Emission Estimation Technique Manual

for

Copper Concentrating, Smelting and Refining
EMISSION ESTIMATION TECHNIQUES
FOR
COPPER CONCENTRATING, SMELTING AND REFINING

TABLE OF CONTENTS

1.0 INTRODUCTION 1
1.1 Context of this Manual 1
1.2 EETs Should Be Considered As “Points Of Reference” 2
1.3 Hierarchical Approach Recommended in Applying EETs 3
1.4 NPI Emissions in the Environmental Context 3
1.5 NPI Reporting Requirements 4
1.6 Use of this Manual 4

2.0 PROCESS DESCRIPTION 5
2.1 General 5
2.2 Copper Concentrating 6
2.2.1 General 6
2.2.2 Grinding 7
2.2.3 Flotation 7
2.2.4 Thickening 7
2.3 Smelting/Electro-Refining Copper 9
2.3.1 General 9
2.3.2 Smelting 9
2.3.3 Electro-refining of Copper 15
2.4 Leaching/Solvent Extraction/Electrowinning 15
2.4.1 Leaching 15
2.4.2 Solvent Extraction 16
2.4.3 Electrowinning Copper 16

3.0 ANCILLARY ACTIVITIES AND ASSOCIATED FACILITIES 18
3.1 Ancillary Activities 18
3.1.1 Acid Plant 18
3.1.2 Trace Metal Recovery 18
3.2 Associated Facilities 22
3.2.1 Fuel and Organic Liquid Storage 22
3.2.2 Fossil Fuel Electric Generation 22
3.2.3 Combustion Engines 22
3.2.4 Other Facilities 22
3.3 Maintenance Activities 23

4.0 POSSIBLE EMISSIONS 24
4.1 Reporting Thresholds 26
# Coppers Concentrating, Smelting and Refining

## Table of Contents cont’

### 5.0 EMISSION ESTIMATION

- **5.1 Emission Estimation Techniques**
  - 5.1.1 Direct Measurement
  - 5.1.2 Engineering Calculations
  - 5.1.3 Mass Balance
  - 5.1.4 Emission Factors
- **5.2 Acceptable Reliability and Uncertainty**
  - 5.2.1 Direct Measurement
  - 5.2.2 Mass Balance
  - 5.2.3 Engineering Calculations
  - 5.2.4 Emission Factors
- **5.3 NPI Reporting Steps**

### 6.0 EMISSIONS TO AIR

- **6.1 Background**
  - 6.1.1 Fugitive Emissions
  - 6.1.2 Point Source Emissions
- **6.2 Furnace and Smelter Emissions**
  - 6.2.1 Direct Measurement
  - 6.2.2 Mass Balance
  - 6.2.3 Emission Factors
- **6.3 Dust and PM<sub>10</sub>**
  - 6.3.1 Direct Measurement
  - 6.3.2 Emission Factors
- **6.4 Metals in Dust**
  - 6.4.1 Direct Measurement
  - 6.4.2 Emission Factors
- **6.5 Acid Mist**
  - 6.5.1 Direct Measurement
  - 6.5.2 Mass Balance
  - 6.5.3 Engineering Calculations
- **6.6 Emissions from Associated Facilities and Ancillary Activities**
  - 6.6.1 Emission Estimation for Fuel
  - 6.6.2 Air Emissions from Fuel and Organic Liquid Storage
  - 6.6.3 Air Emissions from Fossil Fuel Electric Power Generation
  - 6.6.4 Emissions from Internal Combustion (Stationary) Engines
  - 6.6.5 Maintenance Activities - Emission Factors for Solvent Degreasing

### 7.0 EMISSIONS TO WATER

- **7.1 Background**
  - 7.1.1 Run-off and Erosion
  - 7.1.2 Discharge of Treated Process Waters
  - 7.1.3 Discharge of Sewage and Domestic Wastewaters
  - 7.1.4 Spills to Surface Water
# COPPER CONCENTRATING, SMELTING AND REFINING

## Table of Contents cont’

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>EMISSIONS TO LAND</td>
<td>60</td>
</tr>
<tr>
<td>8.1</td>
<td>Background</td>
<td>60</td>
</tr>
<tr>
<td>8.2</td>
<td>Groundwater Modelling - Fates and Trajectories</td>
<td>60</td>
</tr>
<tr>
<td>8.3</td>
<td>TSF Seepage</td>
<td>61</td>
</tr>
<tr>
<td>8.3.1</td>
<td>Direct Measurement</td>
<td>61</td>
</tr>
<tr>
<td>8.3.2</td>
<td>Modelling</td>
<td>62</td>
</tr>
<tr>
<td>8.3.3</td>
<td>Mass Balance</td>
<td>63</td>
</tr>
<tr>
<td>9.0</td>
<td>EXAMPLES OF APPLICATION OF EETS</td>
<td>66</td>
</tr>
<tr>
<td>9.1</td>
<td>Sulfur Dioxide</td>
<td>66</td>
</tr>
<tr>
<td>9.1.1</td>
<td>Background</td>
<td>66</td>
</tr>
<tr>
<td>9.1.2</td>
<td>Direct Measurement</td>
<td>66</td>
</tr>
<tr>
<td>9.1.3</td>
<td>Mass Balance</td>
<td>67</td>
</tr>
<tr>
<td>9.2</td>
<td>Cyanide</td>
<td>69</td>
</tr>
<tr>
<td>9.2.1</td>
<td>Mass Balance</td>
<td>69</td>
</tr>
<tr>
<td>9.2.2</td>
<td>Emission Factors</td>
<td>72</td>
</tr>
<tr>
<td>9.3</td>
<td>Carbon Disulfide</td>
<td>73</td>
</tr>
<tr>
<td>10.0</td>
<td>BEST PRACTICE</td>
<td>76</td>
</tr>
<tr>
<td>10.1</td>
<td>Control Technologies for Air Emissions</td>
<td>76</td>
</tr>
<tr>
<td>10.1.1</td>
<td>Concentrating</td>
<td>77</td>
</tr>
<tr>
<td>10.1.2</td>
<td>Processing Site</td>
<td>77</td>
</tr>
<tr>
<td>10.1.3</td>
<td>Site</td>
<td>78</td>
</tr>
<tr>
<td>10.2</td>
<td>Control Technologies for Water Emissions</td>
<td>79</td>
</tr>
<tr>
<td>10.3</td>
<td>Control Technologies for Land Emissions</td>
<td>79</td>
</tr>
<tr>
<td>11.0</td>
<td>GLOSSARY OF TECHNICAL TERMS AND ABBREVIATIONS</td>
<td>80</td>
</tr>
<tr>
<td>11.1</td>
<td>Definitions</td>
<td>80</td>
</tr>
<tr>
<td>11.2</td>
<td>Abbreviations</td>
<td>81</td>
</tr>
<tr>
<td>12.0</td>
<td>REFERENCES</td>
<td>82</td>
</tr>
<tr>
<td>12.1</td>
<td>References Cited</td>
<td>82</td>
</tr>
<tr>
<td>12.2</td>
<td>References Not Cited</td>
<td>83</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>SOURCES OF EXISTING DATA</td>
<td>84</td>
</tr>
<tr>
<td>A1</td>
<td>Existing Data &amp; Research</td>
<td>84</td>
</tr>
<tr>
<td>A2</td>
<td>Process Monitoring</td>
<td>85</td>
</tr>
<tr>
<td>A3</td>
<td>Licences &amp; Reporting</td>
<td>85</td>
</tr>
<tr>
<td>A4</td>
<td>Approvals Data</td>
<td>86</td>
</tr>
<tr>
<td>A5</td>
<td>Regulatory Data</td>
<td>86</td>
</tr>
<tr>
<td>A6</td>
<td>Suppliers</td>
<td>86</td>
</tr>
<tr>
<td>A7</td>
<td>Inventory</td>
<td>87</td>
</tr>
</tbody>
</table>
COPPER CONCENTRATING, SMELTING AND REFINING

LIST OF FIGURES, TABLES AND EXAMPLES

Figure 1.1 - Scope of the Copper Concentrating, Smelting and Refining EET Manual and its Potential Relationship with Other EET Manuals 2

2.1 - Copper Flotation Cell 8
2.2 - Olympic Dam Process 11
2.3 - Port Kembla Process 13
2.4 - Mount Isa Process 14
2.5 - Typical Leaching, Extraction and Electrowinning 17

3.1 - Sulfuric Acid Plant 19
3.2 - Typical Slimes Treatment Process 21

6.1 - Emissions Estimation for Smelter and Refinery Operations 46
6.2 - Refined Mass Balance Model 47

8.1 - Bore Hole Arrangement for TSFs 61
8.2 - TSF Water Balance 63

9.1 - Estimating SO₂ Emissions 67
9.2 - Mass Balance SO₂ Calculations for Example 9.1 68
9.3 - Cyanide Emissions 70
9.4 - Mass Balance Approach to Cyanide Emissions from TSFs 70

Table 4.1 - NPI-Listed Substances Likely to Trigger Reporting, and Proposed Methods for Determining Threshold Exceedance 24

4.2 - NPI Triggers as Related to Metal Concentration in Ore 27

5.1 - Techniques Available for Estimating Emissions of NPI Substances from Copper Concentrating, Smelting and Refining 32

6.1 - Emission Factors for SO₂ from Primary Copper Smelters 48
6.2 - Emission Factors for Primary Copper Smelters 50
6.3 - Particulate (PM₁₀) Emission Factors for Copper Smelting 51
6.4 - Fugitive Particulate Emission Factors for Primary Copper Smelting 51
6.5 - Lead Emission Factors for Primary Copper Smelters 52
6.6 - Emission Factors for Solvent Emissions 55

7.1 - West Australian Water Corporation Wastewater Treatment Design Criteria for Total Nitrogen and Phosphorus 58
9.1 - Percentage of Natural Degradation of Cyanide Due to Volatilisation 73
COPPER CONCENTRATING, SMELTING AND REFINING

LIST OF FIGURES, TABLES AND EXAMPLES cont’

Example 6.1 - Using Fuel Analysis Data 54
  9.1 - Mass Balance Technique for Estimating SO₂ 68
  9.2 - Breakdown of Xanthates 75
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 Copper Concentrating, Smelting and Refining.

The scope of this document is to outline methods that can be used by the copper 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 copper commencing with the delivery of ore to the processing facilities through to the production of +99% pure copper, using either the concentrating, smelting and electro-refining process, or the heap-leach and electrowinning process, or variants of these.

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

Ancillary activities such as an acid plant, slimes treatment, and tailings storage facilities (TSFs) are covered in this manual. Associated activities such as power generation - combustion engines, and fuel and organic storage facilities are covered briefly in this handbook. These activities are covered comprehensively by separate EET manuals.

The emission of NPI substances from a processing facility’s tailings 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: Copper Concentrating, Smelting & Refining

HANDBOOK: Copper 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 copper 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 particular site characteristic related to cyanide speciation, mineralogy and pH.

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, energy generation equipment, and water treatment.

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 exceed 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 assist 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 received 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 copper 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.

1.6 Use of this Manual

This manual is structured to allow facilities to work through the issues that require addressing 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 applied 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 copper 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.

