

SNAP CODE:	030305
SOURCE ACTIVITY TITLE:	PROCESSES WITH CONTACT <i>Primary Zinc Production</i>
NOSE CODE:	104.12.06
NFR CODE:	1 A 2 b / 2 C 5
ISIC:	2420

1 ACTIVITIES INCLUDED:

The activities relevant for the primary zinc production are:

- Transport and storage of zinc ores
- Concentration of zinc ores
- Oxidation of zinc concentrates with air (roasting process)
- Production of zinc by the electrochemical or the thermal process
- After-treatment of zinc

A description of the process together with a brief description of the associated process steps (e.g. sintering) is provided in Section 3. Detailed descriptions of the associated process steps can be found in chapter B331.

2 CONTRIBUTION TO TOTAL EMISSIONS:

The contribution of gaseous emissions released from primary zinc production to total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]											
		SO ₂	NO _x	NMVOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃	TSP*	PM ₁₀ *	PM _{2.5} *	
Primary Zinc Production	030305												
Typical contribution		0.1	-	-	-	0	-	-	-	-	0.046	0.083	0.104
Highest value											0.116	0.194	0.236
Lowest value											0.001	0.002	0.002

* EU PM_{2.5} Inventory project for EU25 for the year 2000 (TNO, 2006), contribution to total national emissions, excluding agricultural soils

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

The contribution of heavy metal emissions from primary zinc production to the total heavy metal emissions, according to IWAD [9], are given in Table 2.2.

Table 2.2: The contribution of heavy metal emissions from primary zinc production to the total emissions of the IWAD study [9]

Contribution to total emissions (%)					
Cd	Cr	Cu	Ni	Pb	Zn
18.0	0	0	0	0.7	25.6

0 = emissions are reported, but the exact value is below the rounding limit

3 GENERAL

3.1 Description of activities

Primary zinc is produced from ores which contain 85 wt% zinc sulphide and 8-10 wt% iron sulphide (zinc concentration about 50 wt%). The ores also contain metal sulphides such as lead, cobalt, copper, silver, cadmium and arsenic sulphide.

The ores are oxidized with air giving zinc oxide, sulphur oxide and zinc ferro. Chlorine and fluorine are removed from the combustion gas and the sulphur oxide is converted catalytically into sulphuric acid.

The electrochemical zinc production process

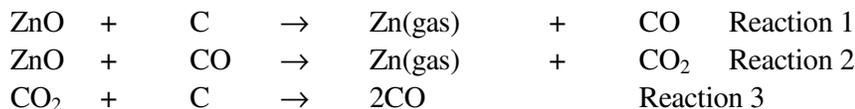
The roasted ores are leached in electrolytic cell acid. The zinc oxide dissolves in the acid solution, but the zinc ferro does not. After a separation step the raw zinc sulphate solution goes to the purification process and the insoluble matter to the jarosite precipitation process.

In the jarosite precipitation process, the insoluble matter of the roast is in good contact with ammonia and iron containing solution (contains also zinc and other metals) from the second leaching process. The iron precipitates, forming the insoluble ammoniumjarosite $[(NH_4)_2Fe_6(SO_4)_4(OH)_{12}]$. After separation the zinc containing solution goes to the first leaching process and the insoluble matter to a second leaching process. The insoluble matter is contacted in the second leaching process with a strong acid solution. The zinc ferro and almost all the other metals dissolve in the strong acid solution. After separation the zinc and iron containing solution is returned to the jarosite precipitation process where the iron and the insoluble matter are removed.

The raw zinc sulphate solution from the first leaching process is purified by adding zinc dust. Because of the addition of the zinc dust the metals copper, cobalt and cadmium are precipitated as metal. After filtration of the purified zinc sulphate solution the zinc electrolytic is separated from the solution. The electrolytically produced zinc sheets are melted in induction ovens and cast to blocks. The zinc alloys can also be produced by adding low concentrations of lead or aluminium.

The thermal smelting zinc production process

Roasted zinc is heated to a temperature of about 1100 °C (temperature > boiling point is needed) in the presence of anthracite or cokes. At that temperature zinc oxide is reduced and the carbon monoxide is formed from the carbon source. The carbon monoxide reacts with another molecule of zinc oxide and forms carbon dioxide:



Because reaction 2 is reversible (at lower temperatures zinc oxide is reformed) the concentration of carbon dioxide has to be decreased. The concentration of carbon dioxide is decreased by reaction with the carbon source.

