Combustion in the Manufacturing Industry

SNAP CODE : 030106

SOURCE ACTIVITY TITLE: **COMBUSTION IN BOILERS, GAS TURBINES & STATIONARY ENGINES**
Other Stationary Equipments

NOSE CODE:

NFR CODE: 1 A 2 a-f

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

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SNAP CODE: **030203**

SOURCE ACTIVITY TITLE: **PROCESS FURNACES WITHOUT CONTACT**
Blast Furnaces Cowpers

NOSE CODE: **104.12.01**

NFR CODE: **1 A 2 a**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from the industrial combustion of blast furnace gas in cowpers (cupolas).

Other emissions of blast furnaces are covered by the following SNAP-codes of the category “Processes in Iron and Steel Industries and Collieries”.

• Blast furnace charging	SNAP code 040202, see chapter B422
• Pig iron tapping	SNAP code 040203, see chapter B423

Figure 1 gives a key plan of a blast furnace process including a blast furnace cowper.

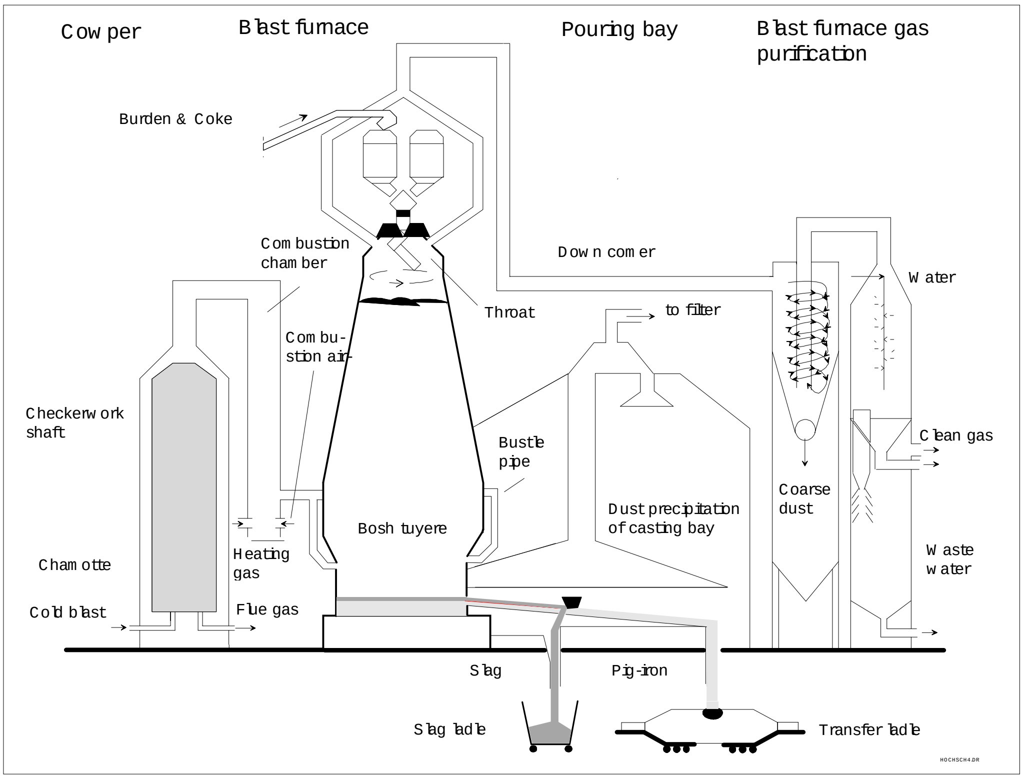

Figure 1: Flow diagram of the blast furnace process /cf. 9/

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from blast furnace cowpers to total emissions in countries of the CORINAIR'90 inventory is given as follows:

Table 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_2O	NH_3
Blast Furnaces Cowpers	030203	0.1	0.2	0	0	1.6	1.3	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

Here, the blast furnace is described as a whole in order to understand the role of the blast furnace cowpers within the overall process. Detailed information concerning emissions other than from blast furnace cowpers is given in chapters B422 and B423.

The blast furnace operates as a countercurrent process. Iron ore sinter and size-graded iron ore, coke and limestone are charged as necessary into the top of the furnace. Preheated air is introduced through a large number of water-cooled nozzles at the bottom of the furnace (tuyeres) and passes through the descending charge. Carbon monoxide is produced, which reacts with the heated charge to form molten high-carbon iron, slag and blast furnace gas. /2, 7/ The molten iron and slag are periodically discharged from tap holes.

3.2 Definitions

Blast furnace	refractory-lined shaft furnace. The ore and the preheated air (coming from the cowper) are charged countercurrently (see also section 3.3). In a blast furnace the iron ore is reduced to pig iron by using the reaction of coke (coming from the coke oven plant) and oxygen as energy source, producing CO as reduction agent (for further details see chapters B422 and B423).
Cowpers	process unit, which is fired by blast furnace gas for indirect preheating of air.

3.3 Techniques

Blast furnace gas (off-gas) released at the top of the furnace is collected and is used as fuel for the cowpers. Typical fuels used for the cowpers are natural gas, coke oven gas and blast furnace gas. But also liquid fuels can be used which require different types of burner. In some countries (e.g. Sweden) a blend of coke oven and blast furnace gas is used as fuel /5/.

In order to facilitate the combustion of blast furnace gas, dust removal is necessary. In most cases a cyclone and a one or two-stage cleaning device are installed. The primary cleaner is normally a wet scrubber which removes 90 % of the particulates. The secondary cleaner is normally a high-energy wet scrubber (usually a venturi) or an electrostatic precipitator. Cleaned blast furnace gas contains less than 0.05 g/m^3 of particulates. /2, 3/

3.4 Emissions

Blast furnace gas contains about 21 - 28 % CO, inert components (50 % N_2, 23 % CO_2), some sulphur compounds and high amounts of dust (from iron ore, sinter and coke) /cf. 7, 8/. CO_2 originates from the complete oxidation of carbon in the blast furnace. Some blast furnace cowpers use a blend of blast furnace gas and alternative fuels. The most common alternative is coke oven gas, but also natural gas can be used.

Relevant pollutants are carbon monoxide (CO) and carbon dioxide (CO_2). Sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and CH_4) and nitrous oxide (N_2O) are of less relevance. Emissions of dust which may contain heavy metals, are also of relevance /cf. 3/. Emissions of ammonia (NH_3) are not relevant. Emissions of carbon monoxide (CO) occur due to incomplete combustion of blast furnace gas components.

3.5 Controls

Due to the low relevance of SO_2 and NO_x emissions, reduction measures for these pollutants are normally not installed.

4/5 SIMPLER AND DETAILED METHODOLOGY

Both methodologies refer to the calculation of emissions based on emission factors and activities, which are jointly discussed in the following. The “simpler methodology” is considered as an overall approach, where activity data refer to production figures. The “detailed methodology” is considered as the recommended approach, where activity data concerning the fuel consumption in blast furnace cowpers is available in a plant specific way. The simpler and the detailed methodologies cover all relevant pollutants.

The annual emission is determined according to Equation (1) by an activity and an emission factor:

$$E_i = EF_i \cdot A \tag{1}$$

E_i annual emission of pollutant i
EF_i emission factor of pollutant i
A activity

The activity A and the emission factor EF_i have to be determined on the same level of aggregation by using available data. The CORINAIR90 methodology requires for blast furnace cowpers activity data, which is related to fuel consumption in [GJ/a].

4.1 Simpler methodology

The simpler methodology corresponds to an approach, which takes into account activity rates derived from data of comparable installations or from literature data. Here, it is assumed, that the required activity data (according to CORINAIR90) are not available (see Equation (1)). In practice, statistics (see also Section 6), which often provides only the production of pig iron in [Mg/a], have to be used.

In order to approximate activity data referring to the energy input into blast furnace cowpers in [GJ/a] the specific blast furnace gas consumption and the lower heating value have to be taken into account as given e.g. in Equation (2):

$$A_{COR} = F \cdot H_u \cdot A_{Stat} \tag{2}$$

A_{COR}	activity in CORINAIR-compatible unit (energy input [GJ])
F	specific blast furnace gas consumption (blast furnace gas/pig iron produced [m^3/Mg pig iron])
H_u	lower heating value of coke oven gas [GJ/m^3]
A_{stat}	activity directly obtained from statistics (pig iron production [Mg])

For the determination of the energy input only the gas consumption by the blast furnace cowpers has to be taken into account. The production of blast furnace gas can be given as about 1,300 to 2,000 m^3/Mg crude steel. About 25 % of the blast furnace gas obtained is used for the cowpers /4/. Country specific conditions have to be taken into account, e.g. one of the two Swedish iron and steel plants uses 46 % of the blast furnace gas produced and 18 % of the coke oven gas produced for combustion in cowpers /5/. Blast furnace gas has a lower heating value of about 2,790 to 3,350 kJ/m^3 /2/.

4.2 Detailed methodology

The detailed methodology corresponds to a plant specific approach, which takes into account as far as possible plant specific informations. Here, CORINAIR90 compatible activity data for blast furnace cowpers (related to the type of fuel consumed in [GJ/a]) are directly available (Equation (1)).

4.3 Emission factors

Emission factors for SO_2, NO_x, NMVOC and CH_4, CO, CO_2, and N_2O in mass pollutant/mass product [g/Mg] and in mass pollutant/energy input [g/GJ] are given in Table 2 (see section 8) based on literature data.

6 RELEVANT ACTIVITY STATISTICS

The following statistics for pig iron production can be used for the determination of the amount of blast furnace gas produced:

- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1994
- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992

Statistics concerning the fuel consumption of blast furnace cowpers are not available.

7 POINT SOURCE CRITERIA

Integrated iron and steel plants with a production capacity of more than 3 million Mg/a have to be treated as point sources according to the CORINAIR90 methodology. Blast furnace cowpers included in these integrated iron and steel plants have to be considered as parts of the point source.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 2 contains emission factors for blast furnace cowpers. Blast furnace cowpers are mostly fired by blast furnace gas; other types of fuel, which have been reported in CORINAIR90, are given in footnotes. A blend of blast furnace gas and coke oven gas is not taken into account.

Table 2: Emission factors for blast furnace cowpers

Type of fuel[1]			NAPFUE code	Emission factors						
				SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC[4] [g/GJ]	CH_4[4] [g/GJ]	CO[5] [g/GJ]	CO_2[3] [kg/GJ]	N_2O [g/GJ]
g	gas	natural	301	0.5 - 8[2]	15 - 50[2]	2.5 - 5[2]	2.5 - 5[2]	10 - 200[2]	55 - 56[2]	1.5 - 3[2]
g	gas	coke oven	304	12 - 25[2]	15 - 146[2]	2.5 - 6.2[2]	2.5 - 112[2]	10 - 70[2])	42 - 46[2]	1 - 3[2]
g	gas	blast furnace	305	0.93 - 56[2]	13 - 145[2]	5 - 6.2[2]	112[2]	10 - 69[2]	100 - 290[2]	1 - 3[2])

[1] The following fuels have been reported within CORINAIR90, but it can be assumed, that their relevance is very low:
sub-bituminous coal: NAPFUE 103; NMVOC 10; CH_4 10; CO 15; N_2O 12 [g/GJ][2]
coke oven coal: NAPFUE 107; NO_x 141; NMVOC 2; CH_4 0.03; CO 120; CO_2 15 10^3-108 10^3; N_2O 3 [g/GJ][2]
residual oil: NAPFUE 203; SO_2 223-305; NO_x 112-521; NMVOC 3; CH_4 3-112; CO 13-15; CO_2 76 10^3 -78 10^3; N_2O 2.8-14 [g/GJ][2]
gas oil: : NAPFUE 204; NMVOC 2.5-6.2; CH_4 2.5; CO 12; CO_2 74 10^3; N_2O 14 [g/GJ][2]

[2] CORINAIR90 data

[3] CO_2: 367 - 385 kg/Mg pig iron: conventional blast furnace (1989) /6/

[4] VOC: 198 g/Mg iron: conventional blast furnace, average /6/

[5] CO: 640 - 5,023 g/Mg product: conventional blast furnace process (1989) /6/

9 SPECIES PROFILES

Species profiles for oxides of sulphur and nitrogen are comparable to those released from combustion installations. Details can be found in chapter B111 “Combustion Plants as Point Sources” (section 9).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors and activities.

At this stage emission factors are only applicable when using 100 % blast furnace gas. Further work should be invested toward providing activity data for a representative split of the fuel gases used and in providing corresponding emission factors e.g. for a blend of blast furnace and coke oven gas. CORINAIR90 data can only be used in order to give a range of emission factors.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) would provide a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from blast furnace cowpers can be obtained by taking into account the

- time of operation, and
- variation of load depending on the demand for iron and steel.

Data for the annual time of operation in iron and steel plants should take into account that

- iron and steel plants produce during the whole year and blast furnace gas is continuously released.

Data for the variation in the demand for iron and steel can only be obtained directly from plant operators.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on “Concepts for Emission Inventory Verification” different verification procedures can be recommended. Verification procedures considered here are principally based on the verification of emission data on a national level and on a plant level.

Emission data for blast furnace cowpers can be verified on territorial unit level (e.g. national level) by comparing the annual emissions related to a territorial unit to independently derived emission estimates (e.g. obtained by using population equivalents). Another possibility is the use of emission density comparisons of e.g. emissions per capita or emissions per GDP between countries with comparable economic structures.
Verification on a plant level takes into account e.g. the number of blast furnace cowpers within the iron and steel plants considered. The verification on a plant level relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

17 REFERENCES

/1/ CITEPA (ed.): CORINAIR - Emission Factor Handbook; Paris; 1992

/2/ and US-EPA (ed.): Compilation of the Pollutant Emission Fraction; Version 1; Stationary Point Area Sources; 1986; AIR CHIEF Version 2.0 Beta; 1992

/3/ Economic Commission of Europe (ed.): Task Force on Heavy Metals Emissions; State-of-the-Art Report; Prague; 1994

/4/ Krumm, Wolfgang: Mathematische Modellierung und Optimierung der Energieverteilung im integrierten Hüttenwerk; in: Energieerzeugung VDI; Düsseldorf (Germany); 1989

/5/ Ms. Froste, Mr. Kvist, Mr. Lannerblom: Personal communication; 1995

/6/ Annema, J. A.; Albers, R. A. W.; Boulan, R. P.: Productie van Primair Ijzer en Staal; RIVM-report 736301131; RIZA-report 92.003/31; 1992

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/8/ Havenaar, P.; Santen, D. J.; Verrier, K.: Blast furnace gas fired co-generation plant; in: Combustion Technology 1994, VGB Technische Vereinigung der Großkraftwerkbetreiber e.V. (ed.), Essen (Germany); 1994

/9/ Rentz, O.; Püchert, H.; Penkuhn, T.; Spengler, T.: Produktionsintegriertes Stoffstrommanagement in der Eisen- und Stahlindustrie; Konkretisierung des § 5 Abs. 1 Nr.3 BImSchG; Umweltbundesamt Berlin (ed.); Deutsch-Französisches Insitut für Umweltforschung; Karlsruhe; 1995 (to be published)

18 BIBLIOGRAPHY

19 RELEASE VERSION; DATE AND SOURCE

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Source: Otto Rentz, Dagmar Oertel
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20 POINT OF ENQUIRY

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SNAP CODE: **030204**

SOURCE ACTIVITY TITLE : **PROCESS FURNACES WITHOUT CONTACT**
Plaster Furnaces

NOSE CODE: **104.11.01**

NFR CODE: **1 A 2 f**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from plaster furnaces as part of the production of plaster, depending on the technology applied (see section 3.3).

Basic steps of a typical gypsum manufacturing process, producing crude gypsum, is shown as an example in Figure 1. In this process gypsum is crushed, dried, ground, and calcined.

