisation although pH is the most significant factor.

This percentage degradation is dependent, however, 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 in Table 9.1.

Table 9.1 - Percentage of Natural Degradation of Cyanide Due to Volatilisation

pH	Percentage of Natural Degradation Due to Volatilisation
6	90%
7	90%
8	80%
9	60%
10	20%
11	0%
12	0%

(Source: Based on Ellis, 1997; Simovic, 1984)

This data is applied using the equation below:

Equation 9.5

$$MV_{HCN} = C_{CN^-} * V_{slurry} * V/100$$

where:

MV_{HCN} = mass of HCN volatilised from TSFs (kg)
C_{CN^-} = free cyanide concentration in TSF return water (kg/m^3)
V_{slurry} = volume of water/slurry throughput to TSF per year (m^3)
V = volatilisation rate (%)

9.3 Carbon Disulfide

The *Nickel EET Manual* has a detailed discussion on the use of emission factors for carbon disulfide. This section of *the Nickel EET Manual* has been adapted for this manual and follows.

Sodium ethyl xanthate (SEX), $C_2H_5OS_2Na$, is widely used in Australia in flotation/concentration processes. SEX is used as a collector, to alter the hydrophobic/hydrophilic nature of the mineral surface, which aids in the flotation of the sulfide complexes. It decomposes in the presence of moisture and/or heat to produce carbon disulfide, which is an NPI reportable substance. When SEX is used as a flotation agent it is mixed with water, usually at a concentration of approximately 10%. The majority of the SEX is retained within the froth, which contains the lead concentrate, whilst the remainder (approximately 1%) will report to the TSF. The ultimate fate and decomposition of xanthate is not fully known. However for the purposes of NPI reporting it can be assumed that 0.2% of SEX will decompose hydrolytically to release carbon disulfide (CS_2)

Xanthate breakdown is influenced by a number of factors. Within the lead 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); and
- Hydrolytic 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 to be applied based on their use of xanthate types.

Depending on the process operation at a particular site. The lead concentrating, smelting and refining area will generally be alkaline. However at some facilities this may be very difficult to achieve. TSFs are also likely to be alkali, although the geochemistry of the ore being handled may result in the TSF becoming acidic.

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 following equations:

Equation 9.6a

Alkali Conditions (pH>7):

$$\text{Moles of } CS_2 \text{ emitted (kg)} = 0.2\% * 0.5 * \text{Mass of Xanthate} * {}^{MW_{CS_2}}\!/_{MW_{xanthate}}$$

Equation 9.6b

Acidic Conditions (pH<7):

$$\text{Moles of } CS_2 \text{ emitted (kg)} = 0.2\% * 1.0 * \text{Mass of Xanthate} * {}^{MW_{CS_2}}\!/_{MW_{xanthate}}$$

Example 9.2 - Breakdown of Xanthates

A facility uses 150 kg of Sodium Ethyl Xanthate (SEX) and for each mole of SEX used, 0.5 moles of CS_2 are produced (alkali conditions)

Molecular weight of CS_2 (MW_{CS_2}) = 76g
Molecular weight of SEX ($MW_{xanthate}$) = 144g

$$\text{Emissions of } CS_2 \text{ (kg)} = 0.002 * 0.5 * \text{Mass of Xanthate} * MW_{CS_2} / MW_{xanthate}$$

$$= 0.002 * 0.5 * 150 \text{ kg} * 76 \text{ g}/144 \text{ g}$$

$$= 0.08 \text{ kg}$$

10.0 Best Practice

The *NPI Guide* has been developed to provide information on the type and extent of emissions from Australian industries. Encompassed in the reporting requirement is addressing how emissions will be reduced. Best practice requires every reasonable effort on behalf of the company to minimise emissions.

When reducing the emissions from a lead processing facility there are three recommended approaches:

- ***Process modification:*** This not only includes using different equipment and reagents that produce less reportable emissions but also encompasses the integration of process streams to maximise energy transfer and the utilisation of by–products, eg. the formation of sulfuric acid. In addition, the NPI trigger levels for Category 1 and 1a substances are not based on the concentration leaving the facility but on the amount "used/handled", thus process modification also includes changes in inventory handling and control (ie order raw materials only as needed).
- ***Containment:*** Where possible all ore, feed products, waste, reaction equipment and product should be contained, either in sealed containers, bunded, in dams, or within a room under negative pressure. If not contained suitable mechanisms should be incorporated to reduce the likelihood of emission, eg. using a windbreak around stockpiles, tarps on trucks.
- ***Treatment:*** All discharge streams should be treated prior to release: this includes removal of all dust from gases before they are vented and the processing of effluent through a waste water treatment facility.