The vaporized zinc is condensed by external condensers.

3.2 Definitions

Zinc concentrate	Enriched zinc ores which contain 85 wt% zinc sulphide and 8-10 wt% iron sulphide. The overall zinc concentration is about 50 wt%.
Roasting process	The zinc concentrate is oxidized, converting the zinc sulphide to zinc oxide, and partly to zinc ferro. The off-gas contains sulphur dioxide and traces of chlorine, fluorine and mercury. These compounds are removed by an air cleaning process (sulphur dioxide is converted into sulphuric acid). The solid product of the roasting process is called roast good.
First leaching process	The leaching process is the dissolving of the zinc oxide in an acid solution. The insoluble matter is separated and transported to the jarosite precipitation process.
Jarosite precipitation process	During the jarosite precipitation process the dissolved iron is precipitated. The iron is converted to ammoniumjarosite which does not dissolve in strong acid solution. The solution is transported back to the first leaching process and the insoluble matter (ammoniumjarosite, zinc ferro and other metals) is transported to a second leaching process.
Second leaching process	The insoluble matter of the jarosite precipitation process is contacted with a strong acid solution. The zinc ferro and several metals dissolve in the acid solution, but the jarosite does not. The solution with dissolved zinc and metals is transported back to the jarosite precipitation process and the insoluble matter is removed from the process (jarosite).

Purification process	During the purification process the traces of metal pollution in the zinc sulphate solution are removed by adding zinc dust. These metals would disturb the electrolytic separation of the zinc and decrease the quality of the electrolytic precipitate. The metals are removed by filtration from the purified zinc sulphate solution.
Electrolytic zinc production	Zinc is electrolytically separated from the purified zinc sulphate solutions. The zinc precipitates on the electrodes and can be removed as zinc sheets.
Thermal smelting process	Roasted zinc concentrates are melted at about 1100 °C in the presence of a carbon source. Zinc oxide is reduced to zinc and vaporized.
Zinc condensation	Vaporized zinc is condensed in several traps.
Casting process	The zinc sheets are melted and the zinc melt is casted in blocks which are suitable for transport.

3.3 Emissions

The emissions of particulate matter and heavy metals (zinc and cadmium) take place during the receipt and storage of the zinc ores and during the production. The receipt and storage of the zinc ore take place under a covering to reduce the emission. The emissions during production occur from tanks, ovens and separation equipment. These emissions can be decreased by changing some constructions.

The emission to the atmosphere by the thermal smelting process can be decreased by cleaning the condensed air. The thermal smelting production process leads to increased emission of metals.

Pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic gaseous compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O), and ammonia (NH₃). According to CORINAIR90 the main relevant pollutant is SO₂ (see also table 2.1).

Each of the two smelting processes (externally heated, electrothermic reduction) generates emissions along the various process steps. More than 90 % of the potential SO₂ emissions from zinc ores is released in roasters (for details see chapter B331). About 93 to 97 % of the sulphur in the feed is emitted as sulphur oxides. Concentrations of SO₂ in the off-gas vary with the type of roaster operation. Typical SO₂ concentrations for multiple hearth, suspension and fluidised bed roasters are 4.5 to 6.5 %, 10 to 13 % and 7 to 12 %, respectively [2].

Additional SO₂ is emitted from the sinter plant; the quantity depends on the sulphur content of the calcine feedstock. The SO₂ concentration of sinter plant exhaust gas ranges from 0.1 to 2.4 % [3].

3.4 Controls

Sulphur dioxide emissions from the roasting processes are often recovered at on-site sulphuric acid plants. No sulphur controls are used on the exhaust stream of sinter plants. Extensive desulphurisation before electrothermic retorting results in practically no SO₂ emissions from these devices [2,3].

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers¹:

- Tier 1: a method using readily available statistical data on the intensity of processes (“activity rates”) and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.
- Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.
- Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR} \times \text{EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

¹ The term “Tier” is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tiers 3), to estimate emissions of gaseous pollutants from the cement production is based on measurements or estimations using plant specific emission factors - guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

If detailed information about the local situation is available this should prevail over the use of general emission factors. Reference emission factors for comparison with users own data are provided in Section 8.2.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of primary zinc, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of cement produced by various types of industrial technologies employed in the zinc industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 "Choice of activity statistics".