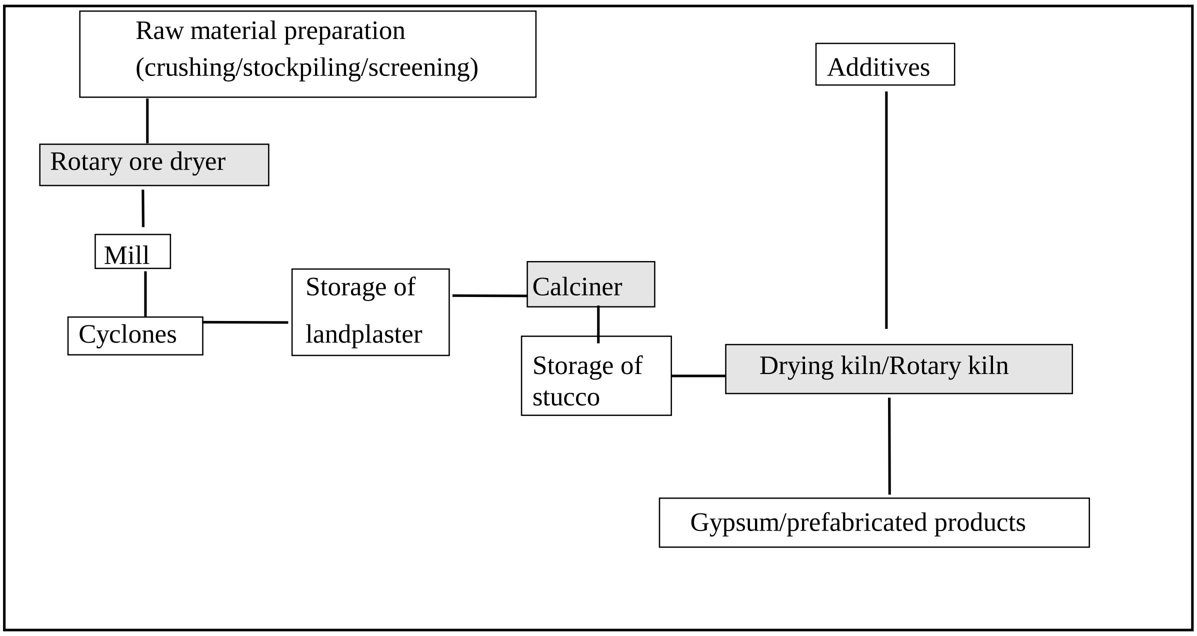

Figure 1: Basic steps of gypsum manufacturing process

Only combustion emissions are considered in this chapter (marked process steps in Figure 1).

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from plaster furnaces to the total emissions of the CORINAIR90 inventory is given as follows.

Table 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_2O	NH_3
Plaster Furnaces	030204	0	0	-	-	0	0	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

Gypsum (calcium sulphate dihydrate $CaSO_4 \cdot 2\ H_2O$) is a naturally occurring mineral which is processed into a variety of products such as a Portland cement additive, soil conditioner, industrial and building plasters or gypsum wallboard /1/.

Gypsum ore, from quarries and underground mines, is crushed and stockpiled near a plant. As needed, the stockpiled ore is further crushed and screened. If the moisture content of the mined ore is greater than about 0.5 wt.-%, the ore must be dried in a rotary dryer or a heated roller mill. Ore dried in a rotary dryer is conveyed to a roller mill. The ground gypsum leaves the mill in a gas stream and is collected in a product cyclone. Ore is sometimes dried in the roller mill by heating the gas stream, so that drying and grinding are accomplished simultaneously and no rotary dryer is needed. The finely ground gypsum ore is known as landplaster, which may also be used as a soil conditioner. /3/

3.2 Definitions

Plaster, gypsum	These expressions are often used synonymously. In this chapter plaster is used for dehydrated landplaster (produced at lower temperatures of ca. 200 °C) and gypsum is used for calcinated landplaster (produced at higher temperatures of ca. 900 °C).

3.3 Techniques

In order to obtain boiled plaster (calcium sulphate semihydrate $CaSO_4 \cdot \frac{1}{2}\ H_2O$), the gypsum ($CaSO_4 \cdot 2\ H_2O$) must be partially dehydrated at a temperature of about 120 °C. After further dehydration of the boiled plaster at a temperature of about 200 °C, stucco is obtained. Then after calcination at a temperature of about 1,300 °C building plaster is formed.

Two different combustion techniques are used: kettle calciners (combustion without contact between product and flue gas), and rotary kilns (combustion with contact between product and flue gas). In practice, plaster is obtained by dry processing in kettle calciners at a temperature of about 120 to 180 °C. α-Gypsum is also obtained by dry processing mostly within directly fired rotary kilns at a temperature of about 300 - 900 °C.

Normally, plaster is fed to kettle calciners or flash calciners, where it is heated to remove three-quarters of the chemically bound water to form stucco. Calcination occurs at approximately 120 to 150 °C and 1 Mg of gypsum calcines to about 0.85 Mg of stucco. /1/
In kettle calciners, the plaster or the gypsum is indirectly heated by hot combustion gas passed through flues in the kettle and the stucco product is discharged into a “hot pit” located below the kettle. Kettle calciners may be operated in either batch mode or continuous mode. In flash calciners, the plaster or the gypsum is in direct contact with hot gases and the stucco product is collected at the bottom of the calciner. /1/

Some plants use residual fuel oil, but the majority uses clean fuels such as natural gas or distillate fuel oil. /3/ For the heating of rotary kilns shell burners are installed which are fed by gas or oil.

3.4 Emissions

Particulate matter is the dominant pollutant in gypsum processing plants; combustion sources emit mainly gaseous pollutants. Here only emissions released from plaster furnaces are considered.

Relevant pollutants are sulphur oxides (SO_x), nitrogen oxides (NO_x) and carbon dioxide (CO_2). Emissions of volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO) and ammonia (NH_3) are of less relevance. Normally, emissions of nitrous oxide (N_2O) are not relevant[1]. Emissions of heavy metals are of less relevance.

Emissions of sulphur dioxide (SO_2) in the flue gas of plaster furnaces depend on the sulphur content of the fuel used and are mostly relevant for the production of calcinated plaster. For the case of combustion with contact in rotary kilns a sulphur retention of SO_2 occur at higher temperatures.

The formation of nitrogen oxides (NO_x) can be split into “fuel-NO”, “thermal-NO” and “prompt-NO” as discussed in the chapter “Combustion Plants as Point Sources” (section 3). For the production of gypsum the dominating NO_x formation mechanism mainly depends on the operation temperature.

Emissions of heavy metals depend on the type of fuel used and are only relevant when using heavy fuel oil. Most heavy metals (As, Cd, Cr, Cu, Ni, Pb, Zn, V) are normally released as compounds (e.g. as chlorides) in association with particulates (see also chapter B111 on “Combustion Plants as Point Sources” (section 9). In the case of combustion with contact in rotary kilns the intake by the feed material has to be considered too, but also a heavy metal retention in the raw material occurs.

3.5 Controls

SO_2 emissions of plaster furnaces are only controlled by the use of low sulphur fuels (e.g. switch from oil to gaseous fuels containing less sulphur).

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[1] The amount of N_2O reported in CORINAIR90 (see Table 1) is considered to be too high.

For the control of NO_x emissions from plaster furnaces only primary measures are relevant (e.g. optimisation of furnace conditions and/or burners).

For the control of particulate matter fabric filters are often used. Electrostatic precipitators (ESP) are installed at rotary ore dryers, roller mills, kettle calciners and conveying systems. Although rotary ore dryers may be controlled separately, emissions from roller mills and conveying systems are usually controlled jointly with kettle calciner emissions. Moisture in the kettle calciner exit gas improves the ESP performance by lowering the resistivity of the dust. /cf. 3/

4/5 SIMPLER AND DETAILED METHODOLOGY

Here both approaches refer to the calculation of emissions based on emission factors and activities, which are jointly discussed in the following. The “simpler methodology” is considered as an overall approach, where activity data refer to production figures. The “detailed methodology” is considered as the recommended approach, where activity data concerning the fuel consumption in plaster furnaces is available in a plant specific way. The simpler and the detailed methodologies cover all relevant pollutants.

The annual emission is determined according to Equation (1) by an activity and an emission factor:

$$E_i = EF_i \cdot A \qquad (1)$$

E_i	annual emission of pollutant i
EF_i	emission factor of pollutant i
A	activity

The activity A and the emission factor EF_i have to be determined on the same level of aggregation by using available data. The CORINAIR90 methodology requires for plaster furnaces activity data, which are related to the type of fuel consumed in [GJ/a].

4.1 Simpler methodology

The simpler methodology corresponds to an approach, which takes into account activity rates derived from data of comparable installations or from literature data. Here, it is assumed, that the required activity data (according to CORINAIR90) are not available (see Equation (1)). In practice, statistics (see also section 6), which provides often only the amount of plaster produced in [Mg/a], have to be used.

In order to approximate activity data referring to the energy input into plaster furnaces in [GJ/a] the specific energy consumption has to be taken into account as given e.g. in Equation

(2):

$$A_{COR} = F \cdot A_{Stat} \qquad (2)$$

A_{COR}	activity in CORINAIR-compatible unit (energy input [GJ])
F	specific energy consumption (energy input/mass plaster produced [GJ/Mg])
A_{stat}	activity directly obtained from statistics (mass plaster produced [Mg])

However, the simpler approach leads to significant uncertainties. Therefore, no emission factors are provided in this edition.

4.2 Detailed methodology

The detailed methodology corresponds to a plant specific approach, which takes into account as far as possible plant specific information. Here, CORINAIR90 compatible activity data for plaster furnaces (related to the type of fuel consumed in [GJ/a]) are directly available (Equation (1)).

Emission factors for the pollutants SO_2, NO_x, NMVOC, CH_4, CO, CO_2 and N_2O are given in Table 2 (see section 8) based on literature data depending on the type of fuel used. Emission factors related to the product are given in footnotes.

6 RELEVANT ACTIVITY STATISTICS

The following statistics can be used to determine the amounts of plaster produced or energy consumed:

- United Nations (ed.): Industrial Statistics Yearbook 1991; Volume I: Commodity Production Statistics; New York 1993; ISIC 2909-02 (Mining and quarrying: crude gypsum)

7 POINT SOURCE CRITERIA

Plaster furnaces should be considered as area sources. Gypsum plants are considered as point source according to the CORINAIR90 methodology, only if the whole plant emits more than 1,000 Mg/year of SO_2, NO_x, NMVOC or NH_3. In this case, plaster furnaces within a gypsum plant have to be reported collectively as part of a gypsum plant.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 2 contains emission factors for the relevant pollutants based on literature data. Oil and gas are mainly used as fuels, but in several plants solid fuels are burned.

Table 2: Emission factors for plaster furnaces

Type of fuel				NAPFUE code	Emission factors						
					SO_2	NO_x[5]	NMVOC[6]	CH_4	CO	CO_2	N_2O
					[g/GJ]	[g/GJ]	[g/GJ]	[g/GJ]	[g/GJ]	[kg/GJ]	[g/GJ]
s	coal	hc	sub-bituminous	102	680[3]	249[3]	15[3]	15[3]	79[3]	98[3]	14[3]
s	coal	hc	coke oven coal	107	0.4 - 436[3]	0.3 - 249[3]	15[3]	15[3]	22 - 1,534[3]	105[3]	14[3]
s	coke		petroleum	110	275[3]	249[3]	1.5[3]	1.5[3]	79[3]	97[3]	14[3]
s	biomass		wood	111	5.2[3]	249[3]	48[3]	32[3]	1,429[3]	92[3]	4[3]
l	oil		residual	203	1,260 - 1,323[3]	150 - 249[3]	3[3]	3[3]	79[3]	76[3]	14[3]
l	oil		gas	204	305[3]	249[3]	1.5[3]	1.5[3]	79[3]	73[3]	14[3]

Type of fuel				NAPFUE code	Emission factors						
					SO_2 [g/GJ]	NO_x[5] [g/GJ]	NMVOC[6] [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
g	gas		natural	301	[4]	249[3]	4[3]	4[3]	83[3]	55[3]	3[3]
-	not specified		-	-		800-1,400[1][2] g/Mg product					

[1] EPA /2/

[2] 800 g/Mg for rotary ore dryer, 1,400 g/Mg for continuous kettle calciner and flash calciner

[3] CORINAIR90 data

[4]	SO_x	9,611	g/Mm^3 fuel	Mineral products, process heaters (NAPFUE 301) /2/
[5]	NO_x	800	g/Mg product	Gypsum, rotary ore dryer /2/
		1,400	g/Mg product	Gypsum, continuous kettle calciner and flash calciner /2/
[6]	VOC	2	g/Mg product	Gypsum, rotary ore dryer, (NAPFUE 301) /2/
		10	g/Mg product	Gypsum, continuous kettle calciner and flash calciner (NAPFUE 301) /2/
		33.6	g/m^3 fuel	Mineral products, process heaters, (NAPFUE 203) /2/

9 SPECIES PROFILES

For combustion without contact species profiles for oxides of sulphur and nitrogen are comparable to those released from combustion installations. Details can be found in chapter B111 on “Combustion Plants as Point Sources” (section 9).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors and activities. CORINAIR90 data can only be used to give a range of emission factors. Further work should be invested to develop emission factors by taking into account technical or fuel dependent parameters.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Spatial disaggregation can be achieved by the relation to the number of industrial employees in industrial areas, the number of plants in the area considered, etc.

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) provides a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from plaster furnaces can be obtained by taking into account the

- time of operation and
- variation of load.

Data for the annual time of operation should take into account, that

- plants produce plaster during the whole year,
- the production of plaster in kettle calciners is a discontinuous process.

The load of a gypsum plant is determined by the variation of production due to varying demand for products. Information concerning the variation in the demand for plaster can only be obtained directly from plant operators.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on “Concepts for Emission Inventory Verification”, different general verification procedures can be recommended. Verification procedures for activity data and emission factors can be related on a national level and on a plant level.

Emission data for plaster furnaces can be verified on a territorial unit level (e.g. national level) by comparing the annual emissions related to a territorial unit to independently derived emission estimates (e.g. obtained by using population equivalents). Another possibility is the use of emission density comparisons of e.g. emissions per capita or emissions per GDP between countries with comparable economic structures.

Verification on a plant level takes into account e.g. the number of plaster furnaces within the plants considered. The verification on a plant level relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

17 REFERENCES

/1/ US-EPA (ed.): Compilation of Air Pollutant Emission Factors, Vol. 1: Stationary Point and Area Sources, 1985; AIR CHIEF Version 2.0 Beta; 1992

/2/ EPA (ed.): AIRS Facility System, EPA-Document 450/4-90-003; Research Triangle Park; 1990.

/3/ US-EPA (ed.): AP42-CDrom; 1994

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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Source: Otto Rentz, Dagmar Oertel
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20 POINT OF ENQUIRY

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SNAP CODE: **030205**

SOURCE ACTIVITY TITLE: **PROCESS FURNACES WITHOUT CONTACT**
Other Furnaces

NOSE CODE: **104.01.01**

NFR CODE: **1 A 2 f**

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

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SNAP CODE: **030301**
040209

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Sinter and Pelletizing Plants
Sinter and Pelletizing Plants (Except Combustion 030301)

NOSE CODE: **104.12.02**
105.12.09

NFR CODE: **1 A 2 a**
2 C 1

1 ACTIVITIES INCLUDED

The sinter process is an ore pre-treatment step in the production of iron, non-ferrous metals and other special materials.

This chapter does not address sinter plants in the non-ferrous metal industry; these plants should be covered by the chapters in SNAP 040300.

With respect to the iron and steel industry, this chapter only addresses travelling grate sintering which is by far the most important technique for iron ore sintering. The discontinuous pan sintering process as well as the rotary kiln process are now used at very few plant and are not discussed here. In addition, other agglomeration processes like pelletisation, briquetting and nodulisation are not considered here.

2 CONTRIBUTION TO TOTAL EMISSION

Table 2.1 Contribution to total emissions of the CORINAIR 90 inventory (*up to 28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%] (including emissions from nature)**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Sinter Plants	030301	1.3	1.0	0.1	0.1	4.9	0.4	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

Emissions of dust, heavy metals and POPs from sinter plants are also relevant but limited information is available. Europe-wide data on dust emissions is not readily available, but the PM10 contribution of sinter production to the UK's National Atmospheric Emissions Inventory for 1998 is given in Table 2.2.

Table 2.2 Contribution of cement production to the total emission of PM10 in the UK

Compound	**Contribution (%)**
PM10	1.5

Table 2.3 gives the contribution of sinter plant to total emissions of heavy metals and POPs from the OSPARCOM-HELCOM-UNECE emission inventory. For many heavy metals and POPs, but particularly in the case of PCDD/Fs, contribution to total emission may vary significantly from country to country and could be large (up to 50%).

Sinter plant are unlikely to be a significant source of sulphurhexafluoride (SF_6), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs), (ETC/AEM-CITEPA-RISOE 1997, ref. 30).

Table 2.3 Contribution to total POP and heavy metal emissions of the OSPARCOM-HELCOM-UNECE emission inventory (up to 39 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions (including emissions from nature) [%]**										
		As	Cr	Cu	Pb	Cd	Hg	Ni	Zn	PCBs	PCDD/Fs	PAH
Sinter plant	030301 / 040209	1.0	2.9	2.3	2.8	3.2	1.6	1.2	0.8	0.5	15	0

3 GENERAL

3.1 Description of activities

The sintering process is a pretreatment step in the production of iron where fine particles of metal ores are agglomerated by combustion. Agglomeration of the fine particles is necessary to increase the passageway for the gases during the blast furnace process. The strength of the particles is also increased by agglomeration.