The document has been developed for the copper concentrating, smelting and refining industry and has been based on the EET Manual for Nickel Concentrating, Smelting and Refining.
2.0 Process Description

2.1 General

Copper is found in the earth’s crust primarily as chalcopyrite (CuFeS$_2$), with other sulfide ores, such as bornite (Cu$_5$FeS$_4$), covellite (CuS) and chalcocite (Cu$_2$S), and oxide ores (CuO) also mined in Australia. Australia has 6% of the world’s known copper resources, ranking it fourth in resources and fifth in production behind Chile, USA, Canada and the former USSR. Copper and its alloys are used in many different industries, including the electrical, telecommunications, building, and computer industries, primarily because copper is a very good conductor of electricity and heat while also being very ductile, malleable, and easy to work. These properties make copper ideal for electrical wiring, electric motors, household plumbing, motor vehicle radiators, and for thin tubing in air conditioning/heating systems.

The Mount Isa mine is the largest producer of copper in Australia, as well as producing lead, and zinc concentrate. The Olympic Dam copper-uranium-gold deposit in South Australia is the largest recently discovered deposit, and was found in 1975. Other important deposits are located at North Parkes copper-gold in NSW, the Nifty copper deposit in Western Australia, CSA copper-lead-zinc and Girilambone deposits in New South Wales, the Mt. Lyell deposit in Tasmania, and the copper and copper-gold deposits at Selwyn in Queensland.

Copper is produced via two distinct processes, smelting/electro-refining and heap leach/solvent extraction/electrowinning. Smelters are operated at Mount Isa, Olympic Dam and Port Kembla; refineries are operated at Townsville (for the Mount Isa copper), Port Kembla, and Port Pirie (as an ancillary process to the lead-zinc refinery). However, prior to the ore undergoing these processes the copper must be liberated from the majority of waste rock. Depending on the mineralogy of the ore, this is typically achieved in three stages, crushing, grinding and flotation. The grade of the copper concentrate depends largely on the mineralogy of the ore and the degree of recovery, for example a concentrate of pure chalcopyrite will contain nearly 35% Cu compared to a concentrate of pure bornite of 63% Cu, and chalcocite which would contain nearly 80% Cu.

Copper production from concentrate, via smelting and electro-refining, involves a combination of pyrometallurgical and electrometallurgical processes. The concentrate is fed to a primary furnace that produces either copper matte (65% Cu) or blister copper (97% Cu). Where copper matte is formed the copper is primarily in the form of Cu$_2$S, which is converted (oxidised) to produce blister copper. As saleable copper needs to be of a high purity (up to 99.99%) the copper is cast into anodes and electrolytically refined. This processing method is used at Mount Isa and Port Kembla, and is the principal means of copper production at Olympic Dam.

An increasingly important alternative to conventional copper smelting and refining is solvent extraction/electrowinning technology. The main method involves heap leaching copper on-site at the mine, by exposing the ore (and gangue) to sulfuric acid solutions, thus dissolving the sulfide/oxide minerals. Processes are also being developed that use alkaline solutions and biological agents to dissolve the minerals. The sulfate solution is purified via solvent extraction, where an organic solvent selectively partitions different
sulfates into the organic phase. A similar process is also used at Olympic Dam to recover residual copper and also uranium from the tailings stream after copper flotation. Some ten percent of Olympic Dam’s copper is produced by solvent extraction and electrowinning.

Following solvent extraction the purified solution is fed into an electrolytic cell and copper deposits onto the cathodes. This copper can then be stripped off the electrode and may be sold directly as cathode copper sheets, or cast into bars, ingots or slabs with a purity of up to or over 99.99%. A version of this process uses concentrated ore and conducts the leaching circuit in autoclaves, percolators or vat (agitation) tanks. This allows more ore to be leached in a shorter time frame, as well as greater control over the reaction. However, it is a very expensive process to establish and maintain. In either circuit the acid for the leaching is a recycle from the electrowinning cell.

Distinct processes are applied to the concentrating, and the smelting and refining of the ores. 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 copper mines produce concentrate only, for smelting elsewhere (such as at the Port Kembla smelter), or may be fully integrated, producing final refined copper product from ore on-site (Olympic Dam). Thus, not all sections of this manual will be relevant to each facility. Facilities are not expected to report on substances they do not emit or produce, nor on processes they do not undertake (e.g. facilities that import concentrate more than likely will not need to consider carbon disulfide as an emission).

Copper concentrating, and copper smelting/electro-refining, are described in Sections 2.2 and 2.3 respectively. Leaching/solvent extraction/electrowin is described in Section 2.3.3.

### 2.2 Copper Concentrating

Concentrate produced from sulfide ore can often be sent directly to the smelter after drying. With copper oxide ores and mixed sulfide-oxide ores, copper may be chemically leached from the ore, bypassing some of the physical separation processes. A combination of flotation and leaching (Section 2.3.3) may be used for mixed sulfide-oxide ores.

#### 2.2.1 General

Copper minerals are usually present as fine grains throughout the rock, with complexes such as chalcopyrite (CuFeS₂) and chalcocite (Cu₂S) being the most abundant copper minerals mined in Australia. Current processing techniques can economically recover copper from ore with a minimum grade of approximately 2%. Thus for off-site smelting and refining, to reduce transport costs, the valuable ore must first be liberated from the waste rock, and separated as a concentrate.
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 to reduce the particle diameter to less than 10 mm. A conveyer then transports the crushed ore to rod and ball mills where it is ground into a fine powder. Alternatively the ore delivered from the mine may be autogenously ground.

The next stage of separation is the liberation of chalcopyrite and other valuable sulfide minerals from the waste rock particles to form a concentrate. The copper sulfide concentrating process is presented in Figure 2.1. Concentrating is carried out in a flotation device; one such device is the Jameson flotation cell.

2.2.2 Grinding

Crushed ore is ground autogenously or in rod and ball mills to further reduce the particle size and aid in the separation of gangue. Copper ore is directed to the copper flotation circuit.

2.2.3 Flotation

Finely ground copper ore and water are combined in a series of flotation cells (Figure 2.1) 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 minerals while the collector changes the surface tension of different minerals. This allows the pyrite and copper-rich particles to attach to the air bubbles and float to the surface of the liquid forming a froth. The pH modifier helps produce a higher grade of 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 copper and iron sulfides. The tailings, which contain the waste minerals, are transferred to a scavenger cell, which separates any residual copper composites from the tailings and recycles them to the flotation cell.

The gangue minerals are unaffected and pass through the flotation cells and are disposed of as residue, usually in a purpose-built facility, 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 flowsheets to identify which reagents are used and any possible compounds that may form.

2.2.4 Thickening

The froth is skimmed off the top of the cell and the resulting copper rich slurry is thickened. Flotation increases the grade of the ore, which may contain as little as 2% copper, to a concentrate assaying between 27% to 60% copper. The thickened concentrate is filtered and dried before being transported to the smelter.
CONCENTRATING COPPER ORE

INPUTS
Crushed Ore

Sodium isobutyl xanthate
Di-thiophosphate
(aeropromoter)
Interfroth 68
Sodium hydrogen sulfide
AL 3003 (flocculant)

Nitric acid
Hydrogen peroxide

Coherex binding agent

PROCESS
Grinding
Flotation Cells
Thickeners
Filtration, Drying
Copper concentrate

Tailings
Tailings sand for backfill

POTENTIAL EMISSIONS
Dust  PM$_{10}$
Metals

Activator Products
Copper disulfide

PM$_{10}$
Cyanide
Metals

Cyanide complexes

Figure 2.1 - Copper Flotation Cell
2.3 Smelting/Electro-Refining Copper

2.3.1 General

The smelting and electro-refining of a copper concentrate is conducted in three basic steps, smelting, anode casting, and electro-refining.

2.3.2 Smelting

The first stage of the smelting process is to convert the copper sulfide complexes into molten copper, by smelting the ore in the presence of oxygen enriched air, according to the following reaction.

\[ \text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2 \]

To prevent the oxidation of the molten copper a silica flux is added to the concentrate, which results in iron, and other impurities, forming silica compounds such as iron (II) silicate (FeSiO₃) in a slag layer on top of the copper preventing exposure to oxygen, and hence oxidation. This slag layer can be removed, and the molten copper can be tapped off and further refined. In some copper smelters this process is conducted in a series of furnaces, which provides the opportunity to recycle and reprocess the slag to ensure that the majority of copper present in the ore is refined. Alternately the slag may be treated in a separate furnace to recover residual copper, or it may be otherwise returned to the process.

Flash furnace smelting consists of blowing fine dried sulfide concentrates (mainly borrite) and silica flux with air, oxygen enriched air or oxygen blast into a shaft-type furnace maintained at approximately 1250°C. Entry of these materials into the hot furnace results in the sulfide minerals, of the concentrate reacting rapidly with the oxygen of the blast. This leads to controlled oxidation of the iron and sulfur in the concentrate, a large evolution of thermal energy, and the melting of solids. The products of flash furnaces are molten copper metal, molten slag containing iron oxides plus gangue and flux oxides, in addition to furnace gases which are rich in sulfur dioxide.

The slag typically contains as much as twenty percent copper. The copper content of the slag can be recovered in a slag-cleaning furnace, often electric. The flash furnace off-gas contains anywhere from 10 to 80% by volume sulfur dioxide (SO₂). The thermal energy in this gas is recovered in a waste heat boiler and the SO₂ is converted into sulfuric acid. Approximately 3-15 per cent of the furnace charge exits the furnace as dust in the off gas, primarily in the form of oxidised concentrate which is collected in electrostatic precipitators, and may be recycled to the furnace for copper recovery.

Copper from the flash furnace (and the slag-cleaning furnace), that is referred to as blister copper is passed to anode furnaces for purification by fire refining, before being cast into anodes for electro-refining (Section 2.3.3). Fire refining comprises an oxidation phase (by injection of oxygen) to remove sulfur, followed by a reduction phase (such as by injection of LPG) to remove excess oxygen. Following fire refining, the copper purity may be about 99.6%.
Olympic Dam Process

At the Olympic Dam operation (Figure 2.2) the copper concentrate is dried, mixed with the appropriate fluxes and fed into the reaction shaft of the flash smelter, along with 70 - 95% oxygen enriched air. The fine concentrate reacts, or “flashes”, instantaneously. Molten copper and slag fall to the hearth of the smelter where they separate (the slag floats on the molten copper) and the slag is removed periodically by tapping. The molten “blister copper”, which contains approximately 0.6% sulfur, is tapped from the flash furnace, and passes into one of two anode furnaces for further purification by fire refining. The slag from the flash smelter contains about 20% copper as oxide and is passed to an electric furnace to recover additional copper, which is also fed into the anode furnaces. Slag from the electric furnace, which contains approximately 4% copper, is returned to the concentrator for re-processing.

The sulfur dioxide gas, which exits the smelter and anode furnaces, is filtered to remove any dust. The dust is recycled back into the flash furnace and the gas is fed into the sulfuric acid plant where it is converted into sulfuric acid (the sulfuric acid plant is discussed in more detail in Section 3.1). This acid is used in the hydrometallurgical section of the plant for leaching the ore and in the electrolytic cells. There is, however, a shortfall in acid production from concentrate, and burning imported sulfur in the acid plant compensates this for.