7 POINT SOURCE CRITERIA

The primary zinc production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors for use with simpler methodology

Table 8.1: Emission factors for primary zinc production

Pollutant	Emission Factor	Emission Factor	Units
	<i>Limited control</i>	<i>Abatement</i>	
Arsenic	100	1	g/tonne zinc
Cadmium	100	50	g/tonne zinc
Copper	250	25	g/tonne zinc
Mercury	20	6	g/tonne zinc
Lead	500	150	g/tonne zinc
Zinc	7000	700	g/tonne zinc
Particulate matter*			
TSP		500	g/tonne zinc
PM ₁₀		400	g/tonne zinc
PM _{2.5}		300	g/tonne zinc

Source: Pacyna et al, 2002

* CEPMEIP emission factors for a conventional plant with ESP, settlers, scrubbers; moderate control of fugitive sources. See also table 8.2d for more details and explanation on the uncertainty.

8.2 Reference Emission Factors for Use With Detailed Methodology

The emission factor for ore handling is calculated with the following formula:

$$\text{Emission} = \{[\text{Mass}]_{\text{dust}} * [\text{Mass}]_{\text{ore}} * [\text{Metal composition}]_{\text{dust}}\} * [\text{Zinc}]_{\text{production}}^{-1} \quad [\text{Formula 1}],$$

where

[Mass] _{dust} :	Loss of mass during receipt of ore (weight percentage);
[Mass] _{ore} :	Yearly average received mass of zinc ores (tonnes);
[Metal composition] _{dust} :	Average weight percentage of metals in dust;
[Zinc] _{production} :	Total yearly produced mass zinc (tonnes).

The emission factor, summarizing all processes with vaporisation of heavy metal containing off-gas is calculated using:

$$\text{Emission} = \{\text{Flow}_{\text{gas}} * d * [\text{Metal composition}]_{\text{gas}}\} * [\text{Zinc}]_{\text{production}}^{-1} \quad [\text{Formula 2}],$$

where

[Flow] _{gas} :	Gas flow of a certain subprocess which emits heavy metals to air (m ³ *year ⁻¹);
d:	Duration of the period of emission of heavy metals to air (per subprocess) (year);
[Metal composition] _{gas} :	Average concentration of heavy metals in emitted gas (g m ⁻³ gas);
[Zinc] _{production} :	Total yearly produced zinc (tonnes).

The emissions can vary widely depending on the ore used and the abatement measures applied, see Table 8.2a for reported emission factors. The emission factors given in Table 8.2b were prepared for the PARCOM-ATMOS Emission Factors Manual 1992. The factors

for the emissions are based on the information from Table 8.2a. Table 8.2c contains fuel related emission factors for primary zinc production based on CORINAIR90 data in g/GJ unit. Technique related emission factors, mostly given in other units (e.g. g/Mg product) are listed in footnotes. Table 8.2d presents emissions factors from the CEPMEIP database on particulate matter emissions (TSP, PM₁₀ and PM_{2.5}) for three different type of plants, old, conventional and modern.

Table 8.2a: Emission factors for the primary zinc production (g.Mg⁻¹ product) as reported by several countries/authors

Compound	Germany [4]		Poland [5]		Netherlands [6]	Pacyna [7,8]	
	thermal	electrolytic	thermal	electrolytic	electrolytic	thermal	electrolytic
Cadmium	100	2	13	0.4-29	0.5	500 ¹⁾	0.2
Lead	450	1	31-1000 ²⁾	2.3-467	-	1900	-
Mercury	5-50	-	-	-	-	8	-
Zinc	-	-	420-3800	47-1320	120	16000	6

¹⁾ with vertical retort: 200 g/Mg product; with Imperial Smelting Furnace: 50 g/Mg product.

²⁾ limited abatement.

Table 8.2b: Proposed emission factors for primary zinc production (g/Mg product)

Substance	Emission factor	
	thermal	electrolytic
Cadmium	¹⁾	1
Lead	500	5
Mercury	20	-
Zinc	10000	100

¹⁾ depends on technology deployed (see Table 8.2a)

Table 8.2c: Emission factors for primary zinc production

				Emission factors					
Fuel		NAPFUE- code	SO ₂ ³⁾ [g/GJ]	NO _x ⁴⁾ [g/GJ]	NMVOC ⁵⁾ [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [g/GJ]
s coke	hc coke oven	107	463 ²⁾	35 ²⁾				105 ²⁾	
1 oil	residual	203	1,030-1,470 ¹⁾	150 ¹⁾			15 ¹⁾	76 ¹⁾	14 ¹⁾
1 oil	gas	204	1,410 ¹⁾	100 ¹⁾			12 ¹⁾	73 ¹⁾	