The activities in the sinter plants include:

- treatment of the ores by crushing and sieving;
- mixing of treated ores, coke and flux compounds;
- combustion and agglomeration of a mixture of crushed ores, coke, small sintered agglomerates and flux compounds;
- sieving of the sintered agglomerates;
- cleaning of the combustion off-gases;
- transport and handling operations occurring between the above mentioned activities.

3.2 Definitions

Mixing of the ores	The ores are mixed with residual material, fuel (coke, breeze), and flux compounds. This is necessary for preparing the ore for the sintering process.
Crushing process	The ores are crushed to increase the contact area for the sintering. The sinter cake is crushed to improve the transportation to the furnace blasting process.
Sieving process	The crushed ores are sieved to prevent the ores which require further crushing from entering the sinter process. The crushed sinter cakes are sieved to prevent small sintered particles entering the furnace process.
Sintering process	During sintering ore particles, flux compounds and other material are agglomerated by the combustion of the coke / breeze. The temperature must stay below the melting temperature of the metals in the ores.
Air cleaning process	The air of the combustion and cooling process is cleaned by removing dust and sometimes other pollutants.
Basicity of sinter mixture	Basicity of the mixture may be an important parameter influencing the emissions of SO_2. It is defined by relation of the following compounds (fractions expressed as weight %): basicity = $(CaO + MgO)/(SiO_2 + Al_2O_3)$
POM	Polycyclic organic matter

3.3 Techniques used during the sintering process

The sintering process is used for several primary metal production processes, each having different designs. During sintering, fine-grained, smeltable ores, in particular iron ore, are agglomerated into compact lumps **by heating nearly to the melting or softening point**. Melting tends to occur at the grain boundaries leading to a caking of the material.

Before the sintering, the various substances are first mixed and, if desired, granulated. The iron ores are agglomerated on conveyor sinter installations, the conveyor belts consist of a large number of wagons. These wagons that have been linked up as an endless conveyor belt which can be as big as 4 m in width and 100 m in length. The fine ore to be sintered is moistened and fed on to the circulating grid together with coke breeze and additives such as limestone, quick lime, olivine or dolomite. Burners above a heat-resistant grate belt heat the material to the required temperature (1100-1200 °C). This causes the fuel in the mixture to be ignited. The combustion then is self supporting and provides sufficient heat, 1300 to 1480 °C, to cause surface melting and agglomeration of the mix. The carbon burns with the aid of the air sucked through the grid into the mixture, resulting in the flame front being moved through the sintering bed. On the underside of the sinter strand a series of windboxes is situated that draw combusted air down through the material bed into a common duct, leading to gas cleaning devices (ref. 1). The sintering processes are completed once the flame front has passed through the entire mixed layer and all fuel has been burnt.

The fused sinter is discarded at the end of the sinter strand, where it is crushed and screened. Undersize sinter is recycled to the mixing mill and goes back to the strand. The remaining sinter product is cooled in open air or in a circular cooler with water sprays or mechanical fans. The cooled sinter is crushed and screened for a final time, then the fines are recycled, and the product is sent to the blast furnaces to be charged (ref. 1).

The most common types of sinter coolers used include circular or straight line moving beds, quiescent beds, or shafts. Air or water is used as the cooling medium in these coolers, with air being prevalent in newer plants and water being dominant in older plants (refs. 2, 3).

Technical data which are typical for the plants operating in W-Europe are listed in Table 3.1:

Table 3.1 Range of technical parameters of European sinter plants

Parameter	**Range**	**Ref.**
width [m]	2,5-4,5	(ref. 4)
area [m²]	50-400 (1)	(ref. 4)
specific flue gas flows [m³/t sinter]	1800-2000	(ref. 5)
flue gas flows [million m³/h]	up to 1.5	(ref. 4)
height of sinter layer	ca. 250 -650 mm	(ref. 6)
coke input [kg/ton sinter]	38-55	

(1) some small installations are reported to be in operation in Poland, another one in Germany (sintering of iron containing return and filter materials)

The sinter plant plays a central role in an integrated iron and steel works for making use of production residues which would have to be disposed otherwise. Slags from steel production, filter dusts of diverse flue gas cleaning systems (including those applied to the sinter plant itself) and various iron-containing materials from residue treatment are recycled in the sinter plant. Recycling may lead to an enrichment of relevant compounds, particularly heavy metals. Some residue materials like roll mill scale may be contaminated with organic compounds (oils), being precursors for PAH and PCDD/F formation. An example of input material composition is shown in the Table 3.2 below.

Table 3.2 Example of input material composition to sinter plant

Material	% (1)
hematite	81.3
magnetite	2.7
returns	7.9
pellet abrasions	2.2
blast furnace dust	0.3
steel work dust	0.6
roll scale	1.3
limestone	9.4
olivine	3.5
coke breeze	5

[1] related to dry mixture

Chlorine compounds can enter into the sinter installation by means of the additive coke slack as well by the ore from its natural chloride contents. Furthermore, returned materials such as certain filter particles, scale and sludges from waste water treatment, which are added to the materials to be sintered, can also increase the chlorine content of the substances used. This is reflected in the waste gases from sinter installations which contain inorganic gaseous chlorine compounds.

An alternative process is pelletisation, where no combustion is necessary.

By 2010 a new technology called "converted blast furnace" or "melting-reduction technology" is expected to be operational. For this process sintering, pelletisation, and coke input will no longer be necessary (ref. 7).

3.4 Emissions

3.4.1 Emitted compounds

Of the 8 CORINAIR standard gaseous compounds, all except ammonia are known to be emitted by sinter plants.

- SO_2 emissions mostly originate from sulphur contained by the coke used as fuel. Actual emissions may be further dependent on the basicity of the mixture. With CaO dominated mixtures SO_2 production is decreased by increasing basicity. From MgO dominated mixtures about 97% of the sulphur content is converted to SO_2. The major fraction of the total SO_2 emission is generated in the hot part of the sinter belt (near the end), (ref. 5).
- Nitrogen oxides are mainly emitted as NO due to rapid downcooling of the flue gases. NO_X emissions originate from nitrogen contained in coke (ca. 80%) and iron ore (ca. 20%), (ref. 5).
- Raw materials contain heavy metals (HM). Dust emissions are generally associated with HM emission. During the sintering process some of the HM may be volatilised or converted into volatile compounds (e.g. chlorides) and can therefore be found in the flue

gas. This mainly concerns Zn, Pb, and Cd. Arsenic is emitted in gaseous form as As_2O_3, passing the dry gas cleaning facilities which are usually operated at 120 °C. Since these volatile compounds form or adsorb to fine particles which are removed by the gas cleaning facilities, they may be accumulated during the sinter return cycle. Moreover, fine particles passing the filters may have a much higher content of these metals than the raw gas dust or the sinter mixture (ref. 5).

- Polycyclic organic material (POM), eg. PAH and PCDD/F, may be formed from chlorine and precursor compounds like oily additives. Potentially, POM emissions may be released from the sinter machine windbox, from the sinter machine discharge point, and from sinter product processing operations (i.e. crushing, screening, and cooling). Because of the high temperatures used in sintering operations, it is probable that sinter plant POM emissions are in both gaseous and particulate matter forms (refs. 2, 8).
- Emissions of fluorides (sintering of ores recovered in Sweden) and hydrochloric acid (use of seawater moistening or coke treatment) have been observed (ref. 4)

3.4.2 Emission points

At a sinter plant, emissions may occur as (‘direct’) stack emissions and - to a minor degree - as fugitive (‘indirect’) emissions during all process steps mentioned above.

- Ambient air is sucked by several windboxes through the mixture to support the combustion process on the sinter belt. After passage of the belt the flue gases are collected, dedusted and released through the main stack.
- The main process steps (like coke crushing, raw material handling, belt charging and discharging, sintering) are usually done within encapsulated or semi-encapsulated housings. The housings may be equipped with suction hoods connected via flue gas cleaning devices to the main stack or to separate stacks. Thus, there may be more than one stack emission point at a given sinter plant.
- Fugitive dust emissions may arise during handling and transportation of the raw materials and of the cooled sinter as well as during maintenance and accidental interrupts of the cyclones or filters. More important, due to the strong thermal convection in the sinter hall’ fugitive emissions through leakages in the roof are likely to occur particularly at the end of the sinter belt.

3.4.3 Abatement measures

Gaseous compounds
Limited information is available about specific control measures for gaseous emissions. A desulphurisation facility is operated at a German plant (ref. 9). Measures for SO_2 and NOx reduction are known from plants operated in Japan (ref. 4).

Dust
Abatement measures are directed to dust emissions. In principle, reduction of dust emission also leads to reduction of emissions for those compounds being bound to particulates. Sinter strand windbox emissions commonly are controlled by cyclone cleaners followed by a dry or wet electrostatic precipitator (ESP), high pressure drop wet scrubber, or baghouse. Crusher and hot screen emissions are usually controlled by hooding and a baghouse or scrubber.

Usually horizontal dry electrostatic precipitators are used; however, less efficient mechanical dedusting devices (e.g cyclone batteries) might be installed in old sinter plants if only protection of the blower wheel rather than environmental protection is intended. Some sinter plants located in CIS countries are reported to have only this low standard abatement technology, others are equipped with wet venturi washers (ref. 10).

POM
Since being identified as a relevant source of dioxins and furans some sinter plants have been equipped with special abatement technologies (e.g. 'Airfine-system', Austria; injection of activated charcoal or open hearth coke in connection with fabric filter) or optimised dedusting facilities ('MEEP' = ESP with rotating electrode), (ref. 6).

4 SIMPLER METHODOLOGY

4.1 Calculation of emission

The simpler methodology involves the combination of emission factors (EF) (eg. mass of emitted compound per tonne of sinter produced) with activity statistics (A) (eg. mass of sinter material produced). Default emission factors are provided in Section 8.1.

5 DETAILED METHODOLOGY

An extensive measuring programme involving off-gas measurements at all relevant emission points is essential to get a clear picture of the actual emissions. Emission measurements should be performed at least at the main stacks connected to the windboxes of the sinter strand and to the hot crushing / sieving facility. This is particularly important concerning emissions of dioxins and furans since there is no way to date to estimate the emissions from different operating conditions.

Reference emissionfactors for comaprison with users own data are provided in section 8.2.

6 ACTIVITY STATISTICS

Standard international compilations of production statistics are available from

- EUROSTAT , Brussels (Iron and Steel, Yearly statistics, Theme 4, Series C);
- the International Iron and Steel Institute , Brussels;
- Wirtschaftsvereinigung Stahl, PO Box 10 54 64, 40045 Düsseldorf, Germany (Statistical Yearbook Iron and Steel Industry);
- National Statistical Yearbooks.

More details of these example data sources for activity statistics are given in Section 17 (References).

7 POINT SOURCE CRITERIA

Sinter plants usually are part of large integrated iron and steel plants connected to high chimneys (> 100 m), and should be regarded as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default emission factors for iron ore sinter plants - simple methodology

Pollutant	**Emission factor**	**Units**
Particulate matter		
Total suspended particulate	2	kg/t sinter
PM10	0.8	kg/t sinter
PM2.5	0.5	kg/t sinter
Arsenic	0.05	g/t sinter
Cadmium	0.08	g/t sinter
Chromium	0.5	g/t sinter
Copper	0.7	g/t sinter
Mercury	0.05	g/t sinter
Nickel	0.24	g/t sinter
Lead	4	g/t sinter
Selenium	0.02	g/t sinter
Zinc	0.9	g/t sinter
Dioxins and furans	15	μgTEQ/t sinter
Hexachlorobenzene	32	μg/t sinter
Polychlorinated biphenyls	200	μg/t sinter
Polyaromatic hydrocarbons	200	mg/t sinter

8.2 Detailed Methodology

This section provides reference emission factors for comparison with users own data.

The following emission factors are given in ref. 28 as recommended values for emission estimation concerning the compounds covered by the Corinair '90 inventory; they are based on the results reported by different sources in Western Europe and the U.S.A. (Annex 1); Emission factors reported for other sinter processes, other countries and additional compounds are given in Annex 1.

Since no assessment of uncertainty is given, data quality rating is generally assumed to be C.

N.B. It is assumed that the emission factors given in the following table were derived originally by relating the entire emission of a pollutant within a time period to the typical input of the mentioned fuels within the same time period, regardless of whether combustion of the fuel really causes any emission of the pollutant. While this procedure leads to chemically inconsistent emission factors it still enables the rough calculation of the entire emission of a plant when just knowing the input amount of one of the fuels used.

Table 8.2a Emission factors for gaseous compounds

Compound	**Emission factor**	**Abatement type**	**Abatement efficiency**	**Fuel type (NAPFUE code)**
	[mg/GJ]		[%]	
Sox	499	Uncontrolled	N/A	Coke breeze (107)
	658	Uncontrolled	N/A	Heating oil heavy (203)
	1410	Uncontrolled	N/A	heating oil light (204)
	4680	Uncontrolled	N/A	natural gas (301)
	5490	Uncontrolled	N/A	coke oven gas (304)
	8600	Uncontrolled	N/A	blast furnace gas (305)
		plus scrubber	90	all fuels
NOx	500	Uncontrolled	N/A	Coke breeze (107)
	134	Uncontrolled	N/A	Heating oil heavy (203)
	100	Uncontrolled	N/A	heating oil light (204)
	530	Uncontrolled	N/A	natural gas (301)
	2350	Uncontrolled	N/A	coke oven gas (304)
	8050	Uncontrolled	N/A	blast furnace gas (305)
		low NOx technology	30	all fuels
		secondary measures (SCR)	70	all fuels
MMVOC	50	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	5	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	1.5	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	14	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	26	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	0.25	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)
CH_4	50	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	4	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	1.5	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	14	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	257	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	257	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)

N/A = not applicable, Data Quality = C

Table 8.2a (continued) Emission factors for gaseous compounds

Compound	Emission factor	Abatement type	Abatement efficiency	Fuel type (NAPFUE code)
	[mg/GJ]		[%]	
CO	10500	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	14	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	13	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	2160	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	35000	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	84000	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)
	109000	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	78000	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	74000	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	55500	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	46000	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	200000	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)
	4	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	10	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	12	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	3	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	2.3	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	3	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)

N/A = not applicable

Data Quality = C

Table 8.2b Emission factors for dust

Process	Emission factor [kg dust/ Mg sinter]	Data quality	Abatement type	Abatement efficiency	Country	Ref
Sintering	4	C	Unabated	0	D	ref. 5
Cooling	3.5	C	Unabated	0	D	ref. 5
Sintering	14	E	Cyclones	60-70 %	CIS	ref. 29
Cooling	3	E	Cyclones	60-70 %	CIS	ref. 29
Sintering	0.3	C	ESP	>90 %	EU	ref. 16
Cooling	0.05	C	multi cyclone,	>90 %	EU	ref. 16
Handling	0.1	D	ESP, bag filters	> 90 %	EU	ref. 16
crushing, blending, sintering	0.25	D	“after abatement”	N/A	EU	ref. 31
Cooling	0.2	D	Cyclones	N/A	EU	ref. 31
Cooling	0.06	D	bag filters	N/A	EU	ref. 31
Windbox	5.56	B	Uncontrolled	N/A	US	ref. 1
Windbox	4.35	A	Uncontrolled (after coarse particles removal)	N/A	US	ref. 1
Windbox	0.8	B	ESP (dry)	N/A	US	ref. 1
Windbox	0.085	B	ESP (wet)	N/A	US	ref. 1
Windbox	0.235	B	Venturi scrubber	N/A	US	ref. 1
Windbox	0.5	B	Cyclone	N/A	US	ref. 1
Sinter discharge	3.4	B	Uncontrolled	N/A	US	ref. 1
Sinter discharge	0.05	B	Baghouse	N/A	US	ref. 1
Sinter discharge	0.295	A	Venturi scrubber	N/A	US	ref. 1
windbox and discharge	0.15	A	Baghouse	N/A	US	ref. 1

8.2c Heavy metal emission

The following factors are based on the emission factors shown in Annex 1. They may be applied to estimate emissions from sinter plants in the western European countries that are commonly equipped with dedusting facilities. For calculation of the possible emission range refer to the values tabled in Annex 1. In view of the higher dust emission reported for sinter plants located in the CIS, higher emissions (about factor 2-3) of heavy metals are likely there.

Table 8.2c Emission factors for heavy metals

Process	**Compound**	**Emission factor [g/ GJ sinter]**	**Data quality**
stack emission	As	0.05	C
	Cd	0.2	C
	Cr	0.2	C
	Cu	0.4	C
	Hg	0.05	C
	Ni	0.2	C
	Pb	8	C
	Se	0.02	C
	Zn	1	C

8.2d POP emissions

Since data on other POP were not available, only emissions of PCDD/Fs are included. Refer to Annex 1 to calculate potential emission range. It should be noticed that extremely high emissions from single plants may dominate the national emission. Therefore the simpler methodology should be applied cautiously.

