National Pollutant Inventory

Emission Estimation Technique Manual

for

Lead-Acid Battery Manufacturing

First published in June 1999

EMISSION ESTIMATION TECHNIQUES
FOR
LEAD-ACID BATTERY MANUFACTURING

TABLE OF CONTENTS

LEAD-ACID BATTERY MANUFACTURING

LIST OF FIGURES AND TABLES

1.0   Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI).   This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in lead-acid battery manufacturing.

EET MANUAL: Lead Acid Battery Manufacturing

HANDBOOK: Battery Manufacturing

ANZSIC CODES :   2853

This Manual was drafted by the NPI Unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government.   It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

2.0 Processes and Emissions

This section provides a brief description of the processes of lead-acid battery manufacturing and identifies likely emission sources of NPI-listed substances.

2.1   Process Description

The lead-acid battery industry is divided into three main sectors: starting, lighting and ignition (SLI) batteries, industrial batteries, and traction batteries. SLI batteries are primarily used in motor vehicles. Industrial batteries include those used for uninterrupted power supply and traction batteries are used to power electric vehicles such as forklifts.

Lead-acid storage batteries are produced from lead alloy ingots and lead oxide. Figure 1 provides an overview of the battery manufacturing process, which is described below.

Battery grids are manufactured either by casting molten lead into moulds, or cutting or stamping lead sheets. The pastes used to fill the grids are a mixture of lead oxide powder, water and sulfuric acid for the positive paste, and the same ingredients in slightly different proportions with the addition of an expander (generally a mixture of barium sulfate, carbon black and organics) for the negative paste. Pasting machines force these pastes into the interstices of the grids, which are made into plates. Plates are cured for a number of days at a temperature of between 30 and 40°C and a relative humidity of 90 percent. During the setting process, crystals of lead sulfate form throughout the mass.

The plates are then stacked in alternating positive and negative positions, with insulators between them. Leads are welded to tabs on each positive and negative plate or in an element during the burning operation. Alternatively, a cast-on connection is used, where positive and negative tabs are independently welded to produce an element. The battery is then charged using either a wet or dry formation process.

In the manufacture of traction batteries, sub-assemblies of lead spines with tubular bags are filled with lead oxide powder using a combination of high frequency and low frequency vibration. Sealed tubes are placed in a solution of diluted sulfuric acid for approximately two hours, then held in a curing chamber for a number of hours. After curing, the plates are pressed and the negative and positive plates are placed alternately in a jig. Terminal posts are attached, then the battery is assembled. After assembly, the cells are charged using a wet formation process.
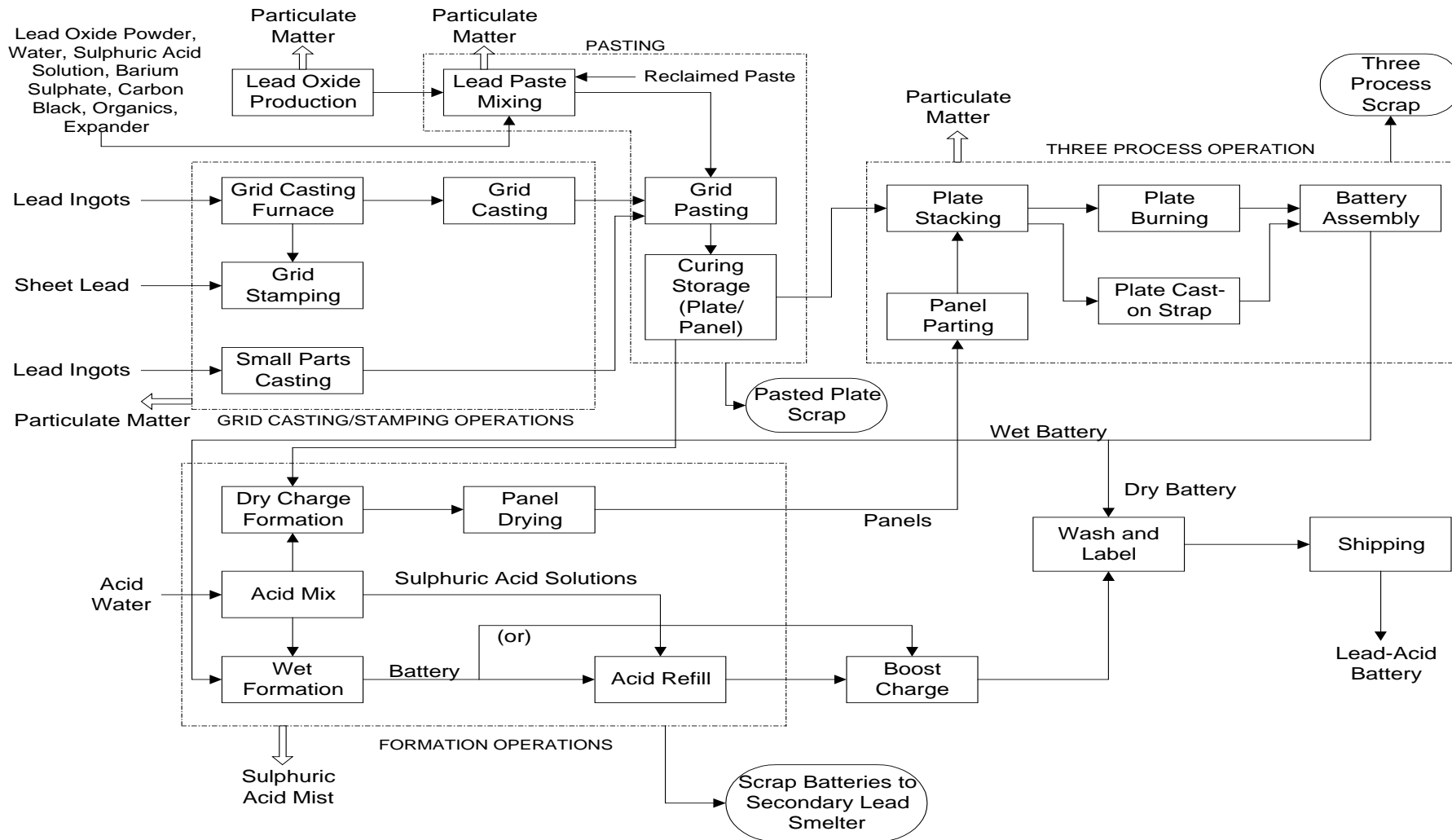
Figure 1 - Basic Process Steps for Battery Manufacturing
Source: USEPA AP-42, 1995.