¹⁾ CORINAIR90 data, area sources (preliminary data)

²⁾ CORINAIR90 data, point sources (preliminary data)

³⁾ SO_x: [1] 2,145,000 g/Mg conc. ore multiple hearth roaster processed
 325 g/Mg conc. ore sinter shand processed
 565 g/Mg conc. ore vertical retort, electrothermal furnace processed
 202,200 g/Mg conc. ore flash roaster processed
 111,750 g/Mg conc. ore fluidised bed roaster processed
 17,209 g/m³ fuel primary metal production, process heaters, NAPFUE 204
 19,006 g/m³ fuel primary metal production, process heaters, NAPFUE 203
⁴⁾ NO_x: [1] 2,397 g/m³ fuel primary metal production, process heaters, NAPFUE 204
 6,591 g/m³ fuel primary metal production, process heaters, NAPFUE 203
⁵⁾ VOC: [1] 24 g/m³ fuel primary metal production, process heaters, NAPFUE 204
 34 g/m³ fuel primary metal production, process heaters, NAPFUE 203

Table 8.2d: Emission factors (kg/ton) for particulates for primary zinc production (CEPMEIP)

Technology	Abatement	TSP	PM ₁₀	PM _{2.5}	Uncertainty
Conventional plant	ESP, settlers, scrubbers; moderate control of fugitive sources	0,5	0,4	0,3	4
Modern plant (BAT)	fabric filters for most emission sources	0,2	0,18	0,16	4
Older plant	Limited control of fugitive sources	6	5	4	4

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in Table 8.2d): The uncertainty in the emission factor for PM_{2.5} from a conventional plant is 4. The emission factor with uncertainty range will therefore be 0.3 kg per tonne primary zinc with an uncertainty range of 0.075 (0.3/4) to 1.2 (0.3x4).

9 SPECIES PROFILES

Since the dust emissions are related to the profile of the ore an ore composition profile could be useful.

10 UNCERTAINTY ESTIMATES

The quality class of the emission factors is estimated to be about B.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The fuel specific emission factors provided in Table 2 are related to point sources and area sources without specification. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested to develop emission factors, which include technical or fuel dependent explanations concerning emission factor ranges.

12 SPATIAL DISAGGREGATION CRITERIA

Not applicable.

13 TEMPORAL DISAGGREGATION CRITERIA

Primary zinc production is usually a continuous process.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency
Compilation of air pollutant emission factors AP-42

PARCOM-ATMOS Emission Factors Manual

16 VERIFICATION PROCEDURES

Emissions might be verified by comparing calculated emissions with the composition profile of the ore.

17 REFERENCES

- 1 EPA (ed.): AIR Facility Subsystem, EPA-Doc. 450/4-90-003, Research Triangle Park, 1990

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- 5 Heavy metals emission to air in Poland for years 1980-1992, Hlawiczka, S., Zeglin, M., Koterska, A., Inst. Ecol. Ind. Areas, Report 0-2.081, Katowice, 1995 (in Polish)
- 6 Spindocument "Productie van primair zink"; Matthijsen, A.J.C.M., Meijer, P.J.; RIVM (reportnr. 736301113); november 1992 (in Dutch)
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- 11 Visschedijk, A.J.H., J. Pacyna, T. Pulles, P. Zandveld and H. Denier van der Gon, 2004, Coordinated European Particulate Matter Emission Inventory Program (CEPMEIP), In: P. Dilara et. Al (eds), Proceedings of the PM emission inventories scientific workshop, Lago Maggiore, Italy, 18 October 2004, EUR 21302 EN, JRC, pp 163 – 174

18 BIBLIOGRAPHY

No additional documents.

19 RELEASE VERSION, DATE, AND SOURCE

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TNO

The Netherlands

Supported by: Otto Rentz, Dagmar Oertel
University of Karlsruhe (TH)
Germany

Updated with emission factors (CEPMEIP) for particulates by:
Tinus Pulles and Wilfred Appelman
TNO
The Netherlands
May 2006

20 POINT OF ENQUIRY

Any comments on this chapter or enquiries should be directed to:

Pieter van der Most

HIMH-MI-Netherlands
Inspectorate for the Environment
Dept for Monitoring and Information Management
PO Box 30945
2500 GX Den Haag
The Netherlands

Tel: +31 70 339 4606
Fax: +31 70 339 1988
Email: pieter.vandermost@minvrom.nl