Table 8.2d Emission factors for PCDD/Fs

Compound	**Process**	**Emission factor (1) [µg I-TEQ/ Mg sinter]**	**Data quality**	**Abatement type**	**Abatement efficiency**	**Country /region**
PCDD/F	sintering	6	C	dedusting, ESP	0% (2)	WEu
PCDD/F	cooling	1	C	dedusting, ESP or cyclones	0% (2)	WEu
PCDD/F	sintering	1.5	D	‘MEEP’ (Moving ESP)	30-70%	D
PCDD/F	sintering	0.5	D	injection of adsorbents/fabric filters	up to 90%	D
PCDD/F	sintering	0.3	C	high performance washer (Airfine)	90%	A

[1] = Note that measurements have shown that there is a significant temporal variation in PCDD/F emissions from sinter plant (about a factor of 2). Also, at one German plant very high PCDD/F emissions were measured (nearly 100 µg I-TEQ/ Mg sinter), showing that variation between plant is likely.

[2] = no significant differences in PCDD/F content measured in raw and clean gas (ref. 6).

9 SPECIES PROFILES

As mentioned in section 3.4 the heavy metal profile of the dust emitted from the hot sintering and crushing/sieving processes are not necessarily related to the profile of the raw materials due to volatilisation and accumulation of some compounds. The following enrichment factors have been observed (ref. 5) :

Table 9.1 Enrichment factors for heavy metals at sinter plant

	Zn	**Pb**	**Cd**
$C_{\text{filter dust}}/C_{\text{Sinter mixture}}$	5	450	30
$C_{\text{clean gas dust}}/C_{\text{Sinter mixture}}$	20	1,300	90

PCDD/F profile information is available from a recent German study (ref. 6). Table 9.2 gives average mass fractions for PCDD/F homologues as revealed by measurement results obtained from 3 plants (5 measurements).

Table 9.2 Species data for PCDD/F from sinter plant

Homologue	**Range [%]**	**mean [%]**
TetraCDF	37-46	40
PentaCDF	26-32	28.5
HexaCDF	10-13	12
HeptaCDF	3.5-5	4
OctaCDF		0.5
TetraCDD	1-5	2
PentaCDD	4-6	4.5
HexaCDD	3-8	5
HeptaCDD	2-4	3
OctaCDD	0-2	1.5

The European IPPC Bureau (ref. 31) includes a graph showing the grain size and weight distribution of dust, based on samples from a number of sinter strands. There are two distinct maxima, one in the range 0.1 – 3 µm, one close to 100 µm. Particles smaller than 0.1 µm and between 3 µm and 80 µm make up a much smaller fraction of the total. The coarse dust can be separated in ESPs with high efficiency. However, the composition of the fine dust, alkali chlorides, reduces the efficiency of ESPs.

The EPA's AP-42 document (ref. 1) gives size distributions for particulate matter emitted from the various stages of sinter production. These are reproduced in Table 9.3.

Table 9.3 Particle size distributions and size-specific emission factors (ref. 1)

Process	Abatement technology	Particle size (µm)	Cumulative mass % < stated size	Cumulative mass emission factor (kg/t)	Quality rating
Windbox	uncontrolled (leaving gate)	0.5	4	0.22	D
		1	4	0.22	
		2.5	6.5	0.28	
		5	9	0.5	
		10	15	0.83	
		15	20	1.11	
			100	5.56	
Windbox	ESP (wet)	0.5	18	0.015	C
		1	25	0.021	
		2.5	33	0.028	
		5	48	0.041	
		10	59	0.05	
		15	69	0.059	
			100	0.085	
Windbox	Venturi scrubber	0.5	55	0.129	C
		1	75	0.176	
		2.5	89	0.209	
		5	93	0.219	
		10	96	0.226	
		15	98	0.23	
			100	0.235	
Windbox	cyclone	0.5	25	0.13	C
		1	37	0.19	
		2.5	52	0.26	
		5	64	0.32	
		10	74	0.37	
		15	80	0.4	
			100	0.5	
Windbox	baghouse	0.5	3	0.005	C
		1	9	0.014	
		2.5	27	0.041	
		5	47	0.071	
		10	69	0.104	
		15	79	0.119	
			100	0.15	
Discharge breaker and hot screens	baghouse	0.5	2	0.001	C
		1	4	0.002	
		2.5	11	0.006	
		5	20	0.01	
		10	32	0.016	
		15	42	0.021	
			100	0.05	

10 UNCERTAINTY ESTIMATES

The main uncertainty relates to the emission factors. The data quality for all emission factors given in this chapter is from C to E. Emissions are likely to vary greatly between different plant and some emission factors are likely to vary by a factor of at least 10. More information is required on the variation of emissions with different types and sizes of process, different abatement etc.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge on abatement techniques, dust removal efficiencies and operating techniques is limited. Emission of PCDD/F may depend strongly on operation conditions and raw material composition; hence, estimation may be very uncertain and measurements are required so that a realistic understanding of the emissions can be developed. Data for other POP remain to be collected.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

This section is not relevant because sinter plant are part of large integrated iron and steel works and therefore should be considered as point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

Sintering can be considered as a continuous process. However, emissions may vary with time (e.g. due to changes in raw material composition)

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;
- Holtmann T., Rentz O., Samaras Z. Zachariadis T., Kulcke K, K.-H. Zierock: Development of a Methodology and a Computer Model for Forecasting Emissions from Relevant Mobile and Stationary Sources, Final Report 1995 (study on behalf of EC, DG XI,, Brussels).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done roughly for metal emissions by calculating the emissions using the factors from section 8 and comparing the results with a mean profile of the ore used. A mass balance over the entire plant may also be a useful check. In case of PCDD/Fs verification can only be done by measurements.

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Eurostat Information Office, Jean Monnet Building B3/88, L-2920 Luxembourg, Tel +352 4301 34567, Fax +352 4364 04

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ANNEX 1 - BACKGROUND EMISSION MEASUREMENT INFORMATION

Emissions of gaseous compounds

Process type	**Iron ore sinter plants**								**Sintering of special materials**	
References	(ref. 11)	(ref. 7)		(ref. 12)		(ref. 13)	(ref. 14)	(ref. 15)	(ref. 7)	
Country or region	Int.	NL		USA		EU	Cz	P	NL	
Abatement	unknown	unabated	with abatement (abatement details unknown)	unknown		unknown	unknown	unknown	unabated	abated
Dimension	g/Mg product	g/Mg crude steel		g/Mg product		g/GJ (NAPFUE 107) (6)	g/GJ	g/Mg	g/Mg crude steel	
SO$_x$	2,000	857	86	1,250 (2)	70 (3)				1,181	118 (7)
SO$_2$						233-632		1200		
NO$_x$	1,500	388	66			300-702	137.9		450	90 (8)
NMVOC	108 (1)					8.5.	14.2	100	347	
VOC		254		700 (2)	25 (4)					
CH$_4$	292 (1)					15	38.4			
CO	20,000-40,000	15,367		22,000 (2)		272		12000	23,000	
CO$_2$		163,265				106			221,000	
N$_2$O						4				
Fluoride (5)		11.6	2					5 6)		
HCl (5)		47	9							

[1] = general, 73 % CH_4 for VOC as 400 g/Mg; [2] = windbox; [3] = cooler; [4] = general for sinter process; [5] = dim: g/Mg sinter; [6] = in the document referred to also emission factors for other fuels are given (NAPFUE 203,204,301,304,305); [7] = with lime scrubber; [8] = with SCR

Dust emissions

[kg dust/Mg sinter produced]

Process type	**Iron ore sinter plants**														
References	(ref. 5)				(ref.10)	(ref. 7)		(ref.16) (6)			(ref. 31)				
Country or region	D				CIS	NL		D;I,B			EU				
Abatement (dust)	unabated		Two field ESP	ESP + fabric filter (3)	unknown (4)	unabated	abated	Dry ESP (3-4 fields)	multi cyclones	dry ESP (2-3 fields) or bag filters	“after abatement”	“after abatement”	“after abatement”	cyclones	bag filters
Dust	2-6 (1)	3-4 (2)	0.135-0.6	<0.006	10-24 (5)	0.675	0.165	0.12-0.34 (7)	0.03-0.12 (8)	0.05-0.2 (9)	< 0.0045	0.09-0.44	0.009-0.25	0.09-0.41	0.037-0.1

[1] = windbox emissions; [2] = crushing and screening; [3] = with injection of lignite activated charcoal and lime; [4] = see description given in 3.4.3; [5] = without sinter cooler 10-18 kg/t; [6] = values calculated from given concentrations with spec flue gas flow; [7] = sintering process, Q_S assumed to be 2000 m³/Mg; [8] = Sinter cooling air (on strand) , Q_S assumed to be 700 m³/Mg; [9] = Sinter handling, Q_S assumed to be 1000 m³/Mg

Heavy metal emissions

[g/Mg sinter produced]

Process type	**Iron ore sinter plants**										
References	ref. 17	ref.18 (1)	ref.18 (2)	ref.19	ref. 20	ref. 21	ref. 7		ref. 5	ref. 6	ref. 22
Country or region	D	D		F	Int.	Int.			D (4)	D (3)	UK (4)
Abatement (dust)	electro-filters	electro-filters		electro-filters	electro-filters	cyclones	unabated	abated	electro-filters	electro-filters	unknown
Compound											
Arsenic (As)	-	0.025	0.009	-	-		0.05	0.01	0.026	0-0.038	
Cadmium (Cd)	-	$3*10^{-4}$	0.09	-	0.02-0.12	0.08	0.13	0.03	0.058	0.024-0.228	0.022
Chromium (Cr)	-	0.13	0.09	0.56	-	-	0.05	0.01	0.161	0.016-0.514	
Copper (Cu)	1	0.25	0.36	0.23	-	-	0.13	0.03	0.437	0.176-0.656	

n.r.a.= No range available

[1] = Diffuse sources, cold; [2] = Abated process emissions; [3]= calculated from given concentrations and spec. flue gas flow, [4]= calculated from reported annual emission with sinter production data

Heavy metal emissions (continued)

[g/Mg sinter produced]

Process type	**Iron ore sinter plants**										
References	ref.17	ref.18 (1)	ref.18 (2)	ref.19	ref. 20	ref. 21	ref. 7		ref. 5	ref. 6	ref. 22
Country or region	D	D		F	Int.	Int.			D (4)	D (3)	UK (4)
Abatement (dust)	electro-filters	electro-filters		electro-filters	electro-filters	cyclones	unabated	abated	electro-filters	electro-filters	unknown
Compound											
Mercury (Hg)	-	$6*10^{-5}$	0.01	-	-	-	0.04	0.01	0.012	0.010-0.106	
Nickel (Ni)	-	0.19	0.14	1.0	-	-			0.240	0.008-0.378	
Lead (Pb)	9	0.13	4.5	2.1	-	15.3	9.92	2.48	2.990	0.360-4.106	0.73
Selenium (Se)	0.02	$1*10^{-4}$	0.019	-	-	-			0.022		
Zinc (Zn)	-	0.13	0.9	2.1	-	-	0.37	0.09	0.678		
Manganese (Mn)									0.966	0.128-1.754	

n.r.a.= No range available

[1] = Diffuse sources, cold; [2] = Abated process emissions; [3]= calculated from given concentrations and spec. flue gas flow, [4]= calculated from reported annual emission with sinter production data

POP emissions

Data are available only for PCDD/Fs

µg I-TEQ/tonne of sinter produced (1)

Process type	**Iron ore sinter plants**									**Sintering of special materials**		
References	ref. 23		ref. 24	ref. 6			ref.25	ref. 26 (2)	ref. 27	ref.24 (8)	ref.25(9)	ref.25(10)
Country or region	A		D	D			NL	S	UK	D	NL	NL
Abatement (dust)	electro-filters	high performance wet scrubbing (‘Airfine’)	electro-filters	Moving electrofilters (‘MEEP’)	fabric filter, activated charcoal	fabric filter, hearth oven coke	electro-filters	electro-filters	electro-filters	electro-filter	fabric filter	washer
PCDD/Fs	4-5 (7)	0.4-1.0	1.3-27.7 (3) 5.9 (4) 0.88 (6)	1.4 (7)	0.24-4.95 (7)	0.04-4.2 (7)	0.3-17	1-2.8	1.2-9	338	0.3	4.5

[1] = I-TEQ: International toxicity equivalents according to NATO/CCMS; [2] = value given in N-TEQ (Toxicity equivalents, nordic model); [3] = windboxes, range except one-case maximum: 94.8 µg I-TEQ/t; [4] = typical value; [6] = sinter cooler; [7] = calculated from reported concentrations and estimate of specific flue gas volume (2000 m^3/t); [8] = sintering of iron containing residue materials; [9] = prod. of artificial gravel; [10] = prod. of phosphates

SNAP CODE : **030302**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Reheating Furnaces Steel and Iron

NOSE CODE: **104.12.03**

NFR CODE: **1 A 2 a**

1 ACTIVITIES INCLUDED

The reheating furnaces are part of the production of primary iron and steel. A detailed description of non-combustion processes in iron and steel industries and collieries can be found in chapters B146 and B422 up to B428. However, in the following, if useful for description, also non-combustion process steps are mentioned.

2 CONTRIBUTION TO TOTAL EMISSION

The emissions of heavy metals from reheating furnaces at iron and steel production plants are relevant on a national level. Emissions of other substances only give a local contribution. For heavy metal emissions, specific figures on relative contributions for this source activity are not available. The average relative contribution from the total iron and steel production industry to the total emission of heavy metals has been presented for European countries in table 1. The data in table 1 is according to Baart *et al.* (1995) [1].

Table 1: Average relative contribution of the production of iron and steel to the total emission of heavy metals in European countries

Compound	Total iron & steel production (%)
Cadmium	22
Chromium	36
Copper	16
Nickel	14
Lead	12
Zinc	33

For emissions other than heavy metals, the contribution from reheating furnaces in steel and iron production to total emissions in countries of the CORINAIR90 inventory is given in table 2.

Table 2: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_2O	NH_3
Reheating Furnaces Steel and Iron	030302	0.3	0.3	0	0	0.2	0.6	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description of activities

Reheating furnaces prepare cool iron material for further processing by an appropriate temperature increase. In soaking pits, ingots are heated until the temperature distribution over the cross section of the ingots is acceptable and the surface temperature is uniform for further rolling into semifinished products (blooms, billets and slabs). In slab furnaces, a slab is heated before being rolled into finished products (plates, sheets or strips). [2]

3.2 Definitions

3.3 Techniques

The type of reheating furnace depends on the site and nature of the intermediate product and the subsequent processing. Coal-fired furnaces are now comparatively rare. Reheating furnaces are normally fired by gas or oil. [3]

3.4 Emissions

Pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2) and nitrous oxide (N_2O). According to CORINAIR90 the main relevant pollutants are SO_x, NO_x and CO_2 (see also table 2). The emissions are released through the stack.

Emissions of sulphur dioxides (SO_x) are directly related to the sulphur content of the fuel. Reheating furnaces are normally fed by low sulphur gas (blast furnace gas, desulphurised coke oven gas or natural gas) or by oil [3].

Nitrogen oxides (NO_x) are formed within the combustion process by conversion of fuel-nitrogen and nitrogen of the combustion air.

Carbon dioxide (CO_2) is a main product of the combustion process and is directly related to the carbon content of the fuel.

3.5 Controls

Emissions are reduced by preceding cleaning of the used blast furnace gas and coke oven gas. No information is available for treatment of exhaust gases from reheating furnaces. [2]

4 SIMPLER METHODOLOGY

The emissions. are inventoried using the default emission factors provided in Table 8.1. These emission factors represent the high end of typical emission factors, and assume limited control technology is in place.

5 DETAILED METHODOLOGY

If an extensive measuring programme is available the emission of heavy metals can be calculated on the basis of the measurements of the dust emission and the composition of compounds over the total process. Reference emission factors are provided for comparison with user’s own data in Table 8.2.

6 ACTIVITY STATISTICS

Standard energy consumption statistics (IEA, UN, International Iron and Steel Institute etc.)

7 POINT SOURCE CRITERIA

The iron and steel plants from which the reheating furnaces are a part are connected to high chimneys (> 100 meter), and can be regarded as point sources . They can be considered to be point sources at a national as well as on a regional level.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

A summary of default emission factors using the simpler methodology for estimating emissions from ordinary steel and iron production are provided in Table 8.1.

8.2 Detailed Methodology

For emissions other than heavy metals, table 8.2 contains fuel use related reference emission factors for reheating furnaces in steel and iron production based on CORINAIR90 data in g/GJ. Technique related emission factors, mostly given in other units (e.g. g/Mg product), are listed in footnotes. In case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account. The specific energy consumption is process and country specific; within CORINAIR 90 a value of 100 GJ/Mg product has been reported.