From the anode furnace, the molten copper, now at approximately 99.6% purity, is cast on a revolving casting wheel into slabs, or copper anodes, which pass to the electrorefinery for production of copper of 99.99% purity. Gold and silver present in the ore pass with the copper through all these stages and are present in the copper anodes. This falls to the bottom of the electrolytic cells as slimes, and the gold and silver is recovered in the slimes treatment plant.

The tailings left from the concentrating process (Section 2.2) contain some ten-percent of the recoverable copper in the ore, plus uranium. This copper, and the uranium, is recovered by acid leaching of the tailings, followed by a two-stage solvent extraction process. This first stage of solvent extraction provides a copper sulfate solution, from which copper is recovered by electrowinning. The second stage of solvent extraction and treatment provides ammonium diuranate, which is calcined to produce uranium oxide concentrate.
Figure 2.2 - Olympic Dam Process

**INPUTS**

- Silica flux
- Oil
- Sulfur
- Coke
- LPG
- Electricity

**PROCESS**

- Concentrate
  - Flash Furnace
  - Electric Furnace
  - Anode Furnaces
  - Slimes Treatment
  - Electrorefining
- Tailings
  - Filter
  - Acid Plant
  - Copper Solvent Extraction
  - Electrowinning
  - Uranium Solvent Extraction
  - Recovery, Calcination

**POTENTIAL EMISSIONS**

- Dust, PM10
- SO2, NOX
- Metals
- SO2, SO3
- H2SO4
- CO
- Metal vapours
- SO2, CO, NOX
- Metal fume
- NOX
- Acid Mist

- Cu 99.99%
- Au 99.99%
- Ag 99.99%
- Cu 99.99%

(Olympic Dam Process Diagram)
**Port Kembla Copper Process**

The primary smelting vessel at Port Kembla Copper is the Noranda furnace (Figure 2.3). Copper concentrates, coal, sand and recycled process materials are fed into the furnace where they are smelted in a molten bath which is blown with oxygen enriched air. Copper matte and slag are produced. Matte is periodically tapped from the Noranda Furnace and transferred to a holding furnace. The slag is cleaned in an electric furnace to recover any residual copper matte and this matte is transferred to the holding furnace. The holding furnace ensures that a constant flow of molten matte is supplied to the Mitsubishi Converting (MIC) furnace.

The first furnace produces a matte containing approximately 65% copper, the majority of which is still within a copper-sulfide complex. The MIC converts the matte into blister copper by the removal of sulfur. In addition, the last traces of the iron impurities are removed in the form of slag. This slag has a high copper content and is recycled to the Noranda furnace. The off-gases from both the Noranda and MIC furnaces and anode furnace during the oxidation cycle are rich in sulfur dioxide and are treated in the acid plant to produce sulfuric acid.

The final stage of the smelting process involves a minor adjustment to the molten blister copper composition within the rotary anode furnaces. The anode copper is cast into a solid anode shape using a casting wheel. These anodes form the feed material to the electro-refining stage.

**Mount Isa Mine Process**

The smelting process utilised to purify Mount Isa ore is similar to that in place at Port Kembla Copper (refer to Figure 2.4). The concentrate is combined with silica flux and lime (when required) and is fed into an Isamelt furnace. This furnace smelts the ore, producing copper matte, slag, and sulfur dioxide. The slag and the matte flow into a holding furnace, where they are separated. The copper matte is transferred to a Pierce Smith converter, where the matte is oxidised to produce blister copper. The blister copper is fed into the anode furnace where additional sulfur dioxide is removed and the copper is cast as anodes. These anodes are electrolytically refined to produce copper with a purity of 99.99% and slimes, which are treated further in a slimes treatment plant to recover precious metals. Sulfur dioxide is produced in each of the furnaces. Currently this gas is released directly to the atmosphere through a stack, however, by arrangement with MIM, WMC is in the process of commissioning an acid plant as part of the Queensland Fertiliser Project.

This project will accept MIM’s smelter gases to produce fertiliser using phosphate rock from the Duchess deposit south of Mount Isa. The project is expected to be commissioned in late 1999, and will reduce MIM’s sulfur dioxide emissions by about 80%.
PORT KEMBLA COPPER PROCESS

**INPUTS**
- Sand
- Coal
- Recycled Process Residues
- Electricity
- Natural Gas
- Limestone
- Return Anodes
- Natural Gas
- Electricity
- $H_2SO_4$
- Lime
- Recycled Process Residues
- Limestone
- Return Anodes
- Natural Gas
- Electricity
- $H_2SO_4$
- Lime

**PROCESS**
- Concentrate
  - Noranda Furnace
  - Slag
  - Cu Matte
  - Dust
  - Filter
  - Acid Plant
  - $H_2SO_4$
- Holding Furnace
- MIC Furnace
  - Blister Cu
  - Cu rich slag for recycling
  - Anode Furnace
  - Anode Casting
  - Electrorefining
  - Cu 99.99%
  - (precious metal recovery)
- Waste Water Treatment Plant
  - Gypsum
  - Water for reuse/discharge

**POTENTIAL EMISSIONS**
- $SO_2$
- $CO$, $NO_X$
- Metal vapours
- $PM_{10}$
- $SO_2$, $SO_3$
- $H_2SO_4$
- Metal fume
- $SO_2$, $NO_X$
- Metal fume
- $CO$, $SO_2$
- $NO_X$
- Metal fume
- Acid mist
Figure 2.4 - Mount Isa Process

MOUNT ISA PROCESS

INPUTS

Silica Flux
Lime

Diesel
Natural Gas

Coal
Natural Gas

Electricity

PROCESS

Concentrate

Isamelt Furnace

SO₂

Filters

SO₂,
NOₓ
Metals

Holding Furnace

Matte Cu

Converter

Blister Cu

Anode Furnace

Anode Casting

Electro-refining

Cu

Slag

SO₂

Acid Plant

H₂SO₄

SO₂,
SO₃
H₂SO₄

SO₂,
Metal fume

NOₓ,
CO, SO₂
Metal fume

Acid Mist

POTENTIAL EMISSIONS
2.3.3 Electro-refining of Copper

Electro-refining is used to refine and purify the anode copper produced from smelting. The copper is electro-refined by casting the molten metal into an anode, which dissolves into the cell electrolyte (typically CuSO₄/H₂SO₄ and more recently HCl) as copper deposits of 99.99% purity on the cathode.

At Mount Isa, Olympic Dam, and Port Kembla Copper the ISAPROCESS of electro-refining is used. The process features the use of permanent stainless steel cathode sheets onto which the purified copper is deposited.

In the refinery the copper anodes are suspended in cells of electrolyte, in-between the cathodes. A high amperage direct electric current passes through the anode and electrolyte to the cathode. Copper dissolves from the anode and is deposited on the stainless steel cathodes. Impurities, including gold and silver drop to the bottom of the tank as slimes. After seven days in the tank the cathode is removed and the copper sheet stripped from the stainless steel cathode, which is returned to the tank. In larger, more automated plants, the copper sheets are removed from the stainless steel cathodes by machine; manual methods are used in some operations. Following stripping, the sheets of high purity copper are bundled for shipment to markets.

The slimes from the tank are collected and may be processed through a series of refining steps (as at Olympic Dam and Mt Isa). These include acid leaching to remove copper, intensive cyanidation (at Olympic Dam) for precious metals extraction and electro-refining processes to produce gold and silver bullion (this purification method is discussed in Section 3.1).

2.4 Leaching/Solvent Extraction/Electrowinning

Copper oxide ores and copper-sulfur-oxide ores can be processed using hydrometallurgical techniques only. This process involves three principal stages, leaching of the ore, solvent extraction for purification and electrowinning of the copper (Figure 2.5).

2.4.1 Leaching

There are many different leaching techniques in use today, including heap and dump leaching, pressure leaching and agitation or vat leaching. In a leach cycle the ore is exposed to either acidic or alkaline solutions (and occasionally to biological activity) to dissolve the minerals and to create an impure pregnant liquor.

Dump leaching and heap leaching treat ores that have not undergone any, or minimal, size reduction preparation. This leaching mechanism has a cycle of months, and in particularly low-grade ore the cycle can take years. The tailings usually remain within the leaching pit. In recent years many refineries have installed autoclaves and agitated tanks, which use concentrate from the flotation cell. As the particle size is very fine the reaction time is reduced to hours, rather than months. This method also provides the operator with greater control over the process.
Where a series of leach vessels is used the leach circuit is usually conducted counter-currently, using acid recycles from the electrolytic cell. This increases the concentration gradient, encouraging more copper to dissolve into solution. This pregnant liquor, and the liquor drained from heap leaching activities, now contains the minerals present in the ore, as dissolved ions. The silicates and other gangue products are transferred to either a tailings dam, or are used as backfill.

2.4.2 Solvent Extraction

Prior to electrolysis of the solution, the pregnant liquor is purified. All metal ions, other than copper, must be removed or they may deposit out with the copper, or cause the evolution of hydrogen from the electrowinning cell. If hydrogen evolves at the anode the cell will run less efficiently, form unwanted by-products, and result in less commercially valuable copper (due to the altered crystal structure).

The solution is typically purified by solvent extraction, an ion exchange mechanism. An extractant (lixiviant) is dissolved in an organic solvent (typically kerosene). This extractant partitions certain ions into the organic phase so that the purified aqueous solution can flow into the cell. This solvent solution can then be scrubbed and stripped to remove the dissolved ions, then the stripped solvent can be recycled as solvent feed.

Continual research is being conducted to develop new purification techniques, particularly as many of the metallic impurities can be sold as valuable by-products. It is recommended that each operation refer to the flowsheet relevant to their purification circuit when reporting NPI emissions.

2.4.3 Electrowinning Copper

The process of electrowinning copper differs from electro-refining as the copper deposits out of the pregnant electrolyte and two non-reactive electrodes are used, as opposed to one non-reactive cathode and a copper anode. A direct current flows from the cathode to the anode, resulting in pure copper depositing out of solution and plating onto the anode. The copper, at a purity of better than 99.99% Cu is periodically stripped from the anode, washed, dried and either sold direct as bundles of copper cathode, or cast into ingots. Any impurities remaining in the electrolyte drop out of solution as anode slime. This slime can either be recycled in the feed to the leach tanks or processed to remove any valuable metals.
Figure 2.5 - Typical Leaching, Extraction and Electrowinning

HEAP LEACH / SOLVENT EXTRACTION / ELECTROWINNING

**INPUTS**
- Ore
- \( \text{H}_2\text{SO}_4 \)
- Organic solvent (e.g., kerosene)
- Diatomaceous earth
- Extractant - Lixivants
- Clay
- Electricity / diesel power station
- Cobalt sulphate
- Guar Gum
- Hydrochloric acid
- Wax
- \( \text{H}_2\text{SO}_4 \)

**PROCESS**
- Crushed Ore
- Heap Leach Pad
- Solvent Extraction
- Electrowinning
- Copper for casting

**POTENTIAL EMISSIONS**
- Dust
- \( \text{PM}_{10} \)
- Leached ore
- Leach solution mist
- Dissolved metals
- Diatomaceous earth waste
- Solvent and extractant vapours
- Clay waste
- Electrolyte mist
- Lead
- Wax waste
- Electrode slime
- Diesel combustion products
3.0 Ancillary Activities and Associated Facilities

A number of by-products from copper refining can be converted into saleable products through ancillary activities. The sulfur dioxide gas released from the furnaces can be used to produce sulfuric acid. When the copper is electro-refined the anode slimes, which are deposited in the electrolytic cells, can be purified to recover precious metals such as gold and silver.