2.2 Emission Sources and Control Technologies

The following section provides a general description of NPI-listed substances likely to be emitted from lead-acid battery manufacturing facilities. However, you should refer to the full list of reportable substances in the NPI Guide to determine if your facility handles any other substances not discussed in this document.

2.2.1 Emissions to Air

Air emissions may be categorised as:

Fugitive Emissions

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include volatilisation of acids from open vessels, particulate or lead emissions from casting or stamping processes, or spills and materials handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions. Emission factor EETs are the usual method for determining losses through fugitive emissions.

Point Source Emissions

These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere. The most likely listed substances to be emitted from the lead-acid battery manufacturing process are particulate matter (PM_{10}), lead, sulfuric acid and some trace metals.

Air emission control technologies, (eg. electrostatic precipitators, fabric filters or baghouses, and wet scrubbers), are commonly installed to reduce the concentration of substances in process off-gas before stack emission. Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been used in emission estimation, the collection efficiency of the abatement equipment needs to be considered. Guidance on applying collection efficiencies to emission factor equations is provided in later sections.

With regards to emission controls for PM_{10}, in the absence of measured data, or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 90% should be used in the emission factor equation to calculate actual mass emissions. This default should only be used if there is no other available control efficiency.

2.2.2 Emissions to Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

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 water monitoring data exists, emissions to water can be calculated based on a mass balance, engineering calculation or using emission factors. The substance most likely to be emitted to water from a lead-acid battery manufacturing facility is lead.

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.*)

2.2.3 Emissions to Land

Emissions of substances to land on-site include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids and may contain listed substances. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries; and
- unintentional leaks and spills.

3.0 Emission Estimation Techniques

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

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

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

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; and
- emission factors.

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

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

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this handbook does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

> **You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site-specific emission factors, you may use these if approved by your relevant environmental authority.**

You should note that the EETs presented in this manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie. the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

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.

3.1   Direct Measurement

You may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement. For the sampling data to be adequate and able to be used for NPI reporting purposes, it would need to be collected over a period of time, and to be representative of operations for the whole year.

3.1.1   Sampling Data

Stack sampling test reports often provide emissions data in terms of kilograms per hour or grams per cubic metre (dry standard). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative (ie. normal) operating conditions. You should be aware that some tests undertaken for a State or Territory licence condition may require the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions.

Equation 1 can be used to estimate emissions of a substance to the atmosphere from battery manufacturing processes using facility-specific sampling data.