Table 8.1 Default emission factors - simpler methodology

Pollutant	**Emission factor**	**Units**
PM10	650	g/tonne steel
Arsenic	1.44	mg/tonne steel
Cadmium	0.48	mg/tonne steel
Chromium	24	mg/tonne steel
Copper	24	mg/tonne steel
Mercury	0.5	mg/tonne steel
Lead	38	mg/tonne steel
Zinc	84	mg/tonne steel
Dioxins and furans	0.2	µgTEQ/tonne cement
Hexachlorobenzene	11	µg/tonne cement
Polyaromatic hydrocarbons	24000	mg/tonne steel

Table 8.2 Emission factors for reheating furnaces in steel and iron production – detailed methodology

					Emission factors							
	Fuel			NAPFUE -code	SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]	NH_3 [g/GJ]
S	coal	hc	Coking	101			$15^{1)3)}$	$15^{1)}$	$12^{1)}$	$94^{1)}$	$3^{1)}$	
S	coal	hc	Steam	102	$992^{3)}$	$150^{3)}$	$15^{1)}$	$15^{1)3)}$	$120^{1)}$, $70^{3)}$	$94^{1)}$, $98^{3)}$	$14^{3)}$	
S	coal	hc	sub-bituminous	103	$1,267^{3)}$	$100^{3)}$	$4^{3)}$	$4^{3)}$	$20^{3)}$	$52^{3)}$	$3^{3)}$	
S	coal	bc	brown coal/lignite	105	$2,358^{3)}$	$150^{3)}$	$20^{3)}$	$100^{3)}$	$18^{3)}$	$86^{3)}$	$3^{3)}$	
S	coke	hc	coke oven	107	$351^{3)}$	$150^{3)}$	$15^{1)3)}$	$15^{1)3)}$	$70^{1)3)}$	$108^{1)}$, $105^{3)}$	$3^{1)}$, $14^{3)}$	
S	coke	bc	coke oven	108	$650^{3)}$	$150^{3)}$	$8^{3)}$	$15^{1)}$	$18^{3)}$	$86^{3)}$	$3^{3)}$	
S	coke		Petroleum	110	$2,000^{3)}$	300	$1.5^{3)}$	$1.5^{3)}$	$70^{3)}$	$97^{3)}$	$10^{3)}$	
L	oil		Residual	203	$1,323^{1)}$ $143\text{-}1,503^{3)}$	100- $240^{3)}$	$3\text{-}5^{1)}$ $3^{3)}$	$3\text{-}5^{1)3)}$	$15^{1)}$, 12- $15^{3)}$	$76\text{-}78^{1)}$ $73\text{-}78^{3)}$	$3\text{-}14^{1)}$ $2\text{-}14^{3)}$	
L	oil		Gas	204	$94\text{-}1,410^{3)}$	$80\text{-}100^{3)}$	$2.5^{1)}$ $1.5^{3)}$	$2.5^{1)}$, $1.5^{3)}$	$12^{1)3)}$	$74^{1)}$ $69\text{-}74^{3)}$	$3^{1)}$ $2\text{-}14^{3)}$	
L	oil		shale-oil	211	$503^{1)}$	$158^{1)}$			$13^{1)}$			
G	gas		Natural	301	$0.87\text{-}58^{1)}$ $0.3\text{-}58^{3)}$	$58\text{-}187^{1)}$ $58\text{-}125^{3)}$	$2.5\text{-}4^{1)}$ $1\text{-}4^{3)}$	$2.5\text{-}4^{1)}$ $1\text{-}5^{3)}$	$5.5\text{-}13^{1)}$ $8\text{-}25^{3)}$	$55\text{-}56^{1)}$ $52\text{-}57^{3)}$	$1.5\text{-}3^{1)}$ $0.8\text{-}3^{3)}$	
G	gas		liquified petroleum gas	303	$0.04^{3)}$	$100^{3)}$	$2.1^{3)}$	$0.9^{3)}$	$13^{3)}$	$65^{3)}$	$1\text{-}3^{3)}$	
G	gas		coke oven	304	$23\text{-}715^{1)}$ $60^{3)}$	$84\text{-}207^{1)}$ $85^{3)}$	$2.5^{1)3)}$	$2.5^{1)3)}$	$12\text{-}17^{1)}$ $15^{3)}$	$42\text{-}46^{1)}$ $45^{3)}$	$3^{1)}$, $1^{3)}$	
G	gas		blast furnace	305	$57\text{-}831^{1)}$ $18\text{-}830^{3)}$	145- $831^{1)}$ $25\text{-}830^{3)}$	$0.25\text{-}2.5^{3)}$		$12\text{-}69^{1)}$ $10\text{-}14^{3)}$	$192^{1)3)}$ $290^{3)}$	$3^{1)}$, $1\text{-}2.4^{3)}$	
G	gas		coke oven and blast furnace gas	306	$0.53^{1)}$	$151^{1)}$		0.25- $2.5^{3)}$	$14^{1)}$	$205^{1)}$		
-	not specified		-	-	$400^{2)}$	$400^{2)}$	$5^{2)}$					

1) CORINAIR90, point sources (preliminary data)
2) EPA 1990 [4]
3) CORINAIR90 data, area sources, (preliminary data)

9 SPECIES PROFILES

The origin of the heavy metals emission is the dust production. The emission factors as presented are therefore related to the profile of the dust. This profile however is dependent on the ores used.

10 UNCERTAINTY ESTIMATES

Not available.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspects discussed here are related to emission factors and activities.

The fuel specific emission factors provided in table 3 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.

Uncertainties also occur concerning the activity covered due to the fact, that a single fuel (e.g. oil) or a mixture of blast furnace and coke oven gas can be used. Further work should be invested in a representative split of fuel gases used (activity data) and in providing corresponding emission factors e.g. for a blend of blast furnace and coke oven gas.

For heavy metals, knowledge on emission factors, abatement techniques, dust removal efficiencies and operating techniques is very limited; measurement data of composition of dust is poor.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Iron and steel production is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Not available.

16 VERIFICATION PROCESSES

Verification of the emissions can be done for metal emissions by calculating the emissions using the factors from the PARCOM ATMOS manual and comparing the results with a mean profile of the ore used. A mass balance over the entire plant may also be a useful check.

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[1] A.C. Baart, J.J.M. Berdowski, J.A. van Jaarsveld; Calculation of atmospheric deposition of contaminants on the North Sea; IWAD; ref. TNO-MW-R 95/138; TNO MEP; Delft; The Netherlands; 1995

[2] US-EPA (ed.): AP 42 CD-Rom; 1994

[3] Parker, Albert (ed.): Industrial Air Pollution Handbook; Maidenhead, Berkshire (England); 1978

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18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE, AND SOURCE

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SNAP CODE: **030303**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Grey Iron Foundries

NOSE CODE: **104.12.04**

NFR CODE: **1 A 2 a**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within grey iron foundries. The grey iron foundries are in general part of production processes for a wide range of metal products. A detailed description of non-combustion processes in iron and steel industries and collieries can be found in chapters B146 and B422 up to B428.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from grey iron foundries to total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 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_2O	NH_3
Grey Iron Foundries	030303	0	0	0	0	1.4	0.1	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

For heavy metal emissions, no specific figures for this source activity are available. The average relative contribution from the total iron and steel production industry and the production of pig iron to the total emission of heavy metals has been presented for European countries in table 2. Grey iron foundries can be considered a part of the production of pig iron. The data in table 2 is according to Baart *et al.* (1995). /1/

Table 2: Average relative contribution of the production of iron and steel and the production of pig iron to the total emission of heavy metals in European countries.

Compound	**Total iron & steel production (%)**	**Pig iron production (%)**
Cadmium	22	-
Chromium	36	3.7
Copper	16	-
Nickel	14	3.0
Lead	12	-
Zinc	33	-

- = not available

3 GENERAL

3.1 Description of activities

Foundry activities are generally part of the following type of industrial activities:

- Malleable foundries
- Nodular foundries, for instance:
  - machine construction
  - automobile and bicycle industry
- Lamellar foundries, for instance:
  - sewer pipe foundries, accessories for tubes
  - tubes for heating purposes
  - machine construction parts
  - automobile industry
- Steel foundries

The activities of the foundries can be seperated in five parts:

- pretreatment of shot metals
- production of casting models
- smelting of metals with flux compounds and treatment of smelt
- casting of metal smelt in casting models
- treatment of castings

The activities, the composition, the scaling and the use of raw materials of the foundries depend strongly on the products made by the foundries and on economic aspects. The casting process is described in section 3.3.

3.2 Definitions

Pretreatment of the raw materials	Some raw materials need to be pretreated since they are not always suitable for the casting process.
Smelting process	The shot metals and flux compounds are mixed with cokes and heated by combustion of the cokes to a temperature above the melting point of iron (»1500 °C). These processes can be either batchwise, or continuous.
Production of casting models	A casting model is made of sand with a chemical binding agent, or of clay bounded sand. The shape of the casting model is the inverse of the casting to be produced. The casting model can only be used once, because after solidification of the metal smelt the casting will be destroyed.
Metal smelt	The shot metals used in the smelting process contain mainly iron. Since shot materials are used the iron may be contaminated with other metals.
Treatment of the metal smelt	The treatment of the metal smelt is a process intended to increase the quality of the smelt. Increase of quality is necessary for the casting process or the properties of the product.
Casting process	The casting process is the pouring of the drained off metal smelt in a casting process and the solidification of the metal smelt.

3.3 Techniques

The casting starts with the pretreatment of the metals. This pretreatment consists of breaking big parts of shot metals, and mixing the metals with the flux compounds. Three types of smelt ovens are commonly used: dome ovens, electro ovens and tumbler ovens. These ovens are described in section 3.3.1.

After the metal smelt is drained from the ovens, the quality of the smelt can be improved by deslagging with slag binding compounds, desulphurating with fine cokes and calcium carbide, inoculation with ferro alloys (based on ferro silica) and nodulisation with magnesium.

The drained metal smelt is casted in a casting model. The casting method is specific for the products. The production of the casting models is described in paragraph 3.3.2. After solidification of the metal smelt the casting model is removed. Cleaning of the casting is generally done by shot peening. Besides shot peening the casting can be been grinded, rolled, chopped and milled. Sometimes the castings will also be treated by glowing, or hardened, tared, red-leaded, painted or lacquered.

3.3.1 Smelt ovens

Dome oven	The dome oven is a continuous operating installation. In the shaft the smelt aggregate is accumulated via an opening in the side wall. Alternately the cokes and the metals are added. During the filling of the shaft the cokes are lighted and the metal smelts and flows into the oven.
Electro oven	The metals and flux compounds are smelted by electric lighting of the petrol cokes. The process is discontinu.
Tumbler oven	The tumbler oven is heated by an oil lighted flame. The metals direct heated by the flame will melt. The turning of the tumbler assures that the metals will be heated on both sides.

3.3.2 Production of casting models

The casting models can be classified in two categories, namely the clay bounded sand models for the light casting production and the models of sand with a chemical hardener. The clay bounded sand model is strengthened by compression. The sand contains concrete, water and coal powder for the production of a smooth structure on the the casting. The casting model made of sand with the chemical agent is also strengthened by compressing during which process the chemicals are polymerized in the sand.

3.4 Emissions

The main emissions of the casting process are emissions of dust and gaseous compounds. The emissions occur during the smelting process, the production of the casting model and the treatment of the castings. The main emission is dust which contains metal oxides like iron and silica oxide. Also some solvents may be part of the emissions into air.

The emissions of dust depend strongly on the type of oven used for the smelting process and quality of the process management.

Gaseous compounds released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O) and ammonia (NH_3). The emissions are released through the stack. According to CORINAIR90 the main relevant pollutants are CO and CO_2 (see also table 1).

Coke burned in cupola furnaces produces several pollutants. Incomplete combustion of coke causes carbon monoxide emissions and the coke sulphur content gives rise to sulphur dioxide emissions. /3/

Electric arc furnaces produce CO emissions which result from combustion of graphite from electrodes and carbon added to the charge. Hydrocarbons (NMVOC) result from vaporisation and incomplete combustion of oil residues remaining on the scrap iron charge. /3/

Electric induction furnaces release negligible amounts of hydrocarbon and carbon monoxide emissions. /3/

3.5 Controls

Possible areas for improvement in emission control are:

Dome oven	Treatment of off-gas with bagfilters and electrofilters
Electro oven	Treatment of off-gas with bagfilters or electrofilters
Tumbler oven	Treatment of off-gas with bagfilters, use of low sulphur containing oil, lime injection combined with bagfilters
Smelt treatment	Treatment of off-gas with bagfilters
Sand preparation	Use of bagfilters and wet scrubbers
Model production	Good humidity control. For the sand model production with the chemical hardened binding resin the choice of the resin can influence the emission.

A cupola furnace typically has an afterburner as well, which achieves up to 95 % efficiency. The afterburner is located in the furnace stack to oxidise CO and burn organic fumes, tars and oils. /3/

Electric induction furnaces are typically uncontrolled since they emit negligible amounts of hydrocarbons and carbon monoxide. /cf. 2/

4 SIMPLER METHODOLOGY

Multiplying the emission factor with the appropriate energy consumption or production figure yields the emission.

5 DETAILED METHODOLOGY

The quality of an estimation of emission is strongly dependent on the management of the process. The estimation of the main emission sources should be based on measurements at the different process stages.

6 RELEVANT ACTIVITY STATISTICS

European statistics for the production of iron, steel and malleable iron castings in the European Community are available. For energy consumption statistics, data from the IEA can be used.

7 POINT SOURCE CRITERIA

Foundries can vary strongly in size. Small foundries can be treated as area source. At the national level big foundries or a concentration of foundries in a small area would be treated as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 3 contains fuel related emission factors for grey iron foundries based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg charged), are listed in footnotes. In case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. At this stage no data for the definition of appropriate conversion factors are available.

Table 3: Emission factors for grey iron foundries[7]

					Emission factors							
	Type of fuel			NAPFUE code	SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]	NH_3 [g/GJ]
s	coal	hc	steam	102	130-160[1]	12-80[1]	15-57[1]	5-15[1]	20[1]	93-94[1]	4-5[1]	
s	coal	bc	briquettes	106	44[1]	12[1]	15-57[1]	6.3-15[1]		97[1]	3.5[1]	
s	coke	hc	coke oven	107	100-584[1] , 92-593[2]	12-220[1] , 12-45[2]	0.5-80[1]	0.5-6.3[1]	97[1]	105-110[1], 105[2]	3-4[1]	
s	coke	bc	coke oven	108	650[1]	150[1]	5[1]	15[1]	18[1]	86[1]	3[1]	
l	oil		residual	203	143-930[1]	100-175[1]	3-57[1]	3-6.3[1]	10-15[1]	73-78[1]	2-10[1]	
l	oil		gas	204	55-94[1]	50-100[1]	1.5-57[1]	1.5-8[1]	10-20[1]	74[1]	2[1]	
g	gas		natural	301	0.3-8[1], 1[2]	50-100[1] ,145[2]	2.5-57	2-6.3[1]	10-20[1], 8[2]	53-60[1], 55[2]	1-3[1]	
g	gas		liquified petroleum gas	303	0.04[1]	100[1]	2.1[1]	0.9[1]	131)	65[1]	1[1]	
g	gas		coke oven	304	12-54[1] , 54[2]	5.5-50[1] ,5[2]	2.5-80[1]	2.5-6.3[1]	10[1]	44-45[1], 45[2]	1-1.5[1]	

[1] CORINAIR90 data, area sources; [2] CORINAIR90 data, point sources

[3]	SO_x: /1/	450	g/Mg charged	cupola furnace
		90,000	g/Mg charged	reverberatory furnace
		0	g/Mg charged	electric induction furnace
		125	g/Mg charged	electric arc furnace
[4]	NO_x: /1/	50	g/Mg charged	cupola furnace
		2,900	g/Mg charged	reverberatory furnace
		0	g/Mg charged	electric induction furnace
		160	g/Mg charged	electric arc furnace
[5]	VOC: /1/	90	g/Mg charged	cupola furnace
		75	g/Mg charged	reverberatory furnace
		0	g/Mg charged	electric induction furnace
		90	g/Mg charged	electric arc furnace
[6]	CO: /1/	72,500	g/Mg charged	cupola furnace
		0	g/Mg charged	reverberatory furnace
		0	g/Mg charged	electric induction furnace
		9,500	g/Mg charged	electric arc furnace

[7] It is assumed, that emission factors cited within the table are related to combustion sources in grey iron foundries; other process emissions are not covered.

For the situation in the Netherlands, the following can be proposed for heavy metal emissions:

Emission factors are calculated from measurements in mixtures consisting of 60% of hot blast air cupolas (1500 m^3 Mg^{-1} off-gases) and 40% of cold blast air off-gases (300 m^3 Mg^{-1} off-gases), using an average dust concentration of 300 mg m^{-3}. The emission factors are calculated from formula 1:

Emission =$[\text{Dust}]_{\text{average}}$ x $\text{Flow}_{\text{off-gases}}$ x $[\text{Metal composition}]_{\text{dust}}$ [Formula 1], where

$[\text{Dust}]_{\text{average}}$: Average dust concentration in off-gases
$\text{Flow}_{\text{off-gases}}$: Average flow of off-gases
$[\text{Metal composition}]_{\text{dust}}$: Average weight percentage of metal composition in dust

The emission factors are given in table 4.