Appendix B of the *NPI Guide* lists additional emission reduction activities, including inventory control, spill and leak prevention, raw material modifications, process modifications, cleaning and degreasing, surface preparation and finishing, and product modifications. This appendix also includes the Activity Codes that should be quoted when reporting reduction activities.

Emission control technologies commonly used in the Australian lead processing industry are considered in the following sections. These technologies, in some companies, are combined with environmental management systems to reduce the overall adverse environmental impact of lead processing.

10.1 Control Technologies for Air Emissions

Air emissions are measured at the point of creation, this does not take into account the fate of the emission, for example sulfur dioxide is measured at the stack, not the site boundary. The three main components of air emission produced at a lead smelter/refinery are dust, metal fumes and sulfur dioxide gas.

10.1.1 Concentrating

A site can minimise air emissions from ore concentrating if they:

- Enclose part or all the process area;
- Keep ore damp, where possible;
- Utilise wet spray suppression systems;
- Enclose transfer points, equipment and the truck loading operation;
- Wet and cover truck loads and stored concentrates;
- Use sprinkler systems on unloading area and stockpiles;
- Incorporate preventative maintenance on machinery to minimise leaks; and
- Store all chemical feeds to the flotation cell in sealed containers.

Tailings Dams

There are two potential air emissions from tailing dams - cyanide and dust. To minimise these emissions facilities may:

- Utilise a wind break to minimise dust generated by the wind;
- Revegetate the dam; and
- Monitor the level of cyanide vaporising.

10.1.2 Processing Site

For loading and unloading areas the following measures should be considered:

- Enclose the areas, where possible;
- Where it is not practical to enclose the area, water spray suppression systems should be installed on the unloading and loading facilities; and

For the storage of raw materials:

- Minimise the amount of raw materials stored outside, maximise storage in sealed bins;
- Sealing compounds should be used for outside storage; and
- Where sealed compounds are not used, it is recommended that the area be protected to minimise exposure to wind eg. a wetting system or wind barrier.

Sinter Plant

- Enclose the vibratory feeders and screens, where possible, and duct gases to a scrubber or fabric filter;
- Collect the hot gas from the front of the sinter plant and directed to an acid plant or a scrubber;
- Pass the gas from the rear of the sinter plant through a scrubber before being emitting into the atmosphere or recirculate the gas back through the sinter after it passes through a cyclone;
- Operate the sinter building (fugitive emissions) under negative pressure;

- Enclose conveyors, screw, shakers etc., and ensure preventative maintenance is undertaken;
- Collect post sinter activities (breaker, rolls, screens) emissions and pass through a venturi scrubber and stack;
- Recycle sinter fines back into the sinter plant; and
- Equip sinter bins with bin vent filters.

Smelting/Refining

- Furnace gases should be directed to a fabric filter;
- Fugitive emissions in the smelter building include dust from uncovered screws and conveyors, discharges from charge outlets, leaks from furnace covers etc. Controls include the enclosure of conveyors and other material handling equipment where practical, operating the building under negative pressure and having a preventative maintenance program in operation; and
- Collect dust and fumes and direct to a fabric filter.

Fuel Storage

There are three main options available to handle emissions from fixed roof tanks. As emissions are directly related to vessel capacity, organic properties of the liquid, tank turnover rate and atmospheric conditions, modification of existing structures provide the best control mechanisms. Options available are:

- Installation of an internal floating roof can dramatically reduce evaporation emissions from fixed rook tanks by 60-90 percent;
- Vapour balancing, essentially vapours are trapped in an empty vessel while the storage vessel is being filled. This vessel is then transported to a vapour recovery system or vented to the atmosphere (the latter providing essentially no control). Vapour recovery can produce control efficiencies ranging from 90 to 98 percent; and
- Vapour recovery systems: these systems condense the collected vapours for reuse. Common units utilise vapour compression, vapour cooling, vapour/solid adsorption and vapour/liquid absorption.

10.1.3 Site

Other dust control measures include:

- Regular damping of unsealed internal roads, or alternatively treat with dust suppression chemicals or oils (subject to EPA approval);
- Regular cleaning and washing of sealed internal roads, with contaminated water being collected, treated and recycled;
- Landscaping and sealing of stockpiles;
- Enclosure and maintenance of conveyors;
- Good material transfer practices (eg. at wharf facilities) in addition to control technology; and
- Utilisation of fabric filters, scrubbers and stacks to treat point source emissions.