Equation 1
$$E_{kpy,i} = (C_i/10^6) * Q * (OpHrs * 3\ 600) * [273 / (273 + T)]$$

where:

$E_{kpy,i}$	=	annual emissions of substance "i", kg/yr
C_i	=	concentration of substance "i" in the gas stream, mg/m^3
Q	=	volumetric flow rate of dry gas, m^3/sec – converted to STP (standard temperature & pressure ie. 0°C & 101.3 kPa)
OpHrs	=	total hours the plant operates per year, hr/yr
T	=	temperature of the gas sample, °C
3 600	=	conversion factor, sec/hr
10^6	=	conversion factor, mg/kg.

Table 1 shows typical sampling data results for lead emissions from Australian lead-acid battery manufacturing facilities. This data may be used with Equation 1 to estimate lead emissions where facility-specific sampling data is unavailable.

Table 1 - Lead Emissions from a Battery Manufacturing Facility

Source	Flow Rate (m^3/sec)	Lead Concentration (mg/m^3)
Oxide mill	2	0.1
Main Extraction	5	0.03
Tubefilling	1	0.02

Source: Queensland Department of Environment and Heritage, 1998.

Example 1 illustrates the application of Equation 1 using the test sampling results from Table 1 and calculates annual lead emissions to atmosphere.

Example 1 - Estimating Pb Emissions Using Sampling Data

A lead-acid battery manufacturer is required to monitor workplace lead emissions as part of its environmental licensing requirement. Table 1 displays the results of sampling undertaken by the facility during the reporting year. The facility operated for 5 760 hours during the reporting year and the sampling temperature was 25° C.

Lead emissions can be estimated from application of Equation 1.

$E_{kpy,Pb}$ = $(C_{Pb}/10^6) * Q * (OpHrs * 3\,600) * [273 / (273 + T)]$

$E_{kpy,Pb}$ (oxide mill) = $(0.1/10^6) * 2 * (5\,760 * 3\,600) * [273 / (273 + 25)]$
= 3.80 kg Pb/yr

$E_{kpy,Pb}$(main extraction)= $(0.03/10^6) * 5 * (5\,760 * 3\,600) * [273 / (273 + 25)]$
= 2.85 kg Pb/yr

$E_{kpy,Pb}$ (tubefilling) = $(0.02/10^6) * 1 * (5\,760 * 3\,600) * [273 / (273 + 25)]$
= 0.38 kg Pb/yr

$E_{kpy,Pb}$ (total) = $E_{kpy,Pb}$ (oxide mill) + $E_{kpy,Pb}$ (main extraction) + $E_{kpy,Pb}$ (tubefilling)
= 3.8 + 2.85 + 0.38
= 7.03 kg Pb/yr

3.1.2 Continuous Emission Monitoring System (CEMS) Data

A continuous emission monitoring system provides a continuous record of emissions over time, usually by reporting pollutant concentration.

Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that pollutant.

You should note that prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data so that the estimate satisfies your relevant environmental authority's requirement for NPI emission estimations.

3.2 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.

3.3 Engineering Calculations

An engineering calculation is an estimation method based on physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

Sulfuric acid emissions from lead-acid battery manufacturing can be estimated by calculating acid concentrations from sulfur trioxide concentrations measured from emissions from the battery charging area. This is based on the assumption that all sulfur trioxide is converted to sulfuric acid. Equation 2 illustrates this calculation.

Equation 2

$$C_{H2SO4} = C_{SO3} * (MW_{H2SO4}/MW_{SO3})$$

where:

C_{H2SO4} = concentration of sulfuric acid (H_2SO_4), g/m^3 or ppm
C_{SO3} = concentration of sulfur trioxide (SO_3), g/m^3 or ppm
MW_{H2SO4} = molecular weight of sulfuric acid, $g/g\text{-mole}$
MW_{SO3} = molecular weight of sulfur trioxide, $g/g\text{-mole}$

Example 2 shows the application of Equation 2.

Example 2 - Conversion of Sulfur Trioxide (SO_3) Concentrations to Sulfuric Acid (H_2SO_4) Concentrations

A lead-acid battery manufacturing facility measures annual average sulfur trioxide concentration of 2 milligrams per cubic metre from a stack servicing the battery charging area. Using Equation 2, sulfuric acid concentrations can be estimated as follows:

$$C_{H2SO4} = C_{SO3} * (MW_{H2SO4}/MW_{SO3})$$
$$= 2 * (98.06/80.06)$$
$$C_{H2SO4} = 2.45 \text{ mg } H_2SO_4/m^3$$

Annual emissions of H_2SO_4 can now be estimated by application of Equation 1.