Table 4: Emission factors for foundries (g.Mg^{-1} product)

Substance	Emission factor [15]	Range [15]
Arsenic	0.3	0.02 - 3.6
Cadmium	0.14	0.006- 0.45
Chromium	1.1	0.09 - 3.0
Lead	7.2	0.24 -15
Nickel	0.5	0.01 - 1.3
Zinc	5.0	2.4 - 7.2

9 SPECIES PROFILES

The heavy metal emissions are related to the metal profile of the dust.

10 UNCERTAINTY ESTIMATES

The emission factors given are based on the data from a small number of measurements, with a rather large variation caused by individual conditions. The quality class of the emission factors other than of CORINAIR90 is estimated to be [D].

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect for heavy metals is the lack of data and adequate measurements.
For emissions other than heavy metals, the weakest aspects discussed here are related to emission factors.

The fuel specific emission factors provided in table 4 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 FOR AREA SOURCES

Not applicable.

13 TEMPORAL DISAGGREGATION CRITERIA

The temporal disaggregation depends on the management of the plant. Some foundries do emit only during Mondays to Fridays from ± 7.00 hour to ± 18.00 hour and others emit continuously.

As result of market conditions a seasonal variation might be present.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

[1] Annual report of the Common Association of Dutch Foundries 1989; AVNEG; 1990
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[16] Environmental Protection Agency; Compilation of air pollutant Emission Factors AP-42
[17] PARCOM-ATMOS Emission Factors Manual.

16 VERIFICATION PROCEDURES

A verification method could be the comparison of the heavy metals emissions calculated with a profile of the composition of the products.

17 REFERENCES

/1/ A.C. Baart, J.J.M. Berdowski, J.A. van Jaarsveld; Calculation of atmospheric deposition of contaminants on the North Sea; IWAD; ref. TNO-MW-R 95/138; TNO MEP; Delft; The Netherlands; 1995
/2/ EPA (ed.): AIR Facility Subsystem, EPA-Doc. 450/4-90-003, Research Triangle Park, 1990
/3/ EPA (ed.): AIR Chief; Version 4.0; 1995
/4/ Air Pollution Aspects of the Iron Foundry Industry; APTD-0806, U.S.-EPA, Research Triangle Park (NC); 1974

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19 RELEASE VERSION, DATE, AND SOURCE

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SNAP CODE: **030304**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Primary Lead Production

NOSE CODE: **104.12.05**

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

The primary lead production process is defined as the production of lead from lead concentrates. A detailed description of other process steps e.g. sintering can be found in chapter B331. However, in the following if useful for description sintering processes are included.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of gaseous emissions released from primary lead 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_2O	NH_3
Primary Lead Production	030304	0.2	0	-	-	0	0	-	-

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 lead production to the total heavy metal emissions, according to IWAD [7], is given in Table 2.2.

Table 2.2. The contribution of heavy metal emissions from primary lead production to the total emissions of the IWAD study [7]

Contribution to total emissions (%)					
Cd	Cr	Cu	Ni	Pb	Zn
1.1	0	0.2	0	1.5	0.3

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

3 GENERAL

3.1 Description of activities

This process contains the classical steps of ore pretreatment and concentration, sintering, smelting, and product refining. Most primary lead smelters also produce other metals to a certain extent. The process route is based on sintering, reduction of sinter in a shaft furnace, and refining of bullion, either pyrometallurgically or hydrometallurgically.

In the sintering process fine particles of metal ores are agglomerated into nodules, briquettes, sinter, or pellets. Also a roasting process is involved in which lead sulphide is converted into lead oxide. Dust emissions result from handling and stockpiling of raw materials or intermediate products. Abatement methods are the use of bag filters, wet scrubbers or electrofilters.

In the smelting process ore, coke, and flux compounds are heated either in a shaft furnace or an electric furnace. Dust abatement can be provided by bag filters or electrofilters. Improved abatement is encapsulation or evacuation of the process.

The refining process is mainly directed at the removal of copper, silver, zinc, and bismuth. Dust emissions mainly occur at the treatment of the different by-product streams.

Several improved processes are either in the pilot stage, or being used at a single plant. However, no general applicable information is available yet.

3.2 Definitions

Sintering process	Agglomeration of ore particles, flux compounds and other material by the combustion of coke.
Roasting process	Oxidation of lead concentrate converting the lead sulphide to lead oxide.

3.3 Techniques

The main techniques for the smelting process are the shaft furnace and the electric furnace process. For refining the main techniques are pyrometallurgical refining and hydrometallurgical refining. Several direct smelting technologies have been under development or are being developed yet. Information about the emissions of these techniques is not yet available.

3.4 Emissions

The main emissions during the primary lead production are dust emissions.

Pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), and nitrous oxide (N_2O). According to CORINAIR90 the main relevant pollutants is SO_2 (see also table 2.1).

The most relevant step with regard to SO_2 emissions is the sintering process (for details see B331). However, only about 7 % of the total sulphur in the ore is emitted as SO_2. The remainder is captured by the slag. The concentration of this SO_2 stream can vary from 1.4 to 7.2 g/m^3, depending on the amount of dilution air injected to oxidise the carbon monoxide and to cool the stream before baghouse particulate removal [1].

Nearly 85 % of the sulphur present in the lead ore concentrate is eliminated in the sintering operation (see chapter B331). In handling process offgases, either a single weak stream is taken from the machine hood at less than 2 % SO_2, or two streams are taken, a strong stream (5 to 7 % SO_2) from the feed end of the machine and a weak stream (less than 0.5 % SO_2) from the discharge end. Single stream operation has been used if there is little or no market for recovered sulphur, so that the uncontrolled, weak SO_2 stream is emitted to the atmosphere.

When sulphur removal is required, however, dual stream operation is preferred. The strong stream is sent to a sulphuric acid plant, and the weak stream is vented to the atmosphere after removal of particulate [1].

Sulphur oxides are also generated in blast furnaces during the smelting process from small quantities of residual lead sulphide and lead sulphates in the sinter feed. The quantity of these emissions is a function not only of the sinter's residual sulphur content, but also of the sulphur captured by copper and other impurities in the slag [1].

3.5 Controls

The dust emissions can be abated by using fabric filters, wet scrubbers or electrofilters. Improvement can be achieved by using encapsulation or evacuation. New approaches are under development.

The SO_2 containing emissions are often used as input for sulphuric acid plants. Here, emissions from combustion and from other process steps are reconciled. Single stage sulphuric acid plants can attain sulphur oxide levels of 5.7 g/m^3, and dual stage plants can attain levels of 1.6 g/m^3. Typical efficiencies of dual stage plants in removing sulphur oxides can exceed 99 %. Other technically feasible SO_2 control methods are elemental sulphur recovery plants and dimethylamine and ammonia absorption processes [1].

4 SIMPLER METHODOLOGY

An approach calculating the emissions from economic or production statistics is feasible. Emission factors are presented in section 8.

5 DETAILED METHODOLOGY

Information about the newer processes mentioned above is not yet available to allow a more detailed methodology to be followed.

6 RELEVANT ACTIVITY STATISTICS

Lead Production Statistics should be available nationally or from international statistics.

7 POINT SOURCE CRITERIA

The primary lead production should be treated as a point source if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The emissions can vary widely depending on the ore used and the abatement measures applied, see Table 8.1 for reported emission factors. The emission factors given in Table 8.2 were prepared for the PARCOM-ATMOS Emission Factors Manual 1992. The factors for the emissions are based on the information from Table 8.1.

Table 8.1. Emission factors for primary lead production (g/Mg product) as reported by several countries/authors

	Sweden [2]		**Poland [3]**			**Germany [4]**	**Pacyna [5,6]**
Compound	limited	improved	limited	improved	unabated	unknown	unknown
Arsenic	3	0.2	16-43	-	-	3	300
Cadmium	3	0.6	10-22	-	-	6	10
Copper	10	4	10	7	-	-	-
Lead	400	200	560-1200	-	-	400	3000
Mercury	-	-	-	-	-	-	3
Zinc	50	20	110	-	680	-	110

Table 8.2.: Proposed emission factors for primary lead production (g/Mg product)

Substance	**Emission factor**		
	limited abatement	improved abatement	unknown level of abatement
Arsenic	3	0.5	10
Cadmium	10	1	15
Copper	10	5	10
Lead	800	200	2000
Mercury	3	3	3
Zinc	80	20	100

The following Table 8.3 contains fuel related emission factors for primary lead production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/m^3) are listed in footnotes. In case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. At this stage no data for the definition of appropriate conversion factors are available.

Table 8.3: Emission factors for primary lead production[6]

					Emission factors						
Type of 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_2O [g/GJ]
s	coal	hc	steam	102	149-520[1]	160[1]	15[1]	15[1]	100[1]	94[1], 99[2]	4[1]
s	coal	hc	sub-bituminous	103	838[2]	39[2]					
s	coal	bc	briquettes	106	149-176[1]	140[1]	15[1]	15[1]	100[1]	97[1]	3.5[1]
s	coke	hc	coke oven	107	149-520[1] , 462-501[2]	140[1], 35[2]	0.5[1]	0.5[1]	100[1]	100-105[1], 105[2]	4[1]
s	coke	bc	coke oven	108	660[1]	200[1]	05[1]	0.5[1]	100[1]	100[1]	4[1]
l	oil		residual	203	149-1,470[1]	150-175[1]	4[1]	4[1]	10-15[1]	76-78[1]	2[1]
l	oil		gas	204	68-1,410[1]	70-100[1]	2.5[1]	2.5[1]	10-12[1]	73-74[1]	2[1]
g	gas		natural	301	0.4-149[1] , 371[2]	50[1], 45[2]	2.5[1]	2.5[1]	10[1]	55-56[1] , 55[2]	1.5[1]

[1] CORINAIR90 data, area sources (preliminary data)

[2] CORINAIR90 data, point sources (preliminary data)

[3] SO_x: /1/ 17,209 · S g/m³ fuel: primary metal production, process heaters, NAPFUE 204, S = sulphur content of fuel
19,006 · S g/m³ fuel: primary metal production, process heaters, NAPFUE 203, S = sulphur content of fuel
Emission factors of SO_2 given here may contain emissions from combustion of fuel as far as emissions from sintering of ore.

[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

[6] It is assumed, that emission factors cited within the table are only related to combustion sources in primary lead production (except of SO_2); other process emissions are not covered.

9 SPECIES PROFILES

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 weakest aspects in the current methodology are the emission factors.

The fuel specific emission factors provided in Table 8.3 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 FOR AREA SOURCES

Not applicable if actively treated on a point source basis.

13 TEMPORAL DISAGGREGATION CRITERIA

The primary lead production as such is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Richtlinien zur emissionsminderung in nicht-eisen-metall-industrien. Umweltbundesamt 1980.
- US-EPA (ed.): AP 42 CD-Rom; 1994

16 VERIFICATION PROCEDURES

A comparison between the profile of the calculated emissions and the composition of the ore could be used as a verification method.

17 REFERENCES

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

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3 Heavy metals emission to air in Poland for years 1980-1992, Hlawiczka, S., Zeglin, M., Kosterska, A., Inst. Ecol. Ind. Areas, Report 0-2.081, Katowice, 1995 (in Polish).

4 Datenerhebung über die Emissionen Umweltgefärdenden Schwermetalle; Jockel, W., Hartje, J.; Forschungsbericht 91-104 02 588, TüV Rheinland e.V. Köln; 1991.

5 Emission factors of atmospheric Cd, Pb and Zn for major source categories in Europe in 1950-1985; Pacyna, J.M.; NILU Report OR 30/91 (ATMOS 9/Info 7); 1990.

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7 Calculation of atmospheric deposition of contaminants on the North Sea, Baart, A.C., Berdowski, J.J.M., Jaarsveld, J.A. van, Wulffraat, K.J., TNO-report TNO-MW-R 95/138, 1995.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE, AND SOURCE

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SNAP CODE: **030305**

SOURCE ACTIVITY TITLE: PROCESSES WITH CONTACT
Primary Zinc Production

NOSE CODE: **104.12.06**

NFR CODE: **1 A 2 b**

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 detailed description of other process steps e.g. sintering can be found in chapter B331. However, in the following if useful for description, sintering processes are included.

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_2O	NH_3
Primary Zinc Production	030305	0.1	-	-	-	0	-	-	-

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:

$ZnO + C \rightarrow Zn(gas) + CO$ Reaction 1
$ZnO + CO \rightarrow Zn(gas) + CO_2$ Reaction 2
$CO_2 + C \rightarrow 2CO$ Reaction 3

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 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 (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), and ammonia (NH_3). According to CORINAIR90 the main relevant pollutant is SO_2 (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 SO_2 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 SO_2 in the off-gas vary with the type of roaster operation. Typical SO_2 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 SO_2 is emitted from the sinter plant; the quantity depends on the sulphur content of the calcine feedstock. The SO_2 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 SO_2 emissions from these devices [2,3].

4 SIMPLER METHODOLOGY

A simpler methodology using economic or production statistics is feasible as a first approach. Emission factors for this approach are however currently lacking.

5 DETAILED METHODOLOGY

If detailed information about the local situation is available this should prevail over the use of general emission factors.

6 RELEVANT ACTIVITY STATISTICS

The statistical data for the primary zinc production can be derived from production 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

The emission factor for ore handling is calculated with the following formula:
$\text{Emission} = \{[\text{Mass}]_{\text{dust}} * [\text{Mass}]_{\text{ore}} * [\text{Metal compositon}]_{\text{dust}}\} * [\text{Zinc}]^{-1}_{\text{production}}$ [Formula 1], where

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

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

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

$[\text{Flow}]_{\text{gas}}$: 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);

$[\text{Metal composition}]_{gas}$: Average concentration of heavy metals in emitted gas (g m^{-3} gas);

$[\text{Zinc}]_{production}$: Total yearly produced zinc (tonnes).

The emissions can vary widely depending on the ore used and the abatement measures applied, see Table 8.1 for reported emission factors. The emission factors given in Table 8.2 were prepared for the PARCOM-ATMOS Emission Factors Manual 1992. The factors for the emissions are based on the information from Table 8.1.

Table 8.1: Emission factors for the primary zinc production (g.Mg^{-1} product) as reported by several countries/authors

	Germany [4]		**Poland [5]**		**Netherlands [6]**	**Pacyna [7,8]**	
Compound	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 8.2.: 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 8.1)

Table 8.3 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 8.3: 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_2O [g/GJ]
s	coke	hc	coke oven	107	463[2)]	35[2)]				105[2)]	
l	oil		residual	203	1,030-1,470[1)]	150[1)]			15[1)]	76[1)]	14[1)]
l	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)

[3)]	SO_x: [1]	2,145,000	g/Mg conc. ore processed	multiple hearth roaster
		325	g/Mg conc. ore processed	sinter shand
		565	g/Mg conc. ore processed	vertical retort, electrothermal furnace
		202,200	g/Mg conc. ore processed	flash roaster
		111,750	g/Mg conc. ore processed	fluidised bed roaster
		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

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

13 TEMPORAL DISAGGREGATION CRITERIA

Primary zinc production is usually a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency
Compilation of air pollutant emisssion 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
2 US-EPA (ed.): AP 42 CD-Rom; 1995
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18 BIBLIOGRAPHY

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SNAP CODE: **030306**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Primary Copper Production

NOSE CODE: **104.12.07**

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

This chapter presents information on atmospheric emissions during the production of copper in primary smelters. More than 80 copper smelters around the world employ various conventional pyrometallurgical techniques to produce more than 90 % of the total copper production (e.g. Pacyna, 1989). Generally there are 3 steps in this process: 1) roasting of ores to remove sulphur, 2) smelting of roaster product to remove a part of the gangue for production of the copper matte, and 3) converting of the copper matte to blister copper. Atmospheric emissions of sulphur dioxide and heavy metals on fine particles occur during all the above mentioned processes.

Both, emissions from fuel combustion in the primary copper plants and industrial processes are discussed here.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions of sulphur dioxide from non-ferrous metal production, particularly copper production contribute less than 10% to the total global emissions of this pollutant. However, copper smelting can be the most important source of sulphur dioxide emissions in certain regions, such as the Kola Peninsula, the Urals, the Norilsk area, and the Fergana region in Russia, Lower Silesia in Poland, and the Gijon region in Spain.