10.2 Control Technologies for Water Emissions

Water emissions include discharges from boiler blow-down, process water from the various activities and floor and site drainage including contaminated stormwater. Lead processing facilities utilise large quantities of water each year, and this process water cannot go straight to sewer so it must either be treated or reused within the facility.

A range of wastewater treatment techniques is used to reduce the adverse environmental impact of water discharges. Examples of such techniques include:

- All drainage points should feed to an impoundment facility, so no liquid waste flows direct to sewer;
- Operation of an Effluent Treatment plant for removal of metals loading and pH control;
- Use of storm water containment facilities;
- Control of floor drain discharges via oil and silt interceptors;
- Recycling of process water wherever practicable;
- Prompt repair of all leaks;
- Use of reed-bed filtering lagoons to minimise water disruption in dams during seasonal storms; and
- Recovery of treated effluent and contained stormwater, for use for dust suppression.

10.3 Control Technologies for Land Emissions

Land discharges are limited to waste materials, ash (for coal fired plant) and ground water contamination.

Control techniques include:

- Utilisation of flyash for cement products;
- Controlled waste landfill or disposal off-site;
- Wet ash dams (not impacted by wind erosion);
- All vehicles and machinery transporting concentrate, should be washed down due to the potential for cross contamination;
- Closely monitoring seepage from containment facilities into ground water;
- Lining tailings dams to minimise ground-water contamination;
- Interception trenches and recovery of contaminated groundwater for on-site treatment;
- Inspection and monitoring program of potential spill or leak sources; and
- Bunding of oil, fuel, electrolytic cells and chemical storage, to reduce the risk of spillage to soil.

11.0 Glossary of Technical Terms and Abbreviations

11.1 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 various ways depending on the emission type. For emissions to air boundary is the point of creation (such as the surface of a liquid for 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.

11.2 Abbreviations

API	American Petroleum Institute
C	Capacity
CO	Carbon monoxide
DCAP	Double Contact Acid Plant
DoME	Department of Minerals and Energy
DM	Direct Measurement
EC	Engineering Calculation
EEA	European Environment Agency
EET	Emission Estimation Technique
EF	Emission Factor
EFR	Emission Factor Rating
EPA	Environment Protection Authority
ESP	Electrostatic Precipitator
ETP	Effluent Treatment Plant
GF	Generic Factor
INV	Inventory
kW	kilowatts
m^3	Cubic meters
MSDS	Material Safety Data Sheets
NEPM	National Environment Protection Measure
NOI	Notice of Intention
NO_x	Oxides of Nitrogen
NPI	National Pollutant Inventory
PAH	Polycyclic Aromatic Hydrocarbons
PM_{10}	Particles which have an aerodynamic diameter equal to or less than 10 micrometers
SCAP	Single Contact Acid Plant
SI	Systeme Internationale
TSP	Total Suspended Particulate
TSF	Tailings Storage Facility
VOC	Volatile Organic Compounds
US	United States of America
US EPA	United States Environmental Protection Agency
WA	Western Australia

12.0 References

12.1 References Cited

1. ANZSIC: Australian and New Zealand Standard Industrial Classification, Australian Bureau of Statistics & NZ Dept of Statistics 1993, ABS Catalogue No 1292.0

2. Background Information for New Source Performance Standards: Primary Copper, Zinc and Lead Smelters, Volume 1: Proposed Standards, EPA-450/2-74-002a, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1974.

3. BPEMIM, Tailings Containment (1995), Best Practice Environmental Management in Mining series, 'Tailings Containment', EPA

4. Carras (1998), Letter to PPK Environment & Infrastructure, CSIRO

5. *EET Manual for Ferrous Foundries*, National Pollutant Inventory, 1998

6. *EET Manual for Fossil Fuel Electric Power Generators*, National Pollutant Inventory 1999

7. *EET Manual for Fuel and Organic Liquid Storage*, National Pollutant Inventory, 1999

8. *EET Manual for Mining*, National Pollutant Inventory, 1999

9. *EET Manual for Nickel Concentrating, Smelting and Refining*, National Pollutant Inventory, 1999

10. Ellis (1997), *Investigation & Modelling of the Natural Decay of Cyanide in a Gold Mine Tailings Pond*, Daniel Ellis, Honours Thesis, University of Western Australia.

11. *Encyclopædia of Chemical Technology*, John Wiley and Sons, Inc. New York, NY, 1967.