Copper 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, power generation and wastewater treatment.

3.1 Ancillary Activities

3.1.1 Acid Plant

A significant environmental problem faced when smelting and refining copper from sulfide ore is the formation of sulfur dioxide bearing gas. There are two methods of removing the gas, either through direct venting or the formation of sulfuric acid. Under current guidelines the formation of sulfuric acid is encouraged, owing to the adverse environmental effects of sulfur dioxide gas. The hot gases emitted during smelting will also contain dust. To remove this dust the gas is typically initially cleaned by a hot gas precipitator followed by a sequence of wet scrubbers. Final cleaning may be conducted using wet electrostatic precipitators.

After cleaning the gas is passed through drying towers to remove water. Then it passes 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 acid may be used within the plant, in the leaching circuit, or may be sold.

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 Trace Metal Recovery

Other metals commonly found in copper ore include nickel, gold, silver, mercury, iron, selenium and tellurium. All of the iron compounds, which are present after processing as oxides and sulfur-oxide compounds, including pyrite, haematite etc., are disposed of as a waste product in the slag or tailings from the leach circuit. The other metals may also be recovered and sold. Typically these metals are either removed from the process as slimes from the electrolytic process, or if leaching is conducted, as a result of solvent extraction. The precious metals can be recovered from the copper anode slimes through a series of digestion and leach stages, followed by cyanidation and electro-refining. The quantity and type of metals recovered from slimes are dependent on the geochemistry of the ore.
Figure 3.1 - Sulfuric Acid Plant

**TYPICAL SULFURIC ACID PROCESS**

**INPUTS**
- Hot gas from furnaces or Elemental sulfur

**PROCESS**
- Hot Gas Precipitators
  - Water to treatment / process
- Wet Scrubbers
- Electrostatic Mist Precipitators
- Drying Towers
  - Water to treatment / process
- Converters
- Absorption Columns
- Acid Cooler and Storage
  - Exit gases
  - 98% Sulfuric Acid

**POTENTIAL EMISSIONS**
- PM$_{10}$
- Dust (may contain heavy metals)
- Metal fume
- Catalyst residue
- SO$_2$, SO$_3$
- H$_2$SO$_4$ (acid mist)
Figure 3.2 is an example of a slimes treatment plant. The slime is removed from the electrolytic cell and filtered to remove any excess electrolyte, then the slime is leached to remove any residual copper as copper sulfate. The residual material is then roasted and smelted in a furnace before being cast as anodes and undergoing the first of two electro-refining stages.

At Olympic Dam, the slimes are subject to additional processing between copper leaching and roasting and smelting. Firstly the process stream is neutralised, then undergoes intensive cyanidation to dissolve all of the silver and gold. Zinc dust is used to precipitate the metallic ions and the cyanide solution is neutralised to ensure that no cyanide in solution is transferred to the Tailings Storage Facility (TSF). The zinc precipitate is leached again to remove all remaining zinc, copper and selenium, and this solution is recycled back to the copper refining process.

After anode casting in the roasting and smelting furnace, the first cell removes the silver as crystals, which are remelted and cast for sale. At the bottom of this cell, the gold forms a mud which can be removed. This mud is releached and the gold is cast into anodes and electrolytically refined, remelted and cast for sale.
Figure 3.2 - Typical Slimes Treatment Process

**SLIMES TREATMENT**

**INPUTS**
- Slimes
- Electrolyte
- \( \text{H}_2\text{SO}_4 \)
- Caustic Soda
- Sodium Cyanide
- Zinc dust
- Reagent
- Flux
- Natural gas
- Electricity
- Acid
- Natural gas
- Electricity
- Natural gas

**PROCESS**
- Slimes
  - Electrolyte recycle to cells
  - Filter
  - Copper Leach
  - Neutralisation
  - Cyanidation
  - Zinc Precipitation
  - Acid Leach
  - Roasting/Smelting
  - Silver Refining Cell
  - Furnace
  - Ag Bullion

**POTENTIAL EMISSIONS**
- \( \text{H}_2\text{SO}_4 \)
- Cyanide complexes
- \( \text{H}_2\text{SO}_4 \)
- \( \text{NO}_X \)
- \( \text{SO}_2 \)
- Acid mist
- \( \text{H}_2\text{SO}_4 \)
- Acid mist
- \( \text{NO}_X \)
- \( \text{SO}_2 \)

This part of the process occurs only at Olympic Dam.

In the generic process the stream undergoes a copper leach then is roasted.
3.2 Associated Facilities

There are 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 copper 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. It is unlikely that the sites will hold any significant quantities of other organic liquids.

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

3.2.2 Fossil Fuel Electric Generation

Fossil fuel electricity generation plants are delineated into steam plants, gas turbines, co-generation and internal combustion engines. In relation to the copper processing industry it is likely that the only fossil fuel electric 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 in remote sites and in 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.

3.2.4 Other Facilities

There are many other associated facilities that may need to be accounted for in NPI reporting. Each facility will need to refer to its own plant flowsheets to aid in identifying these activities. These may include:

- Waste disposal;
- Waste and recycle water treatment;
- Concrete batching (as part of backfill operations); and
- Lime production (as part of wastewater treatment).
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 copper-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 copper 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 copper 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 copper concentrating, smelting and refining facilities. A thorough inventory for each facility will provide a more accurate list. All facilities should refer to the complete list, which is included as Table 2 in the NPI Guide.

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

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

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>TRIGGER</th>
<th>CATEGORY</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony &amp; compounds</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td>Arsenic &amp; compounds*</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Boron &amp; compounds</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td>Cadmium &amp; compounds*</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>Usage (Coincidental production)</td>
<td>1</td>
<td>DM, EC</td>
</tr>
<tr>
<td>Carbon monoxide*</td>
<td>Usage (Coincidental Production)</td>
<td>1</td>
<td>DM, EC</td>
</tr>
<tr>
<td></td>
<td>Or fuel use</td>
<td>2a</td>
<td>DM, INV</td>
</tr>
<tr>
<td>Chromium (III) compounds</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Chromium (VI) compounds*</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Cobalt &amp; compounds*</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td>Copper &amp; compounds</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Cyanide (inorganic) compounds*</td>
<td>Usage</td>
<td>1</td>
<td>INV</td>
</tr>
<tr>
<td>Fluoride compounds*</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or fuel use</td>
<td>2a</td>
<td>INV</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>Usage (Usage &amp; coincidental production)</td>
<td>1</td>
<td>INV, EC, DM</td>
</tr>
<tr>
<td></td>
<td>or fuel use</td>
<td>2a</td>
<td>INV</td>
</tr>
</tbody>
</table>
Table 4.1 - NPI-Listed Substances Likely to Trigger Reporting, and Proposed Methods for Determining Threshold Exceedance

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>TRIGGER</th>
<th>CATEGORY</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead &amp; compounds*</td>
<td>Usage (Ore content &amp; anodes)</td>
<td>1</td>
<td>INV, DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Manganese &amp; compounds</td>
<td>Usage (Ore content &amp; catalyst)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td>Mercury &amp; compounds*</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Nickel &amp; compounds</td>
<td>Usage (Ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td></td>
<td>or power usage</td>
<td>2b</td>
<td>C</td>
</tr>
<tr>
<td>Oxides of nitrogen*</td>
<td>Fuel use</td>
<td>2a</td>
<td>DM, EC</td>
</tr>
<tr>
<td>Particulate matter ≤10 μm*</td>
<td>Fuel use</td>
<td>2a</td>
<td>DM, EF</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>Fuel Use</td>
<td>2b</td>
<td>DM, INV</td>
</tr>
<tr>
<td>Selenium &amp; compounds</td>
<td>Usage (ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
<tr>
<td>Sulfur dioxide*</td>
<td>Fuel use</td>
<td>1</td>
<td>DM, EC</td>
</tr>
<tr>
<td></td>
<td>Power usage</td>
<td>2b</td>
<td>DM, EC</td>
</tr>
<tr>
<td>Sulfuric acid*</td>
<td>Usage (coincidental production &amp; production on-site)</td>
<td>1</td>
<td>INV, EC</td>
</tr>
<tr>
<td>Total nitrogen*</td>
<td>Discharge to surface waters (sewage plants)</td>
<td>3</td>
<td>DM, EF</td>
</tr>
<tr>
<td>Total phosphorus*</td>
<td>Discharge to surface waters (sewage plants)</td>
<td>3</td>
<td>DM, EF</td>
</tr>
<tr>
<td>Total Volatile Organic Compounds</td>
<td>Use or design bulk storage</td>
<td>1a</td>
<td>C, INV</td>
</tr>
<tr>
<td>Zinc &amp; compounds</td>
<td>Fuel use</td>
<td>2a</td>
<td>C, INV</td>
</tr>
<tr>
<td></td>
<td>Usage (ore content)</td>
<td>1</td>
<td>DM, GF</td>
</tr>
</tbody>
</table>

* 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 Table 5.1 and Table 5.2:

** DM Direct Measurement → Direct measurement of NPI reportable emissions in a stream or characterisation of the ore body;

** INV Inventory → Inventory or material usage (eg. 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 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*.

Within the copper industry, trace metals within ore may trigger reporting thresholds, as may the coincidental production of sulfur dioxide from the smelting process and the NPI substance content of process chemicals used at facilities.

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.

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

Direct measurement by representative sampling is the most accurate means of characterising ore and hence determining “usage” of trace metals, as the metal content of ore will vary between and within facilities. In the absence of facility-specific assays, generic ore assays may be used as the basis for reporting of metals “usage”. These generic assays are presented in 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 facility inventories will facilitate the calculation of the mass of NPI substances “used” through their presence in process chemicals. This approach will require recording of the volumes of process chemicals used in a reporting period and determination of the concentration of NPI substances in those chemicals. This data may be available from material safety data sheets (MSDS) or directly from suppliers.

Table 4.2 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

<table>
<thead>
<tr>
<th>Metal conc. in ore (ppm)</th>
<th>Amount of ore treated (millions of tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td>0.2</td>
<td>50</td>
</tr>
<tr>
<td>0.3</td>
<td>33.3</td>
</tr>
<tr>
<td>0.4</td>
<td>25</td>
</tr>
<tr>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>0.6</td>
<td>16.7</td>
</tr>
<tr>
<td>0.7</td>
<td>14.3</td>
</tr>
<tr>
<td>0.8</td>
<td>12.5</td>
</tr>
<tr>
<td>0.9</td>
<td>11.1</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
</tr>
</tbody>
</table>

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

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.
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 handbook, 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.