The contribution of emissions released from primary copper 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_2O	NH_3
Primary Copper Production	030306	0.1	0	-	-	0.2	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Various trace elements can be measured as impurities in copper ores. During the copper production process they are emitted to the atmosphere. This process is the major source of atmospheric arsenic and copper (about 50 % of the global emissions of the element), and indium (almost 90 %), and a significant source of atmospheric antimony, cadmium and selenium (ca. 30 %), and nickel and tin (ca. 10 %) (Nriagu and Pacyna, 1988). The production of copper (and nickel) is the major source of these and other elements in regions with non-ferrous metal production. Contribution of primary copper production emissions of selected trace metals to the total emissions in Europe is presented in Table 2.2 (Pacyna, 1996).

Table 2.2: Contribution to the European emission of trace metals at the beginning of the 1990's (Pacyna, 1996)

Source-activity	SNAP-code	Contribution to the total emissions			
		As	Cd	Pb	Zn
Primary Copper Production	030306	29.4	10.5	4.8	6.2

Primary copper production is unlikely to be a significant source of sulphurhexafluoride (SF_6), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs), (ETC/AEM-CITEPA-RISOE 1997).

3 GENERAL

3.1 Description

The traditional pyrometallurgical copper smelting process is illustrated in Figure 3.1 (EPA, 1993). Typically, the blister copper is fire refined in an anode furnace, cast into "anodes" and sent to an electrolytic refinery for further impurity elimination. The currently used copper smelters process ore concentrates by drying them in fluidized bed dryers and then converting and refining the dried product in the same manner as the traditionally used process (EPA, 1993).

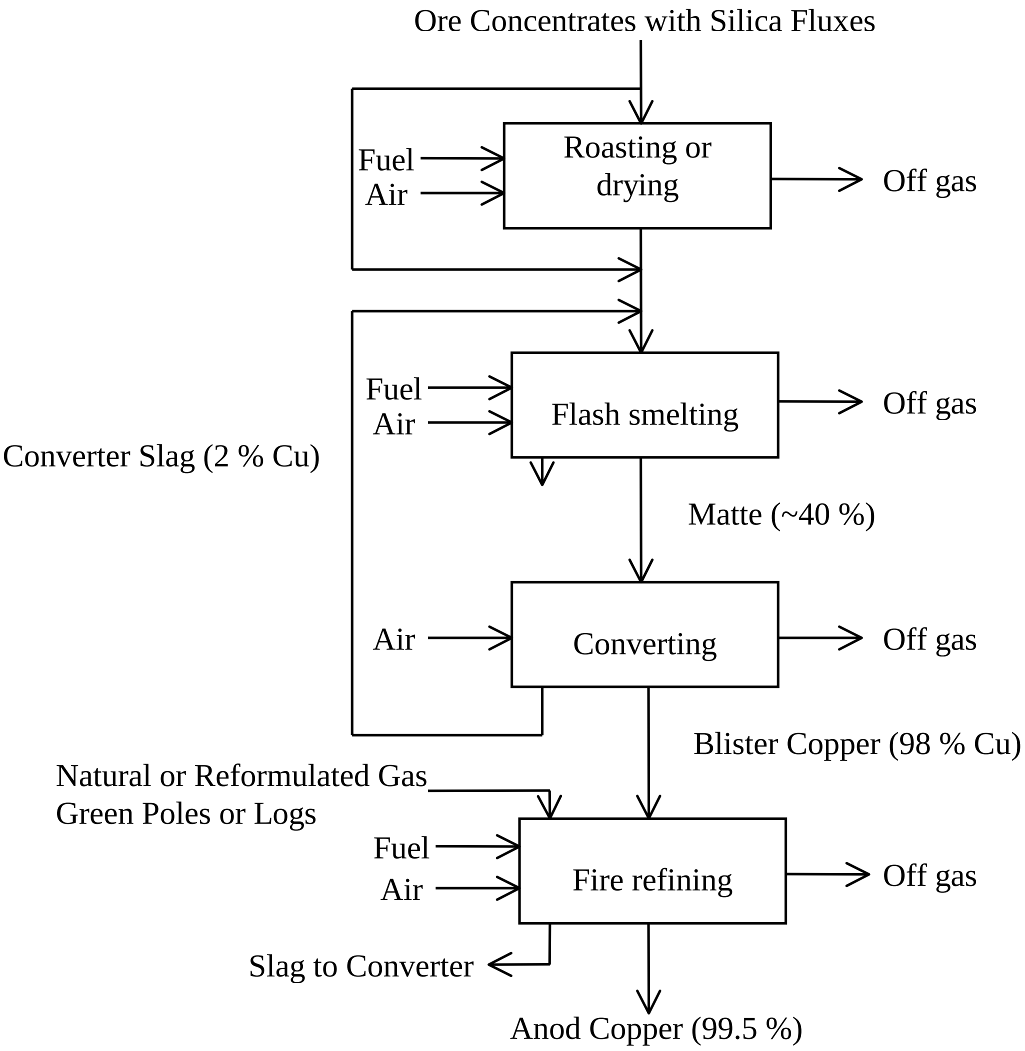
Concentrates usually contain 20-30 % Cu. In roasting, charge material of copper mixed with a siliceous flux is heated in air to about 650 C, eliminating 20 to 50 % of sulphur and portions of volatile trace elements. The roasted product, calcine, serves as a dried and heated charge for the smelting furnace.

In the smelting process, calcines are melted with siliceous flux in a flash smelting furnace to produce copper matte, a molten mixture of cuprous sulphide, ferrous sulphide, and some trace elements. Matte contains usually between 35 and 65 % of copper. Heat required in the smelting process comes from partial oxidation of the sulphide charge and from burning external fuel. Several smelting technologies are currently used in the copper industry, including reverberatory smelting, flash smelting (two processes are currently in commercial use: the INCO process and the OUTOKUMPU process), and the Noranda and electric processes.

In the reverberatory process heat is supplied by combustion of oil, gas, or pulverised coal. The temperature in the furnace can reach 1500 C. Flash furnace smelting combines the operations of roasting and smelting to produce a high grade copper matte from concentrates and flux. Most of flash furnaces use the heat generated from partial oxidation of their sulphide charge to provide much or all of the energy required for smelting. The temperature in the furnace reaches between 1200 and 1300 C. The Noranda process takes advantage of the heat energy available from the copper ore. The remaining thermal energy is supplied by oil burners, or by coal mixed with the ore concentrates. For the smelting in electric arc furnaces, heat is generated by the flow of an electric current in carbon electrodes lowered through the furnace roof and submerged in the slag layer of the molten bath (e.g. EPA, 1993; UN ECE, 1994).

Concerning emissions of air pollutants from the smelting operations, all the above described operations emit trace elements. Flash furnace smelting produces offgas streams containing high concentrations of sulphur dioxide. In contrary, electric arc furnaces do not produce fuel combustion gases, so flow rates are lower and so are the sulphur dioxide concentrations.

Figure 3.1: Typical primary copper smelter process (adapted from EPA, 1993)



The final step in the production of blister copper is converting. The rest of iron and sulphur in the matte is removed in this process leaving molten blister copper. Blister copper usually contains between 98.5 and 99.5 % pure copper with the rest consisting of trace elements, such as gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulphur, tellurium, and zinc. There are various converting technologies applied in the copper production. The temperature in the converting furnace reaches 1100 C.

3.2 Definitions

Roasting -	high-temperature process of the calcine production from ore concentrates.
Smelting -	high-temperature process of the matte production from roasted (calcine feed) and unroasted (green feed) ore concentrates.
Converting -	high-temperature process to yield blister copper from the matte.
Matte -	impure product of smelting of sulphide ores.

3.3 Techniques

A description of primary copper process technology is given in section 3.1.

3.4 Emissions

Pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), trace elements, and selected persistent organic pollutants (POPs). The main relevant pollutants are SO_2 and CO, according to CORINAIR90 (see also Table 2.1) and selected trace elements. Concerning POPs, there are mostly dioxins and furans which are emitted from shaft furnaces, converters, and flame furnaces.

Primary copper smelters are a source of sulphur oxides (SO_x). Emissions are generated from the roasters, smelting furnaces, and converters (see Table 3.1). Fugitive emissions are generated during material handling operations. Remaining smelter operations use material containing very little sulphur, resulting in insignificant SO_2 emissions (EPA, 1995). Here only emissions from combustion processes with contact are relevant.

Table 3.1 shows typical average SO_2 concentrations from the various smelter units.

It can be assumed, that the SO_2 concentrations given in Table 3.1 take into account emissions from fuel sulphur and ore sulphur.

Table 3.1: Typical sulphur dioxide concentrations in off-gas from primary copper smelting sources (EPA, 1995)

Process unit	SO_2 concentration [vol.-%]
Multiple hearth roaster	1.5 - 3
Fluidized bed roaster	10 - 12
Reverberatory furnace	0.5 - 1.5
Electric arc furnace	4 - 8
Flash smelting furnace	10 - 70
Continuous smelting furnace	5 - 15
Pierce-Smith converter	4 - 7
Hoboken converter	8
Single contact H_2SO_4 plant	0.2 - 0.26
Double contact H_2SO_4 plant	0.05

3.5 Controls

Emission controls on copper smelters are employed for controlling sulphur dioxide and particulate matter emissions resulting from roasters, smelting furnaces, and converters. Control of sulphur dioxide emissions is achieved by absorption to sulphuric acid in the sulphuric acid plants, which are commonly a part of copper smelting plants. Reverberatory furnace effluent contains minimal SO_2 and is usually released directly to the atmosphere with no SO_2 reduction. Effluents from the other types of smelter furnaces contain higher concentrations of SO_2 and are treated in sulphuric acid plants before being vented. Single-contact sulphuric acid plants achieve 92.5 to 98 % conversion of SO_2 from plant effluent gas. Double-contact acid plants collect from 98 to more than 99 % of the SO_2. Absorption of the SO_2 in dimethylaniline solution has also been used in US-American smelters to produce liquid SO_2. (EPA, 1995).

Electrostatic precipitators (ESPs) are the common particulate matter control devices employed at copper smeltering facilities. The control efficiency of ESPs often reaches about 99 %. It should be added that most of the trace elements is condensed on very fine particles, e.g. <1.0 um diameter, and the control efficiency for these particles is lower, reaching about 97 % (e.g. Pacyna, 1987a).

A detailed description of control techniques and best available technologies for the primary copper production is available in UN ECE (1994).

4 SIMPLER METHODOLOGY

The simpler methodology for sulphur dioxide emission estimation gives recommendations on a smelter-by-smelter level, taking into account the ore consumption or socio-economic data. Emission factors can be used in the case where no measurements are available. Emission factors for sulphur dioxide depend on the copper production technology, the type and efficiency of control equipment, and sulphur content of copper ores.

Emission factors for trace elements depend on similar parameters to the sulphur dioxide emission factors. For the simpler methodology a mean emission factor can be used together with information on copper production in a given country or region without further specification on the type of industrial technology or the type and efficiency of control equipment. However, if the typical degrees of abatement control are known then this should be taken into account.

5 DETAILED METHODOLOGY

The detailed methodology to estimate emissions of sulphur dioxide from the primary copper production is based on measurements or estimations using emission factors. The measurement and estimation approaches described for “Combustion plants as point sources” chapter B111 can also be used for primary copper production.

The detailed methodology to estimate emissions of trace elements from the primary copper production is similar to the simpler one. However, more information on the type of the process, e.g. roasting, smeltering, or converting, as well as on the type of the industrial technology should be made available. This information shall be used to estimate specific emissions for at least a specific industrial technology.

Measurements of the emission rate and chemical composition of fine particles with < 1.0 um diameter are often carried out at major copper smelters worldwide. The results of these measurements are then used to estimate atmospheric emissions of several trace elements contained as impurities in copper ores.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of copper in primary smelters is widely available from the UN statistical yearbooks (e.g. UN, 1995). This information is satisfactory to estimate emissions with the use of the simpler estimation methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of the metal produced by various types of industrial technologies employed in the copper industry. Therefore, the application of the detailed estimation methodology may be complicated unless the statistical data are available directly from a given smelter.

Some statistical yearbooks provide information about the production of blister copper.

No information is easily available on the content of impurities in the copper ores from different mines or even mining regions.

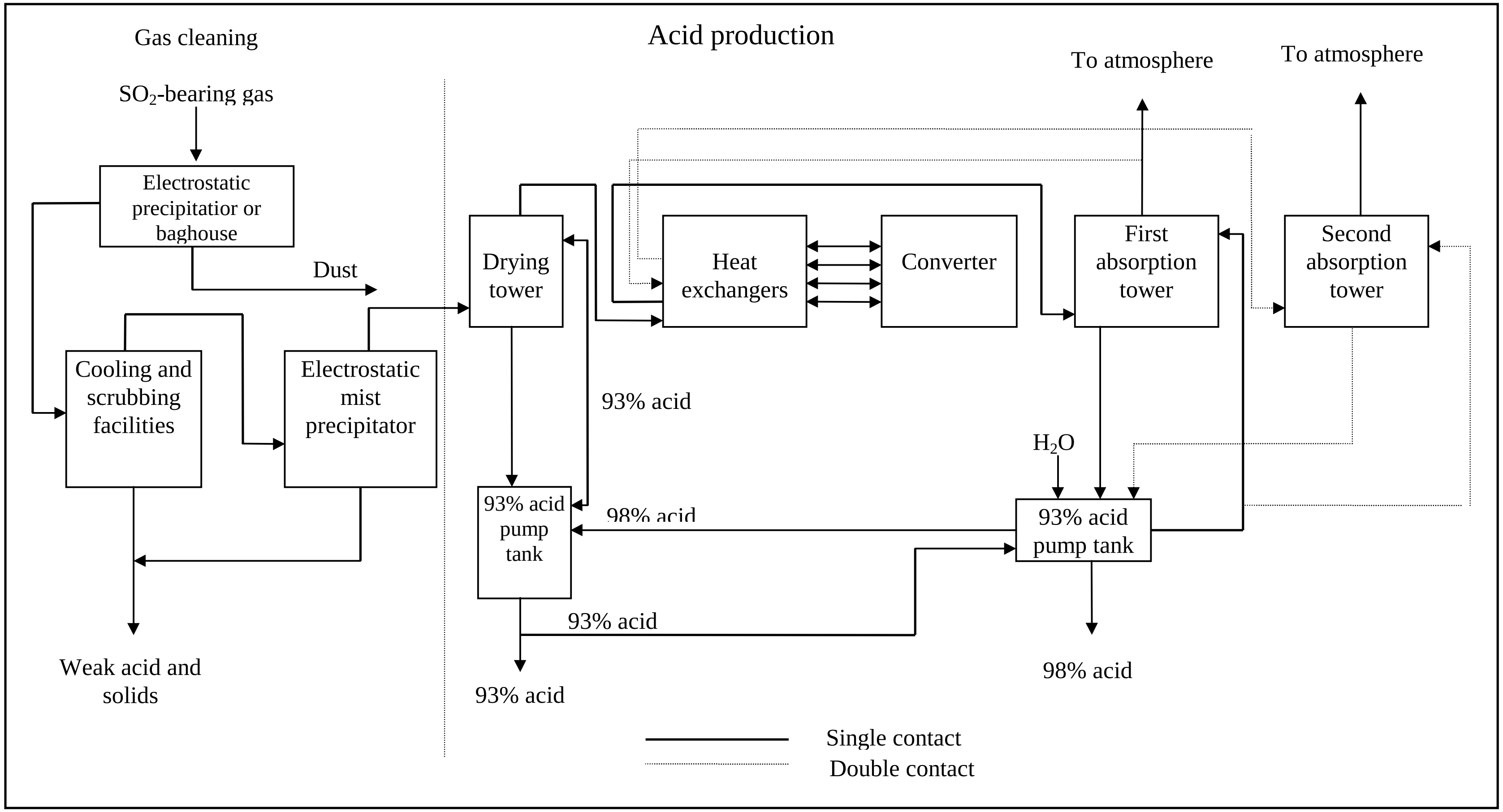
7 POINT SOURCE CRITERIA

Primary copper smelters should be regarded as point sources, very often high point sources, e.g. with over 100 m high stacks if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The traditional roasters produce emissions with an average of 1 to 4 % of sulphur dioxide and 3 to 6 % of the weight of the charged concentrate as particulate. This type of roaster also produces substantial amounts of fugitive emissions. The fluid bed roaster, which is now becoming common, produces between 10 and 15 % of sulphur dioxide; up to 80 % of the calcine concentrate will leave the roaster in the flue gas (Environment Canada, 1982). The flue gases from the traditional smelter furnace contain between 1 and 2 % of sulphur dioxide, which can be increased to 2.5 % by oxygen enrichment of the air. Flash smelting produces sulphur dioxide concentrations as high as 80 % when only oxygen is used, or up to 10 to 15 % when no oxygen is used (Environment Canada, 1982). Finally, the conventional converters produce emissions with sulphur dioxide concentrations ranging from almost 0 to 10 % and averaging about 4 to 5 %. Sulphuric acid is the most common sulphur product recovered from metallurgical gases. A production schematic for single and double contact sulphuric acid plant is shown in Figure 8.1.