3.4   Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source to some common activity associated with those emissions.   Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted divided by the unit weight, volume, distance, or duration of the activity emitting the substance (eg. kilograms of lead emitted per 1 000 batteries produced).

Emission factors are used to estimate a facility's emissions by the application of Equation 3.

Equation 3

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

where:

$E_{kpy,i}$ =   emission rate of pollutant i, kg/yr
A =   activity rate, 1000 batteries/yr
EF_i =   uncontrolled emission factor of pollutant i, kg/1000 battery
CE_i =   overall control efficiency for pollutant i, %.

Emission factors developed from measurements for a specific process may sometimes be used to estimate emissions at other sites. If a company has several processes of similar operation and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources.

Example 3 illustrates the application of Equation 3.

Example 3 - Calculating Lead Emissions Using Emission Factors

Using an emission factor from Table 2 with Equation 3, annual lead emissions from a 3-process operation (plate stacking, burning, and battery assembly) can be calculated. A lead-acid battery manufacturer produces 500 000 batteries a year, which would be equivalent to an activity rate "A", from equation 3, of 500 x 1000 batteries per year. From the emissions factors in Table 2, the midpoint value for lead emissions from the 3-process operation was chosen as the most representative of an average battery manufacturing facility.   The facility has a fabric filter installed to treat stack emissions before being exhausted to the atmosphere.   The fabric filter has an efficiency of 99 % for lead removal from the exhaust stream.

$$
\begin{aligned}
E_{kpy,Pb} \quad &= \quad A * EF_i * [1 - (CE_i / 100)] \\
&= \quad 500 * 5.7 * [1 - (99 / 100)] \\
&= \quad 28.5 \text{ kg Pb/yr}
\end{aligned}
$$

Table 2 - Emission Factors for Particulate Matter, Lead and Sulfur Acid from Storage Battery Production

Process	Emission Factor (kg/1000 batteries)[a,d]			
	Particulate[c]	Lead	Sulfuric Acid	Emission Factor Rating
Grid casting	0.8 - 1.42	0.35 - 0.4	NA	B
Paste mixing	1.00 - 1.96	0.50 - 1.13	NA	B
Lead oxide mill (baghouse outlet)	0.05 - 0.1	0.05	NA	C
3-Process operation	13.2 - 42	4.79 - 6.60	NA	B
Lead reclaim furnace[b]	0.7 - 3.03	0.35 - 0.63	NA	B
Dry formation[e]	NA	ND	14 - 14.7	B
Small parts casting	0.09	0.05	NA	C
Total production	56.82 - 63.2	6.94 - 8	ND	NA

Source: USEPA AP-42, 1995. NA - not applicable. ND - no data available.

[a] Factor units are kg of substance emitted per 1000 batteries produced.

[b] Lead reclaim furnace emission factor range due to variability in lead scrap quality.

[c] Emission factors are for total particulate emissions. A particulate size characterisation analysis of particulate matter from your facility will be required to determine PM_{10} emissions.

[d] Emission factor ranges presented reflect a varying degree of emission controls. "State-of-the-art" facilities may choose the lower range, whereas facilities with few pollution control devices should choose the higher range. In most instances, the midpoint value should be used.

[e] For sulfates in aerosol form, this factor may be considered sulfuric acid emissions. Emission factor does not account for water and other substances that might be present.

4.0 Emission Estimation Techniques: 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 National Pollutant Inventory 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 battery manufacturing facilities. The technique chosen is dependent on available data, 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 the emission factors presented in Section 3.4. of this Manual.

4.1 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 battery manufacturing 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 of batteries.

In the case of CEMS, instrument calibration drift can be problematic and uncaptured data can create long-term incomplete data sets. However, it may be misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment and the corresponding emissions data.

4.2 Mass Balance

Calculating emissions from a battery manufacturing facility using mass balance appears to be a straightforward approach to emission estimations. However, a mass balance requires facilities to consistently track material usage and waste generation with a considerable degree of accuracy. Inaccuracies associated with individual material tracking or other activities inherent in each material handling stage can result in large deviations of 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.

4.3 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from battery manufacturing processes. 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.

4.4 Emission Factors

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 Section 5.0 of this Manual. The emission factor ratings <u>will not</u> form part of the public NPI database.

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

The EFR system is as follows:

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

5.0 References

National Pollutant Inventory Homepage
http://www.npi.gov.au

USEPA, January 1995, *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 12, Metallurgical Industry,* United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA.
http://www.epa.gov/ttn/chief/ap42.html

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

- Emission Estimation Technique Manual for Combustion Engines.