12. G. Sallee, Personal Communication, Midwest Research Institute, Kansas City, MO. June 1970. (as referenced in the *Nickel EET Manual*)

13. Heath et al (1998), *A method for measuring* $HCN_{(g)}$ *emission from CIP / CIL tanks*, CSIRO & Curtin University

14. *Industrial Process Profiles for Environmental Use, Chapter 28 Primary Zinc Industry*, EPA-600/2-80-169, U. S. Environmental Protection Agency, Cincinnati, OH, July 1980.

15. MERIWA Project M241 (1998), *"Saline Tailings Disposal & Decommissioning"*, Australian Centre for Geomechanics [ACG : 1004-98 (A)/(B)]

16. Mt Keith Nickel (1996), *Mt Keith Nickel Project Tailings Storage Upgrade CER*, Jan 1996, for WMC by Woodward Clyde

17. *Particulate Pollutant System Study, Volume 1: Mass Emissions*, APTD – 0743, U. S. Environmental Protection Agency, Research Triangle Park, NC, May 1971.

18. R. B. Jacko and D. W. Nevendorf, "Trace Metal Emission Test Results From A Number Of Industrial And Municipal Point Sources", *Journal of the Air Pollution Control Association*, 27(10):989-994. October 1977

19. Simovic (1984), *Report on Natural Degradation of Cyanides from the Cullaton Lake Gold Mines Effluent,* Environment Canada, Waste Water Technology Centre. NOTE: Referenced through Ellis, 1997

20. *Systems Study For Control of Emissions In the Primary Nonferrous Smelting Industry*, Volume 1, APDT-1280, U. S. Environmental Protection Agency, Research Triangle Park, NC, June 1969.

21. *Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions*, EPA-450/3-77-010, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1977.

22. Telephone conversation with ANCOLD representative, Re. Guidelines on Tailings Disposal and TSFs seepage, NOTE Referenced in *the Nickel EET Manual.*

23. US EPA. June 1999. *Emission Factor Documentation for AP-42, 5th Edition Section 12.6 Primary Lead Smelting, and Section 12.11 Secondary Lead Processing*. United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA. http://www.epa.gov/ttn/chief/ap42.html

24. WMC Report Ref 692 634 (1992), Investigation of Engineering Design Criteria for Xanthate Handling Facilities

12.2 References Not Cited

1. Hayes, P., *Process Principles in Minerals and Materials Production*, Hayes Publishing, Qld 1993

2. Linkson, P., *Extractive Metallurgy Lecture Series*, University of Sydney 1998

Appendix A - Sources of Existing Data

Existing Data

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

Data sources may include the following:

A1 Existing Data & Research

Research projects of interest to industry are often sponsored, such as university Honours, Master or PhD projects. These may be very directed areas of research, such as slag content and leachability or hydrogeological contamination, and results may not be widely available even 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 by measurement, visual means or mass balance; and
- The implementation of dust control strategies.

This data may be applied to emission estimation methods to increase their accuracy either directly through the development of emission factors or indirectly by identifying additional processes within mass balances.

Processing sites 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 sites will have access to geotechnical data and groundwater data for the processing site from work carried out in the past (during exploration or when the refinery was built). 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.

A2 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;
- Slag; and
- TSFs water input and return.

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

- Ammonia;
- Cyanide;
- Sulfur dioxide;
- Acids; and
- Carbon monoxide.

A3 Licences & Reporting

Smelters and refineries may be required to carry out monitoring that can be applied to the requirements of the NPI. This data may include the following parameters:

- Sulfur dioxide;
- Carbon monoxide;
- Sulfuric acid fumes;
- Dust and particulates;
- Metals; including arsenic, selenium, antimony, beryllium, cadmium, lead, mercury, chromium, manganese, cobalt, copper, nickel, and 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.

The 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.

A4 Approvals Data

Lead smelters and refineries may have environmental assessment reports or other approval documents, which contain a range of facility characterisation and operational efficiency data. This information may be applied to emission estimation methods to provide greater accuracy in reported data.

For example from March 1993 all proposals 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.

A5 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.

A6 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 lead process and to TSFs. Another example is the sulfur content of fuel.

A7 Inventory

A facility inventory may be used to identify all inputs to the lead 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.

TableA1 - Inventory of a Lead Processing Facility

INPUTS	Units	Jan	Feb	Mar	...	Dec	TOTAL
Tonnes of ore treated	*tonnes*						
Lead production	*kg*						
Sodium Cyanide	*tonnes*						
Quicklime (78% CaO)	*tonnes*						
(88% CaO)	*tonnes*						
Oxygen	m^3						
Carbon	*tonnes*						
Flocculent	*tonnes*						
Antiscalant	*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*						