The techniques available for estimating emissions of NPI substances from copper concentrating, smelting and refining activities are detailed in Table 5.1, while techniques available for estimating emissions from ancillary activities and associated facilities at copper 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 upon 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 (e.g. 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, i.e. 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 CuSO₄ were emitted to the environment, only the Cu component would be reportable. While CuSO₄ has a molecular weight of 159 the Cu component has a molecular weight of only 63. Reporting of the total CuSO₄ 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 is 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. This data can be used to assist in NPI reporting requirements.

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

The copper 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 emission treatment processes, dependent on the geochemistry of the ore. These are referred to in this manual as “Ancillary Activities” and may include:

- Lead production;
- Zinc production;
- Sulfuric acid production;
- Cadmium production;
- Gold and silver 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 gold is produced 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 facilities estimation methods detailed in this handbook.

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

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 not currently be 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 copper facility will report only one value for SO\textsubscript{2}, which is the summation of all the individual SO\textsubscript{2} emissions across the entire facility.
<table>
<thead>
<tr>
<th>Substances</th>
<th>Concentrating</th>
<th>Smelting</th>
<th>Leaching</th>
<th>Solvent Extraction</th>
<th>Electrolysis</th>
<th>Emissions From:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Slag landfill</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TSFs</td>
</tr>
<tr>
<td>Antimony &amp; compounds</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>W,L</td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td>Arsenic &amp; compounds</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>W,L</td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td>Boron &amp; compounds</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td></td>
<td></td>
<td></td>
<td>DM, MB, EF</td>
<td>DM, MB, EF</td>
</tr>
<tr>
<td>Cadmium &amp; compounds</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>W,L</td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>A</td>
<td></td>
<td>A</td>
<td></td>
<td></td>
<td>W,L</td>
</tr>
<tr>
<td></td>
<td>EC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DM, MB, EF</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W,L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DM, MB, EF</td>
<td></td>
<td></td>
<td></td>
<td>DM, MB, EF</td>
</tr>
<tr>
<td>Chromium (III) &amp; compounds</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>W,L</td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td>Chromium (VI) &amp; compounds</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>W,L</td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td>Cobalt &amp; compounds</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>W,L</td>
<td>W,L</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td></td>
<td></td>
<td></td>
<td>DM, MB, EF</td>
<td>DM, MB, EF</td>
</tr>
<tr>
<td>Copper &amp; compounds</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>W,L</td>
<td>W,L</td>
<td>W,L</td>
</tr>
</tbody>
</table>
Table 5.1 - Techniques Available for Estimating Emissions of NPI Substances from Copper Concentrating, Smelting and Refining Activities cont'

<table>
<thead>
<tr>
<th>Substances</th>
<th>Concentrating</th>
<th>Smelting</th>
<th>Leaching</th>
<th>Solvent Extraction</th>
<th>Electrolysis</th>
<th>Emissions From Slag landfill</th>
<th>TSFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanide (inorganic) compounds</td>
<td>A</td>
<td>MB</td>
<td>A</td>
<td>W, L</td>
<td>W, L</td>
<td>DM, MB, EC</td>
<td></td>
</tr>
<tr>
<td>Flouride compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>W</td>
<td>EC</td>
<td>A, W</td>
<td></td>
<td></td>
<td>W, L, DM, MB, EF</td>
<td></td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>A</td>
<td>EF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organo-tin compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxides of Nitrogen</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulate matter, ≤10μm</td>
<td>A</td>
<td>EF</td>
<td></td>
<td></td>
<td></td>
<td>A, EF, EC</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.1- Techniques Available for Estimating Emissions of NPI Substances from Copper Concentrating, Smelting and Refining Activities cont’

<table>
<thead>
<tr>
<th>Substances</th>
<th>Concentrating</th>
<th>Smelting</th>
<th>Leaching</th>
<th>Solvent Extraction</th>
<th>Electrolysis</th>
<th>Emissions From</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Slag landfill</td>
</tr>
<tr>
<td>Selenium &amp; compounds</td>
<td>A MB</td>
<td>A</td>
<td>A</td>
<td>W, L</td>
<td></td>
<td>W, L</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>A DM, MB, EF</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>A DM, MB, EF</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 Copper Processing

<table>
<thead>
<tr>
<th>Substance</th>
<th>Acid Plant</th>
<th>Slimes Treatment</th>
<th>Fossil Fuel Electric Generation</th>
<th>Fuel &amp; Organic Liquid Storage</th>
<th>Combustion Engines</th>
<th>Waste Water Treatment Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony &amp; compounds</td>
<td></td>
<td>A, MB</td>
<td>A</td>
<td>A</td>
<td>A, MB</td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Arsenic &amp; compounds</td>
<td></td>
<td>A, MB</td>
<td>A</td>
<td>A</td>
<td>A, MB</td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Boron &amp; compounds</td>
<td></td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium &amp; compounds</td>
<td></td>
<td>W, L, MB</td>
<td>A</td>
<td>A</td>
<td></td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td></td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium (III) &amp; compounds</td>
<td></td>
<td>W, L, MB</td>
<td>A</td>
<td>A</td>
<td>A, MB</td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Chromium (VI) &amp; compounds</td>
<td></td>
<td>W, L, MB</td>
<td>A</td>
<td>A</td>
<td>A, MB</td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Cobalt &amp; compounds</td>
<td></td>
<td>W, L, MB</td>
<td>A</td>
<td>A</td>
<td></td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Copper &amp; compounds</td>
<td></td>
<td>W, L, MB</td>
<td>A</td>
<td>A</td>
<td></td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Fluoride</td>
<td></td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td>W, DM, MB</td>
</tr>
</tbody>
</table>
Table 5.2 - Techniques Available for Estimating Emissions of NPI Substances from Ancillary Activities and Associated Activities Related to Copper Processing cont’

<table>
<thead>
<tr>
<th>Substance</th>
<th>Acid Plant</th>
<th>Slimes Treatment</th>
<th>Fossil Fuel Electric Generation</th>
<th>Fuel &amp; Organic Liquid Storage</th>
<th>Combustion Engines</th>
<th>Waste Water Treatment Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Lead &amp; compounds</td>
<td>W, L, MB</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Manganese &amp; compounds</td>
<td>W, L, MB</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td>W, DM, MB</td>
</tr>
<tr>
<td>Mercury &amp; compounds</td>
<td>A, MB</td>
<td>W, L, MB</td>
<td>A, MB</td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Nickel &amp; compounds</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Oxides of nitrogen</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Particulate matter ≤10µm</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DM, MB</td>
</tr>
<tr>
<td>Selenium &amp; compounds</td>
<td>W, L, MB</td>
<td>A, MB</td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>A, DM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A, DB, MB</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>A, W, MB</td>
<td>A, W, MB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2 - Techniques Available for Estimating Emissions of NPI Substances from Ancillary Activities and Associated Activities Related to Copper Processing cont’

<table>
<thead>
<tr>
<th>Substance</th>
<th>Acid Plant</th>
<th>Slimes Treatment</th>
<th>Fossil Fuel Electric Generation</th>
<th>Fuel &amp; Organic Liquid Storage</th>
<th>Combustion Engines</th>
<th>Waste Water Treatment Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DM, EF</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DM, EF</td>
</tr>
<tr>
<td>Total VOCs</td>
<td>A, L, MB</td>
<td>A, EF</td>
<td>A, EF</td>
<td>A, EF</td>
<td>A, EF</td>
<td>A, EF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W, DM, EF</td>
</tr>
</tbody>
</table>

Notes: DM Direct Measurement, MB Mass Balance, EC Engineering Calculations, EF Emission Factor

A Emission to Air, W Emission to Water, L Emission to Land
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 measurement commitments and data that can be applied to the reporting requirements of the NPI. Potential sources of existing data are discussed in Appendix A.

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

Direct measurement data can 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, and including a factor to take into account temperature differences.

**Equation 5.1**

\[
E_i = C_i \times V \times \left[\frac{273}{(273 + T)}\right]
\]

where:

- \(E_i\) = hourly emissions of pollutant i  (kg/hr)
- \(C_i\) = concentration of pollutant i  (kg/m³)
- \(V\) = stack gas volumetric flow rate  (m³/hr)
- \(T\) = gas temperature  (°C)
- 273 = 273 K (0°C)

Where direct measurement is undertaken, it is essential that sampling and source measurement procedures be 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 engineering calculations, 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

A mass balance identifies the quantity of substance going in and out of an entire facility, process, or piece of equipment. Emissions can be calculated as the difference between input and output of each listed substance. Accumulation or depletion of the substance within the equipment should be accounted for in your calculation.
It is essential that the mass balance calculations address all losses and fates of a substance and utilise 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 either 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**

Where a facility uses a listed mineral acid or base, with this acid or base being effectively neutralised in use or during wastewater treatment (to a pH of 6 to 8, as required by most State and Territory effluent standards), even though a threshold is triggered a “zero” emission may be reported. However, if the acid or base is itself transformed into another listed substance 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 coincidental production exceeds 10 tonnes.

Wastewater treatment may precipitate a reportable chemical in 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 not all the chemical is 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 values that are derived from similar operations. Emission factors are a useful tool for estimating emissions where the relationship between the emission and the “use” of substances is well defined. Emission factors are widely used in estimating emissions from combustion sources, 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 a 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

\[ E_i = A \times EF_i \times [1 - CE_i/100] \]

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 copper 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 copper 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 copper 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. EET equations are available for the following types of emissions common to copper concentrating and smelting/refining facilities.

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 (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in 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 “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 in Table 1: NPI Substances, found in Appendix A of the NPI Guide. Substances that are likely to be used at copper 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, and the amount of energy 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, 7 and 8 of this manual, which provide examples of the various estimation techniques used to calculate emissions to air, water and land.
6.0 Emissions to Air

6.1 Background

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

- Stack emissions from smelters;
- The stockpiling, movement and comminution of ore;
- The operation of process plants including electrolytic processing; and
- The operation of tailing storage facilities.

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.

6.1.1 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.

6.1.2 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 filters, or afterburner may “treat” stack emissions prior to their release, reducing their total loading to the atmosphere.

6.2 Furnace and Smelter Emissions

Emissions from copper smelters are principally particulate matter and oxides of sulfur. Fugitive emissions are generated primarily during material handling operations. Copper oxides or sulfides are significant constituents of the particulate matter, but other metals such as arsenic, antimony, cadmium, and mercury may also be present, along with
Copper Concentrating, Smelting, and Refining

metallic sulfates and sulfuric acid mist. Significant emissions of SO\textsubscript{2} occur from various processes associated with primary copper smelting of sulfide ores. Recovery of this SO\textsubscript{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.

6.2.1 Direct Measurement

Direct measurement (or source monitoring) is one of the more accurate methods of estimating air emissions from smelters/converters. Source monitoring programs for air emissions such as SO\textsubscript{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\textsubscript{2} emissions can be found in Section 9.1.

6.2.2 Mass Balance

Emissions (such as sulfur dioxide and metals) from smelting 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/metals content of process inputs and outputs.

It is important that the fates of component substances are considered within the mass balance and that all assumptions are stated. For example, it may be assumed that all sulfur is converted to sulfur dioxide during combustion, and 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. Figure 6.1 shows a typical “box” approach to mass balances.

![Diagram showing mass balance approach to emissions estimation](image)

**Figure 6.1 - Emissions Estimation for Smelter and Refinery Operations**

Air emissions may be estimated where the NPI substance concentrations of the feedstock, product and solid wastes have been effectively characterised.
Sulfur dioxide (SO₂) emissions from converter and smelting 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 in 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](image)

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

### 6.2.3 Emission Factors

It is unlikely that any copper 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. However, some factors have been developed for smelters in the United States, and these are outlined in Table 6.1. The emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source. As these factors have been developed based on American sites they may not be totally comparable with Australian sites.
Table 6.1 - Emission Factors for SO₂ from Primary Copper Smelters
(kg of pollutant/tonne of concentrated ore processed)

<table>
<thead>
<tr>
<th>Process</th>
<th>Sulfur Dioxide</th>
<th>Emission Factor Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate Dryer (CD)</td>
<td>0.5</td>
<td>B</td>
</tr>
<tr>
<td>Electric Furnace (EF)</td>
<td>45</td>
<td>B</td>
</tr>
<tr>
<td>Flash Furnace (FF)</td>
<td>410</td>
<td>B</td>
</tr>
<tr>
<td>Cleaning Furnace (SS)</td>
<td>0.5</td>
<td>B</td>
</tr>
<tr>
<td>Noranda Reactor (NR)</td>
<td>ND²</td>
<td>ND</td>
</tr>
<tr>
<td>Pierce Smith Converter(C)³</td>
<td>410</td>
<td>B</td>
</tr>
</tbody>
</table>

¹ Converter gas effluent, and at some smelters, roaster gas effluent are treated in single contact acid plants (SCAP) or double contact acid plants (DCAP) for SO₂ removal. Typical SCAPs are about 96% efficient, and DCAPs are up to 99.85% efficient in SO₂ removal. Gas cleaning equipment provided to clean the smelter gases prior to passing to the acid plant also remove over 99% of particulate matter. Noranda and flash furnace off-gases are also processed through acid plants and are subject to the same efficiencies as cited for converters and some roasters. In addition to the sources indicated each smelter contains fire refining anode furnaces after the converters. Anode furnaces emit SO₂ in some phases of the refining cycle, and in some plants these gases are collected and passed to the acid plant. However, these emissions are small in magnitude compared with smelter SO₂ emissions.

² ND = no data
³ Converter figures are associated with CD and EF, CD, FF, and SS (410).

(Source: Background Report Primary Copper Smelting, prepared for US Environmental Protection Agency)

6.3 Dust and PM₁₀

6.3.1 Direct Measurement

PM₁₀ 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 estimates.

Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM₁₀ from total PM emissions, a size analysis may need to be undertaken. The weight of the fraction can then be multiplied by the total PM emission rate to produce PM₁₀ emissions. Alternatively, assume that 100% of PM emissions are PM₁₀, ie. assume that all particulate matter emitted to air has an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10µm.
6.3.2 Emission Factors

Processing Areas

The EET Manual for Mining provides emission factors for PM\textsubscript{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 metals 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.
Primary copper smelting generates particulate matter from the smelting furnaces and converters. Fugitive emissions are generated during material handling operations. Particulate emissions vary depending on the configuration of the smelting equipment.

The emission factors in Table 6.2 are based on US information, so they may not be entirely comparable with Australian smelters. The emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source.

### Table 6.2 - Emission Factors for Primary Copper Smelters

<table>
<thead>
<tr>
<th>Process</th>
<th>Particulate (Less than 15µm)</th>
<th>Sulfur Dioxide</th>
<th>Emission Factor Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate Dryer (CD)</td>
<td>5</td>
<td>0.5</td>
<td>B</td>
</tr>
<tr>
<td>Electric Furnace (EF)</td>
<td>50</td>
<td>120</td>
<td>B</td>
</tr>
<tr>
<td>Flash Furnace (FF)</td>
<td>70</td>
<td>410</td>
<td>B</td>
</tr>
<tr>
<td>Cleaning Furnace (SS)</td>
<td>5</td>
<td>0.5</td>
<td>B</td>
</tr>
<tr>
<td>Noranda Reactor (NR)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Pierce Smith Converter (C)</td>
<td>18</td>
<td>410</td>
<td>B</td>
</tr>
</tbody>
</table>

1 Used to recover copper from furnace slag and converter slag.
2 If Pierce Smith converter is in association with CD, FF, and SS or CD and NR no data is available.

(Source: Background Report Primary Copper Smelting, prepared for US Environmental Protection Agency) Particulate emission factors were extracted from the US EPA AP-42 document (1999) Table 12.3-2

The emission factors for PM$_{10}$ in Table 6.2 are based on the following treatment processes. For particulate matter removal, gaseous effluent from roasters, smelting furnaces and converters are usually treated in hot electrostatic precipitators (ESP) at 200 to 340°C or in cold ESPs with gases cooled to about 120°C before being passed to the ESP. Particulate emissions from copper smelters contain volatile metallic oxides that remain in vapour form at higher temperatures, around 120°C. Therefore, overall particulate removal in hot ESPs may range from 20 to 80% and in cold ESPs may be 99%.

Converter gas effluent, and at some smelters roaster gas effluent, are treated in single contact acid plants (SCAP) or double contact acid plants (DCAP) for SO$_2$ removal. Typical SCAPs are about 96% efficient, and DCAPs are up to 99.85% efficient in SO$_2$ removal. Gas cleaning equipment provided to clean the smelter gases prior to passing to the acid plant also removes over 99% of particulate matter. Noranda and flash furnace off-gases are also processed through acid plants and are subject to the same efficiencies as cited for converters and some roasters. In addition to the sources indicated, a smelter may also have fire refining anode furnaces after the converters.

Anode furnaces emit SO$_2$ during some phases of the refining cycle, and in some plants (such as Olympic Dam) these gases are also collected and passed to the acid plant. However these emissions are small in magnitude compared with smelter SO$_2$ emissions.
No published particulate data is available for source emissions from anode furnaces however; fugitive data is available in Table 6.3.

Particulate emissions from various process areas, for primary copper smelting, are presented in Table 6.3. Fugitive emission factors are presented in Table 6.4. These emission factors should be applied carefully. Emission factors for some operations are derived from data from a single facility. Others are based on similar operations in the steel, lead, and zinc industries (USEPA, 1999).

Table 6.3 - Particulate (PM$_{10}$) Emission Factors for Copper Smelting

<table>
<thead>
<tr>
<th>Process</th>
<th>Particulate - PM$_{10}$ (#10µm)</th>
<th>Emission Factor Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pierce Smith copper converter</td>
<td>10.6</td>
<td>E</td>
</tr>
<tr>
<td>Converter slag &amp; copper blow operations</td>
<td>2.1</td>
<td>D</td>
</tr>
</tbody>
</table>


(AP-42 US EPA, 1999 Tables 12.3-16)

Table 6.4 - Fugitive Particulate Emission Factors for Primary Copper Smelting

<table>
<thead>
<tr>
<th>Process</th>
<th>PM$_{10}$</th>
<th>Emission Factor Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pierce Smith Converter</td>
<td>2.2</td>
<td>B</td>
</tr>
<tr>
<td>Pierce Smith Converter slag return</td>
<td>ND</td>
<td>B</td>
</tr>
<tr>
<td>Anode refining furnace</td>
<td>0.25</td>
<td>B</td>
</tr>
<tr>
<td>Slag cleaning furnace$^b$</td>
<td>4</td>
<td>B</td>
</tr>
</tbody>
</table>

* Expressed as mass kg of pollutant/tonne of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal. Factors for flash furnace smelters and Noranda furnace smelters may be lower than reported values. ND = no data

$^b$ Used to treat slags from smelting furnaces and converters at the flash furnace smelter.

(AP-42 US EPA, 1999 Table 12.3-10)

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. The proportion of PM$_{10}$ in the TSP will need to be determined to allow more accurate estimation of the facility’s emissions of these metals. Periodic analysis of dust samples will allow the proportion of PM$_{10}$ in dust 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 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’s 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 or 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 content (including cyanide) of TSF dust emissions should be based on representative sampling of the TSF’s surface matrix.

US EPA document AP-42 includes emission factors for lead from primary copper smelters; these are reproduced in Table 6.5.

### Table 6.5 - Lead Emission Factors for Primary Copper Smelters

<table>
<thead>
<tr>
<th>Operation</th>
<th>Emission Factor $^b$</th>
<th>Emission Factor Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelting $^c$</td>
<td>0.036</td>
<td>C</td>
</tr>
<tr>
<td>Converting $^d$</td>
<td>0.13</td>
<td>C</td>
</tr>
<tr>
<td>Refining</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

$^a$ Reference 2. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal. Based on test data for several smelters with 0.1 - 0.4% lead in feed through out. ND = no data.

$^b$ For process and fugitive emissions totals.

$^c$ Based on test data on reverberatory furnaces. Includes total process emissions from matte tapping and slag skimming operations amount to about 35% and 2% respectively.

$^d$ Includes total of process and fugitive emissions. Fugitives constitute about 50% of total. Based on Pierce Smith converters.

(US EPA AP-42, 1999, Table12.3-18)

6.5 Acid Mist

An increasingly important alternative to conventional copper smelting and refining is solvent extraction/electrowinning technology, in which dilute sulfuric acid is percolated through copper-bearing ore to leach out the copper. The copper is concentrated through solvent extraction and is subsequently recovered by plating onto a starter cathode in a process called electrowinning.

The extraction/electrowinning process is an alternative to smelting but it and its corresponding emission streams are fundamentally different from smelting.
The main emissions to air are leach solution mist from the heap leach process and electrolyte mist from the electrowinning process. Both contain sulfuric acid and copper sulfate.

6.5.1 Direct Measurement

Little direct measurement is possible in an open environment, however some sites do measure airborne sulfuric acid. Others rely on contouring of the plant’s immediate landscape to drain rainfall into the dam or mine pits. This reclaims spray, mist and dust back to the site. This suggests that the process and plant is a relatively closed cycle operation where rainfall washes many emissions back to the plant for re-integration into the process cycle.

6.5.2 Mass Balance

Emissions from extraction/electrowinning operations may be estimated through the use of mass balance. Direct measurement of the process inputs is undertaken, in order to minimise losses (outputs) which need to be replaced to keep the process running. The process fate of the acid mist may be estimated from the additional acid input that is required over time.

6.5.3 Engineering Calculations

Engineering calculations may be used to estimate acid mist emissions from the overall process. The process is designed to operate at a certain level of efficiency, and while variations will occur it may be valid to assume a given performance efficiency under normal operating conditions.

The calculations may utilise the chemical reactions that occur in the leaching and electrowinning processes. In simple terms these would be as follows:

Heap Leach: \[ \text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} \leftrightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \]

Electrowinning: \[ \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \]

6.6 Emissions from Associated Facilities and Ancillary Activities

Associated facilities at copper smelters and refineries can also produce NPI reportable emissions. This section covers the most common associated activities and refers to other existing EET Manuals. The relevant sections from these manuals have been included in the copper EET Manuals in order to create a self-contained manual.
6.6.1 Emission Estimation for Fuel

Fuel analysis is an example of an engineering calculation and can be used to predict \( \text{SO}_2 \), metals, and other emissions based on 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.

Equation 6.1 is the basic equation used in fuel analysis emission calculations. \( \text{SO}_2 \) emissions from combustion can be calculated based on the concentration of sulfur in fuel.

This approach assumes complete (100%) conversion of sulfur to \( \text{SO}_2 \). Therefore, for every kilogram of sulfur (EW = 32) burned, two kilograms of \( \text{SO}_2 \) (MW = 64) are emitted.

**Equation 6.1**

\[
E_{\text{kgpy}, \text{SO}_2} = Q_f * C_i / 100 * \frac{MW_{\text{SO}_2}}{EW_s} * \text{OpHrs}
\]

where:

- \( E_{\text{kgpy}, \text{SO}_2} \) = amount of \( \text{SO}_2 \) emitted (kg/yr)
- \( Q_f \) = fuel use (kg/hr)
- \( C_i \) = pollutant concentration of fuel weight percent %
- \( MW_{\text{SO}_2} \) = molecular weight of \( \text{SO}_2 \) (= 64) (kg/kg-mole)
- \( EW_s \) = elemental weight of S (= 32) (kg/kg-mole)
- \( \text{OpHrs} \) = operating hours (hr/yr)

Example 6.1 illustrates the use of Equation 6.1.

---

**Example 6.1 - Using Fuel Analysis Data**

\( E_{\text{kgpy}, \text{SO}_2} \) 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

\[
E_{\text{kgpy}, \text{SO}_2} = Q_f * C_i / 100 * \frac{MW_{\text{SO}_2}}{EW_s} * \text{OpHrs}
\]

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

\[
= 733 590 \text{ kg/yr}
\]

Therefore, under these operating conditions the amount of \( \text{SO}_2 \) 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

### 6.6.2 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.

### 6.6.3 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 copper 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.

### 6.6.4 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.

### 6.6.5 Maintenance Activities - Emission Factors for Solvent Degreasing

Solvent degreasing within the copper processing industry is related to maintenance activities. Table 6.6 contains emission factors for solvent emissions.

#### Table 6.6 - Emission Factors for Solvent Emissions

<table>
<thead>
<tr>
<th>Solvent Used</th>
<th>Use</th>
<th>Emission Factor(^1) (kg/kg solvent used)</th>
<th>Emission Factor Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane:</td>
<td>Vapour degreasing</td>
<td>0.930</td>
<td>E</td>
</tr>
<tr>
<td>Uncontrolled</td>
<td>Cold Cleaners</td>
<td>0.890</td>
<td>E</td>
</tr>
<tr>
<td>Controlled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethylene:</td>
<td>Vapour Degreasing</td>
<td>0.890</td>
<td>E</td>
</tr>
<tr>
<td>Uncontrolled</td>
<td>Cold Cleaners</td>
<td>0.850</td>
<td>E</td>
</tr>
<tr>
<td>Controlled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene:</td>
<td>Vapour Degreasing</td>
<td>0.910</td>
<td>E</td>
</tr>
<tr>
<td>Uncontrolled</td>
<td>Cold Cleaners</td>
<td>0.870</td>
<td>E</td>
</tr>
<tr>
<td>Controlled</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) 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 (e.g. 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 copper 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.

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing sampling data can be used to calculate annual emissions.

If no wastewater monitoring data exists, emissions to water can be calculated based on a mass balance or using emission factors.

The discharge of listed substances to a sewer or tailings dam does not require you to report to the NPI. However, leakage and other emissions (including dust) from a tailings storage facility are reportable. (See also Section Three of the NPI Guide.)

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.
Copper sulfate is used in heap leach operations and may also be used as a flotation chemical. This substance is generally recycled with process water.

If xanthates are used in the solvent extraction process, they may be partly retained in the solvent and may, as a consequence, be associated with a water emission if the solvent is discharged from the facility to a watercourse.

**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. This method is inherently less accurate than the direct measurement method.

### 7.1.2 Discharge of Treated Process Waters

Smelters and refineries may 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 may then be recycled to the smelting or leaching process or can be sold. The resulting effluent can then be 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

In these calculations only discharges to surface water bodies should be considered.

Direct Measurement

Total nitrogen and total phosphorus loading 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

<table>
<thead>
<tr>
<th></th>
<th>kg per person per day</th>
<th>Indicative Facility Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total nitrogen</td>
<td>0.011</td>
<td>&gt;3500</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>0.0025</td>
<td>&gt;3000</td>
</tr>
</tbody>
</table>

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

**Equation 7.1**

\[
M_{\text{NorP}} = \overline{M}_{\text{NorP}} \times N_{\text{pers}} \times N_{\text{days}} \times \frac{1-E}{100}
\]

where:

- \(M_{\text{NorP}}\) = mass of total Nitrogen or Phosphorus emitted (kg)
- \(\overline{M}_{\text{NorP}}\) = average loading of Nitrogen or Phosphorus per person per day (kg/p/d)
- \(N_{\text{pers}}\) = average number of personnel on-site
- \(N_{\text{days}}\) = 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, or transfer to waste storage facility, of slag or jarosite; and
- Unintentional leaks and spills.

In relation to the copper concentrating, smelting and refining industry, discharges to land such as TSFs, solid waste dumps and waste rock dumps are classed as transfers. Heap leaching of copper ore involves piling the ore in heaps on a prepared impervious base and then leaching with sulfuric acid. 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 or leach heaps would be suited to this approach.
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 displays a typical arrangement for bore hole placement, it should be noted that alternative recovery systems (such as trenches) might 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**

\[ Y_{TSF} = A_{inf} \times K_{hyd} \times \Psi_{hyd} \]

where:

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

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

**Equation 8.2**

\[ Y_{emit} = Y_{TSF} - V_{H2O} \]

where:

- \( Y_{emit} \) = emitted hydraulic loading \( (m^3/\text{day}) \)
- \( Y_{TSF} \) = TSF hydraulic loading \( (m^3/\text{day}) \)
- \( V_{H2O} \) = volume of recovered water \( (m^3/\text{day}) \)

The emission of NPI substances is then estimated.

**Equation 8.3**

\[ M = C_B \times Y_{emit} \times T \]

where:

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

### 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 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](image_url)

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 m³.*

*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 and heap leach pads;
- As dust; and
- As a result of TSF overflow.

The mass balance approach may be utilised to estimate emissions of metals in a manner similar to that used to estimate the emission of cyanide through seepage.

While these seepage rates will be facility-specific, generic seepage rates of between 0 - 10% of return water or heap leach liquors have been quoted within the industry (Mt Keith Nickel 1996, ANCOLD, pers. comm.).

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 or dump/heap leach liquors; and
- The retention of NPI metals by the TSF or pad liner or under-liner. If this is not known, assume retention is nil.

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

**Equation 8.4**

\[ M_M = C_M \times V_{slurry} \times \frac{V}{100} \]

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 are known Darcy’s Law may be applied to calculate hydraulic loadings to the environment. Darcy’s Law is most applicable where an impermeable membrane has not been installed as part of the TSF design. Where an impermeable membrane has been installed, but seepage is known to be occurring, Darcy’s Law may be applied where facilities can estimate the surface area of the liner where its integrity has been compromised.
Equation 8.5

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

where:

- \( V_{\text{seepage}} \) = volume of calculated seepage \( (m^3/\text{day}) \)
- \( K \) = vertical permeability of TSF floor material \( (m/\text{day}) \)
- \( A \) = 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 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

\[ E_M = V_{\text{seepage}} \cdot N_{\text{days}} \cdot C_M \]

where:

- \( E_M \) = emission of the metal \( (kg) \)
- \( V_{\text{seepage}} \) = as above \( (m^3/\text{day}) \)
- \( N_{\text{days}} \) = number of days TSF operated \( (\text{days}) \)
- \( C_M \) = 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 or heap leach liquors;
- 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 is 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

\[ M_{M\text{-seepage}} = M_{M\text{-bore}} - C_{M\text{-bore}} \cdot V_{\text{bore-water}} \]

where:

- \( M_{M\text{-seepage}} \) = 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 \( (kg/m^3) \)
- \( V_{\text{bore-water}} \) = volume of recovered bore water \( (m^3) \)
9.0 Examples of Application of EETs

9.1 Sulfur Dioxide

9.1.1 Background

As there are considerable quantities of sulfur in the copper sulfide ores (Section 2.1), significant sulfur dioxide (SO\textsubscript{2}) emissions occur at various processes associated with primary copper smelting. Recovery of this SO\textsubscript{2} is good environmental practice and may be economically beneficial. Typically the hot gases are usually captured and piped to an acid plant for the manufacture of sulfuric acid. The smelter at Mt Isa currently discharges direct to atmosphere but this will change in the coming year when the smelter gases will be used for sulfuric acid production. Fuel combustion products also contribute to emissions from smelting furnaces.

The use of a sulfuric acid plant to treat copper smelter effluent gas streams requires that particulate-free gas streams with a steady SO\textsubscript{2} concentration of at least three-percent be maintained.

In some plants, SO\textsubscript{2} bearing gases may be also collected from the anode furnaces during some parts of the refining cycle, and these gases are also directed to the acid plant. The remaining smelter operations process material containing very little sulfur, resulting in insignificant SO\textsubscript{2} emissions. Particulate may be emitted from fire-refining operations. Electrolytic refining emissions are negligible.

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 emissions and the discussion below is based on this. The following techniques can be used to estimate the amount of SO\textsubscript{2} emitted.

9.1.2 Direct Measurement

Direct measurement (or source monitoring) is one of the most accurate methods of estimating emissions of SO\textsubscript{2}. Usually, SO\textsubscript{2} emissions are measured at the stack exit points. The gas is emitted from the main furnace eg. Noranda furnace, flash furnace, as well as from converter or subsequent furnace areas eg. anode furnace. All these areas also contribute to fugitive emissions.

Smelters may have stack-monitoring programs designed to meet environmental licence conditions. These conditions generally specify an amount of SO\textsubscript{2} that is not to be exceeded. Ambient SO\textsubscript{2} may also be measured to meet environment and health-related goals.

Elements of the processing of copper 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:

**Equation 9.1**

\[ M_{SO_2} = C_{SO_2} \times V_{SO_2} \times \left( \frac{273}{273+T} \right) \]

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 converter and 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, the diagram shows a simplified approach to SO$_2$ emissions from smelting 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 of the product (matte or anode copper) and waste (slag or slimes).

**Example 9.1 - Mass Balance Technique for Estimating SO₂**

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

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

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. The tonnage represents tonne SO₂ produced, or potential to produce.

**Figure 9.2 - Mass Balance SO₂ Calculations for Example 9.1**

<table>
<thead>
<tr>
<th>Inputs</th>
<th>=</th>
<th>Estimated Outputs</th>
<th>+</th>
<th>Assumed Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 + A2 + A3</td>
<td>=</td>
<td>(B + E + F)</td>
<td>+</td>
<td>(D + C) + Fugitives</td>
</tr>
<tr>
<td>167 570</td>
<td>=</td>
<td>(139 380)</td>
<td>+</td>
<td>(27 280) + Fugitives</td>
</tr>
<tr>
<td>Fugitives</td>
<td>=</td>
<td>167 570 - 166 660</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fugitives</td>
<td>=</td>
<td>910 tonnes of SO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus total amount of SO₂ released to air

\[ = \text{Waste gases} + \text{Acid Plant Gases} + \text{fugitive SO₂} \]

\[ = 27 280 + 910 \]

\[ = 28 190 \text{ tonnes SO₂} \]
9.2 Cyanide

9.2.1 Mass Balance

Sodium cyanide may be used in copper concentrating as an iron depressant, so that pyrite (FeS₂) can be separated from chalcocite (Cu₂S). The stable iron and copper cyanide complexes form on the mineral surfaces which remain in the slurry. In some plants that recover gold as a by-product, cyanide emissions may also result from gold refining operations. It is likely that most copper smelting and refining facilities will trigger the reporting threshold for cyanide.

The NPI requires that inorganic cyanide compounds be 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. This example includes all three emission media as the mass balance approach accounts for all input and output sources.

At Olympic Dam, residual cyanide in the tailings stream are neutralised with ferrous sulfide before being passed to the TSF.

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.

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. These emissions will be classed as emissions to land.

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

\[
MV_{CN} = M_{CN} + M_{CN\text{return}} - M_{CN\text{TSF}} - M_{CN\text{neut}} - M_{CN\text{seep}}
\]

where:

- \(MV_{CN}\) = mass of cyanide lost through volatilisation (kg)
- \(M_{CN}\) = mass of cyanide added to the process (kg)
- \(M_{CN\text{return}}\) = mass of cyanide in TSF return water (kg)
- \(M_{CN\text{TSF}}\) = mass of cyanide carried to TSF (kg)
- \(M_{CN\text{neut}}\) = mass of cyanide neutralised prior to TSF (kg)
- \(M_{CN\text{seep}}\) = mass of cyanide loss in seepage from TSF (kg)

Figure 9.3 - Cyanide Emissions

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% have been quoted within the industry (Mt Keith Nickel 1996, ANCOLD pers. comm. 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).

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**

\[
M_{\text{CNS}} = V_{\text{slurry}} \cdot \frac{V}{100} \cdot C_{\text{CN}}
\]

where:

- \(M_{\text{CNS}}\) = mass of cyanide emitted through seepage \((\text{kg})\)
- \(V_{\text{slurry}}\) = volume of water/slurry throughput to TSF per year \((\text{m}^3)\)
- \(V\) = seepage rate \((\%\)
- \(C_{\text{CN}}\) = concentration of cyanide \((\text{kg/m}^3)\)

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.
**Volutilisation**

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.

### 9.2.2 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 copper processing industry for the purposes of this manual.

Emissions should be reported as mass of CN⁻ using the stoichiometry detailed below:

**Equation 9.4**

\[
M_{CN^-} = M_{HCN} \times 0.54
\]

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 copper processing industry for the requirements of this manual.

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

This percentage degradation is 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

<table>
<thead>
<tr>
<th>pH</th>
<th>Percentage of Natural Degradation Due to Volatilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>90%</td>
</tr>
<tr>
<td>7</td>
<td>90%</td>
</tr>
<tr>
<td>8</td>
<td>80%</td>
</tr>
<tr>
<td>9</td>
<td>60%</td>
</tr>
<tr>
<td>10</td>
<td>20%</td>
</tr>
<tr>
<td>11</td>
<td>0%</td>
</tr>
<tr>
<td>12</td>
<td>0%</td>
</tr>
</tbody>
</table>

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

This data is applied using the equation below:

**Equation 9.5**

\[
MV_{\text{HCN}} = C_{\text{CN}} \times V_{\text{slurry}} \times V / 100
\]

where:

- \( MV_{\text{HCN}} \) = mass of HCN volatilised from TSFs (kg)
- \( C_{\text{CN}} \) = free cyanide concentration in TSF return water (kg/m\(^3\))
- \( V_{\text{slurry}} \) = 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 the Copper EET Manual and follows.

Sodium ethyl xanthate (SEX), C\(_2\)H\(_5\)OS\(_2\)Na, 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 xanthate adsorbs the stable iron and copper cyanide complexes that remain in the slurry. The majority of the SEX is retained within the froth, which contains the copper 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 copper 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 CS₂ 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 CS₂); and
- Hydrolytic decomposition (acidic conditions) of the xanthate ion results in a stoichiometry of 1:1 (xanthate to CS₂).

[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 copper 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. At Olympic Dam, where acid leaching is used to recover residual copper and also uranium, the tailings are acidic in nature.

As the first point of reference, it can be assumed that 100% degradation of xanthate occurs within the processing area, with 0.2% of the degraded xanthate producing carbon disulfide.

On this assumption CS₂ emission may be estimated using the following equations:

**Equation 9.6a**

*Alkali Conditions (pH>7):*

\[
\text{Moles of CS}_2\text{ emitted (kg)} = 0.5 \times 0.2\% \times \text{Mass of Xanthate} \times \frac{MW_{\text{CS}_2}}{MW_{\text{xanthate}}}
\]

**Equation 9.6b**

*Acidic Conditions (pH<7):*

\[
\text{Moles of CS}_2\text{ emitted (kg)} = 1.0 \times 0.2\% \times \text{Mass of Xanthate} \times \frac{MW_{\text{CS}_2}}{MW_{\text{xanthate}}}
\]
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 CS₂ are produced (alkali conditions).

Molecular weight of CS₂ (MW_{CS₂}) = 76g
Molecular weight of SEX (MW_{Xanthate}) = 144g

Emissions of CS₂ (kg) = 0.002 * 0.5 * Mass of Xanthate * \( \frac{MW_{CS₂}}{MW_{Xanthate}} \)
= 0.002 * 0.5 * 150 kg * 76 g/144 g
= 0.08 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. The results of these efforts are evident in the introduction of new processing methods such as the collection of SO₂-bearing gases from anode furnaces, and passing these gases to the acid plant together with the smelter gases.

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

1. **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 and the treatment of anode slimes. 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).

2. **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.

3. **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 copper processing industry are considered in the following section. These technologies in some companies are combined with environmental management systems to reduce the overall adverse environmental impact of copper 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, and for example sulfur dioxide is measured at the stack, not the site boundary. The three main components of air emission produced at a copper 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 and Heap Leach Pads

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.

Heap leach pads may also have a problem with carry-over of sulfuric acid mist:

- Ensure acid distribution systems do not generate fine spray; and
- Make the lined area with collector drains sufficiently larger than the pad area to collect as much acid mist carry-over as possible.

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.
**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 materials 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.

**Leaching**

- Cover leach pit to minimise evaporation of acid;
- Moisten ore before filling the pit; and
- Vent all tank house gases through a scrubber to remove sulfuric acid before release to atmosphere.

**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 mechanism. 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:

- Internal roads that are not sealed should be dampened regularly, or alternatively treated with dust suppression chemicals or oils (subject to EPA approval);
- Sealed internal roads should be regularly cleaned and washed, 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. Copper 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 directly 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 of tailings dams to minimise ground-water contamination;
- Interception trenches and recovery of contaminated groundwater for onsite 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

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>C</td>
<td>Capacity</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>DCAP</td>
<td>Double Contact Acid Plant</td>
</tr>
<tr>
<td>DoME</td>
<td>Department of Minerals and Energy</td>
</tr>
<tr>
<td>DM</td>
<td>Direct Measurement</td>
</tr>
<tr>
<td>EC</td>
<td>Engineering Calculation</td>
</tr>
<tr>
<td>EEA</td>
<td>European Environment Agency</td>
</tr>
<tr>
<td>EET</td>
<td>Emission Estimation Technique</td>
</tr>
<tr>
<td>EF</td>
<td>Emission Factor</td>
</tr>
<tr>
<td>EFR</td>
<td>Emission Factor Rating</td>
</tr>
<tr>
<td>EPA</td>
<td>Environment Protection Authority</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic Precipitator</td>
</tr>
<tr>
<td>GF</td>
<td>Generic Factor</td>
</tr>
<tr>
<td>INV</td>
<td>Inventory</td>
</tr>
<tr>
<td>kW</td>
<td>kilowatts</td>
</tr>
<tr>
<td>m³</td>
<td>cubic meters</td>
</tr>
<tr>
<td>MIC</td>
<td>Mitsubishi Converting Furnace</td>
</tr>
<tr>
<td>MSDS</td>
<td>Material Safety Data Sheets</td>
</tr>
<tr>
<td>NEPM</td>
<td>National Environment Protection Measure</td>
</tr>
<tr>
<td>NOI</td>
<td>Notice of Intention</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Oxides of Nitrogen</td>
</tr>
<tr>
<td>NPI</td>
<td>National Pollutant Inventory</td>
</tr>
<tr>
<td>PAH</td>
<td>Polyaromatic Hydrocarbons</td>
</tr>
<tr>
<td>PM₁₀</td>
<td>Particles that have an aerodynamic diameter equal to or less than 10 micrometers</td>
</tr>
<tr>
<td>SCAP</td>
<td>Single Contact Acid Plant</td>
</tr>
<tr>
<td>SI</td>
<td>Systeme Internationale</td>
</tr>
<tr>
<td>TSP</td>
<td>Total Suspended Particulate</td>
</tr>
<tr>
<td>TSF</td>
<td>Tailings Storage Facility</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>WA</td>
<td>Western Australia</td>
</tr>
</tbody>
</table>
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. BPEMIM, Tailings Containment (1995), Best Practice Environmental Management in Mining series, 'Tailings Containment', EPA


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


15. Inhalable Particulate Source Category Report For the Nonferrous Industry, Contact 68-02-3159, Acurex Corp. Mountain View, CA, August 1986

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


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


### 12.2 References Not Cited


Appendix A - Sources ofExisting Data

Existing Data

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

The 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;
- Sulfur trioxide/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, heap leach pads, and TSFs is suspected monitoring of bore holes may also be undertaken. Parameters may be expressed as soluble or total, and may include:

- pH;
- Conductivity and TDS;
- Standing water level; and
- Metals.
This data may be used:

- Directly where NPI substances are being monitored and reported;
- Indirectly such as dust monitoring where speciation of the dust component may be required; and
- Relationally where the ratio of a monitored parameter can be related to the emissions of an NPI substance.

### A4 Approvals Data

Copper 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 copper 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 copper 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.

### Table A1 - Inventory of a Copper Processing Facility

<table>
<thead>
<tr>
<th>INPUTS</th>
<th>Units</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>...</th>
<th>Dec</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonnes of ore treated</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper production</td>
<td>kg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Cyanide</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quicklime (78% CaO)</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(88% CaO)</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flocculent</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antiscalant</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>litres</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grinding balls</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>kWh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LP Gas</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caustic soda</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potable Water</td>
<td>kl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bore Water Total</td>
<td>kl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decant Water from TSFs</td>
<td>kl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSF dewatering system</td>
<td>kl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSF decant return</td>
<td>kl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSF underdrainage</td>
<td>kl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>