Figure 8.1: Single and double contact sulphuric acid plant schematic (adapted from Environment Canada, 1982)



The production data and maximum sulphur dioxide emissions for sulphuric acid processes are presented in Table 8.1 (Environment Canada, 1982).

Table 8.1: Production data and maximum sulphur dioxide emissions for sulphuric acid processes (adopted from Environment Canada, 1982)

Sulphuric acid recovery process	SO_2 removal	SO_2 concentration in input gas (vol. %)	Maximum sulphur dioxide emissions in gas after treatment
Single contact process	97.5 %	7 %	5.7 g SO_2/m^3
	97.5 %	6 %	4.8 g SO_2/m^3 17 kg SO_2/t H_2SO_4
Double contact process	99.5 %	10 %	1.7 g SO_2/m^3 3.3 kg SO_2/t H_2SO_4
	99.5 %	6 %	1.0 g SO_2/m^3 3.3 SO_2/t H_2SO_4
	99.0 %	10 %	3.5 g SO_2/t H_2SO_4 6.6 kg SO_2/t H_2SO_4
	99.0 %	6 %	1.9 g SO_2/m^3 5.5 kg SO_2/t H_2SO_4

Table 8.2 contains fuel related emission factors for primary copper production based on CORINAIR90 data in [g/GJ].

Table 8.2: Emission factors for primary copper production

					Emission factors						
	Type of fuel			NAPFUE code	SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
s	coal	bc	briquettes	107	632[2]	702[2]				112[2]	
l	oil		residual	203	419-1,470[1], 419-1,030[2]	123-150[1], 123-150[2]	7[1][2]	1[1]	5-15[1], 5-20[2]	76-79[1], 77-79[2]	15[1][2]
l	oil		gas	204	1,410[1]	100[1]			12[1]	73[1]	
Data quality rating					B	B	D	D	C	C	D

[1] CORINAIR90 data, area sources

[2] CORINAIR90 data, point sources

Table 8.3: Emission factors for SO_2 in kg/tonne ore processed, unless specified otherwise (EPA, 1995)

Process type	Abatement type	Abatement efficiency	Emission Factor	Data Quality	Country or Region
Multiple hearth roaster	N/A	N/A	140.00	E	USA
Reverberatory smelting furnace after roaster	N/A	N/A	90.00	E	USA
Converter, all configurations	N/A	N/A	311.50	E	USA
Ore concentrate dryer	N/A	N/A	0.50	E	USA
Reverberatory smelting furnace with ore charge, without roasting	N/A	N/A	160.00	E	USA
Fluidized bed roaster	N/A	N/A	18.00	E	USA
Electric smelting furnace	N/A	N/A	120.00	E	USA
Flash smelting	N/A	N/A	410.00	E	USA
Roasting, fugitive emissions	N/A	N/A	0.50	E	USA
Reverberatory furnace, fugitive emissions	N/A	N/A	2.00	E	USA
Converter, fugitive emissions	N/A	N/A	65.00	E	USA
Anode refining furnace fugitive emissions	N/A	N/A	0.05	E	USA
Slag cleaning furnace, fugitive emissions	N/A	N/A	3.0	E	USA
Converter slag returns, fugitive emissions	N/A	N/A	0.05	E	USA
Slag cleaning furnace	N/A	N/A	3.75	E	USA
Reverberatory furnace with converter	N/A	N/A	160.00	E	USA
Fluidized bed roaster with reverberatory furnace and converter	N/A	N/A	180.00	E	USA
Concentrate dryer with electric furnace, cleaning furnace and converter	N/A	N/A	0.50	E	USA
Concentrate dryer with flash furnace and converter	N/A	N/A	0.50	E	USA
Multiple hearth roaster with reverberatory furnace and converter	N/A	N/A	140.00	E	USA
Fluidized bed roaster with electric furnace and converter	N/A	N/A	300.00	E	USA
Reverberatory furnace after multiple hearth roaster	N/A	N/A	90.00	E	USA
Electric furnace after concentrate dryer	N/A	N/A	120.00	E	USA
Flash furnace after concentrate dryer	N/A	N/A	410.00	E	USA
Electric furnace after fluidized bed roaster	N/A	N/A	45.00	E	USA
Primary metal production, process heaters *1	N/A	N/A	17209xS- -19006xS S=Sulphur content	E	USA

*1 in g/m^3 fuel
N/A = Not available

Technique related emission factors, mostly given in other units (e.g. g/Mg product) are listed in Tables 8.3 through 8.6 for sulphur dioxide, nitrogen oxides, VOCs, and particulate matter. No information exists on the type and efficiency of abatement techniques, but the factors in these tables seem to be valid for emission uncontrolled processes.

Table 8.4: Emission factors for NO_X in kg/tonne ore processed, unless specified otherwise (EPA, 1995)

Process type	Abatement type	Abatement efficiency	Emission Factor	Data Quality	Country or Region
Multiple hearth roaster	N/A	N/A	1.80	E	USA
Reverberatory smelting furnace after roaster	N/A	N/A	2.90	E	USA
Converter, all configurations	N/A	N/A	0	E	USA
Reverberatory smelting furnace with ore charge, without roasting	N/A	N/A	5.15	E	USA
Primary metal production, process heaters *1	N/A	N/A	2400-6600	E	USA

*1 in g/m^3 fuel
N/A = Not available

Table 8.5: Emission Factors for VOC in g/tonne ore processed, unless specified otherwise (EPA, 1995)

Process type	Abatement type	Abatement efficiency	Emission Factor	Data Quality	Country or Region
Multiple hearth roaster	N/A	N/A	4.5	E	USA
Reverberatory smelting furnace after roaster	N/A	N/A	7.5	E	USA
Ore concentrate dryer	N/A	N/A	2.0	E	USA
Reverberatory smelting furnace with ore charge, without roasting	N/A	N/A	1.5	E	USA
Primary metal production, process heaters *1	N/A	N/A	24-34	E	USA

*1 in g/m^3 fuel
N/A = Not available

Table 8.6: Emission factors for particulate matter in kg/tonne ore processed, unless specified otherwise (EPA, 1995)

Process type	Abatement type	Abatement efficiency	Emission Factor	Data Quality	Country or Region
Multiple hearth roaster	N/A	N/A	22.50	E	USA
Reverberatory smelting furnace after roaster	N/A	N/A	25.00	E	USA
Converter, all configurations	N/A	N/A	18.00	E	USA
Ore concentrate dryer	N/A	N/A	5.00	E	USA
Reverberatory smelting furnace with ore charge, without roasting	N/A	N/A	25.00	E	USA
Fluidized bed roaster	N/A	N/A	27.50	E	USA
Electric smelting furnace	N/A	N/A	50.00	E	USA
Flash smelting	N/A	N/A	70.00	E	USA
Roasting, fugitive emissions	N/A	N/A	1.30	E	USA
Reverberatory furnace, fugitive emissions	N/A	N/A	0.20	E	USA
Converter, fugitive emissions	N/A	N/A	2.20	E	USA
Anode refining furnace fugitive emissions	N/A	N/A	0.25	E	USA
Slag cleaning furnace, fugitive emissions	N/A	N/A	4.00	E	USA
Slag cleaning furnace	N/A	N/A	5.00	E	USA
Reverberatory furnace with converter	N/A	N/A	25.00	E	USA
Fluidized bed roaster with reverberatory furnace and converter	N/A	N/A	27.50	E	USA
Concentrate dryer with electric furnace, cleaning furnace and converter	N/A	N/A	5.00	E	USA
Concentrate dryer with flash furnace and converter	N/A	N/A	5.00	E	USA
Multiple hearth roaster with reverberatory furnace and converter	N/A	N/A	22.50	E	USA
Fluidized bed roaster with electric furnace and converter	N/A	N/A	27.50	E	USA
Reverberatory furnace after multiple hearth roaster	N/A	N/A	25.00	E	USA
Electric furnace after concentrate dryer	N/A	N/A	50.00	E	USA
Flash furnace after concentrate dryer	N/A	N/A	70.00	E	USA
Electric furnace after fluidized bed roaster	N/A	N/A	50.00	E	USA
Fire (furnace) refining	N/A	N/A	5.00	E	USA
Reverberatory furnace after fluidized bed roaster	N/A	N/A	25.00	E	USA

N/A = Not available

A list of emission factors for several trace elements emitted from copper smelters is presented in Table 8.7. Results of measurements carried out in various countries were used to estimate these factors. The factors can be differentiated only as those relevant for a smelter with limited or improved control equipment. Limited control of emissions relates to a case of smelter equipped with ESP, the most common emission control installation in copper smelters worldwide, having control efficiency of about 99 %. Improved control of emissions relates to a case of smelter equipped with advanced emission control installation, such as high efficiency ESP, fabric filters, and/or wet scrubbers. Control efficiency of at least 99.9 % should be achieved in such smelter. It is assumed that all major copper smelters in the UN ECE region are equipped with at least limited control installations. Therefore, no uncontrolled emission factors are presented in Table 8.7.

Information available from the above mentioned measurements does not allow for further differentiation of emission factors with respect to either various industrial processes involved in the primary copper production or different production technologies used at present. Therefore, the factors in Table 8.7 can only be used in a simpler emission estimation methodology.

Table 8.7: Compilation of emission factors for primary copper production (in g/tonne Cu produced)

Element	Global Emission Survey (Nriagu & Pacyna, 1988)	Measurements in Poland (Pacyna et al., 1981)	Measurements in Germany (Jockel and Hartje, 1991)	Measurements in Sweden (PARCOM, 1991)	Estimates in Canada (Jaques, 1987)	PARCOM program (PARCOM, 1992)	Suggested	
							Limited control	Impact control
Arsenic	1000-1500	~1000	15-45	100	600	50-100	500-1500	15-50
Chromium					1		1	?
Cadmium	200-400		3-10	15	550	6-15	200-500	3-10
Copper	1700-3600	1700-3600		300	200-12320		1500-4000	200-300
Indium	1-4						1-4	?
Manganese	100-500						100-500	?
Nickel	900				10-3410		900-3000	10-100
Lead	1300-2600	2300-3600	70	250	860-16700	250-2000	1000-4000	50-250
Antimony	50-200	~100			20		50-200	10-20
Selenium	50-150						50-150	10-20
Tin	50-200						50-200	?
Vanadium	5-10						5-10	?
Zinc	500-1000	~970		200		200-850	500-1000	100-200
Bismuth		~150					100-200	?
Mercury			0.06				?	0.10
Control	Unspecified	ESP, ca. 99% efficiency	High efficiency control equipment	Limited abatement (usually ESPs, fabric filter, wet scrubbers)	Based on questionnaires. Most plants use ESPs with 99 % efficiency	Unspecified	Common ESPs with 99% efficiency	Advanced control with at least 99.9% efficiency
Quality Data code	D	C	C	C	E	E	D	D

Concentrations of dioxins and furans in the flue gas after passing the control equipment in the primary copper production are presented in Table 8.8 after a compilation of data by the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Emission Control Committee in Germany (Umweltbundesamt, 1996).

Table 8.8: Concentrations of dioxins and furans in the flue gas after passing the control devices, in ng TEQ/m^{3*1}

Process	Emission Control Device	PCDD/F Concentration	Data Quality Code
1. Shaft furnace:		9.7	D
-old installation	Fabric filter		
-new installation	Fabric filter	1.5 - 2.0	C
2. Converter:			D
-using liquid black copper, and scrap	Fabric filter	0.16 - 0.6	
-using copper matte	ESP	0.001 - 0.005	D
3. Anode kiln	Fabric filter	0.05 -1.1	D
(flame furnace)			
4. Suspended melting	ESP	0.0001 - 0.007	D
furnace			

[*1] The toxic equivalency factor established by NATO/CCMS

In general, concentrations of dioxins and furans in the flue gas after the control device vary substantially due to the large differences in the materials used and different operational processes employed. For new installations controlled with fabric filters the concentrations would be up to 2.0 ng TEQ/m^3, while for older plants these concentrations can be by one order of magnitude higher.

Data from Table 8.8 can be presented in a form of emission factors. These factors would range from 0.25 to 22.0 µg 1-TEQ/tonne of the copper produced.

9 SPECIES PROFILES

At present no reliable information exists on physical and chemical species of trace elements emitted during the primary copper production. It can be assumed that the majority of trace elements volatilized from the ores and then from semi-products in the production process enter the atmosphere on fine particles.

Very general information collected by Pacyna (1987b) appears to indicate that oxides and sulphates are the major chemical forms of atmospheric trace elements from the primary copper production.

10 UNCERTAINTY ESTIMATES

It is rather difficult to assess current uncertainties of emission estimates for pollutants emitted during the primary copper production. The uncertainties of sulphur dioxide emission estimates can be assessed in a similar way as the uncertainties of the estimates for the fossil fuel combustion (see chapter B111).

Recently it was concluded that up to 50 % of uncertainties can be assigned to the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Similar uncertainty can be assigned for emission estimates of these compounds from the primary copper production.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for the primary copper production. This improvement should focus on preparing individual emission factors for major industrial technologies currently employed in roasting, smelting, and converting processes in the copper industry. In this way a detailed approach methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data on the production of the calcines, matte, and blister.

The fuel specific emission factors provided in Table 8.2 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 FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The primary production process is a continuous process. No temporal dissaggregation is needed.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

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16 VERIFICATION PROCEDURES

Estimated emission factors could be best verified by measurements at plants using different industrial technologies.

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18 BIBLIOGRAPHY

No additional documents to those in Section 17.

19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **030307**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Secondary Lead Production

NOSE CODE: **104.12.08**

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

This chapter presents information on atmospheric emissions during the production of lead in secondary lead smelters. There are more than 200 secondary lead smelters in the world and a similar number of refineries, producing about 40% of the total lead production (Pacyna, 1989). Various furnaces, including blast, reverberatory and kettle-type ones, are employed in several production processes, such as storage battery production, lead alkyl manufacture, the manufacture of collapsible tubes, ammunition and plumbing equipment, coating of electrical cables and the casting, grinding, and machining of lead alloys, such as brasses and bronzes, in foundries, etc. This chapter describes the methods to estimate emissions of atmospheric pollutants during the secondary lead recovery from products such as battery plates, cable sheathing, type metal, and various slags and drosses.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

The contribution of emissions released from secondary lead 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_2O	NH_3
Secondary Lead Production	030307	0	-	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

There are several trace elements that can be emitted during the secondary lead production. However, these emissions are not very significant on a global scale. Nriagu and Pacyna (1988) concluded that secondary lead production contributes well below 1 % of the total atmospheric emissions of lead, antimony, selenium, and zinc. The estimated contribution of both primary and secondary lead production to European emissions is given in table 2-2.

However, a secondary lead smelter or refinery can be an important emission source on a local scale.

Table 2-2: Contribution to total heavy metal emissions of the OSPARCOM-HELCOM-UN/ECE inventory for 1990 (up to 38 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Total Lead Production	0403pb	1.0	1.4	-	0.1	0.9	-	1.1	1.1

- = no emissions are reported

Secondary lead production may be a source of polychlorinated dioxins and furans, depending on parameters such as the composition of the raw material (e.g. presence of PVC in battery scrap). European wide emission estimates from this sector are not available.

3 GENERAL

3.1 Description

A secondary lead smelter is defined as any plant or factory in which lead-bearing scrap or lead-bearing materials, other than lead-bearing concentrates (ores) derived from a mining operation, is processed by metallurgical or chemical methods into refined lead, lead alloys or lead oxide. The high proportion of scrap-acid batteries that is re-processed provides feed for the alloy lead market (Barbour et al., 1978).

Secondary lead can be produced using pyrometallurgical or hydrometallurgical processes. Up to now hydrometallurgical processes have only been used at a preliminary stage. The pyrometallurgical processes are subdivided as follows (Rentz et al., 1996):

- battery breaking and processing (scrap preparation),
- smelting of battery scrap materials,
- refining.

In contrast to secondary zinc and copper production, which use a great variety of secondary materials, the recycling of secondary lead materials is concentrated on the processing of scrap batteries, with a world-wide portion of about 80 %. Metal sheets, pipe scraps, sludges, drosses, and dusts play only a minor role as secondary raw materials.

Secondary lead is sometimes combined with primary material for refining. Various pyrometallurgical refining technologies can be applied, depending on the feed material and product specification.

3.2 Definitions

Secondary lead production: - production of lead from materials other than ores.

3.3 Techniques

In general, for the production of secondary lead from battery scrap *two basic process routes* are possible. One route is based on breaking up and dismantling old batteries, and separating the paste, metallics and organics. Melting and reduction is carried out afterwards in different types of furnaces with an additional refining step. The other route is characterised by the direct treatment of complete and undismantled batteries with or without sulphuric acid inside in various smelting furnaces, also with an additional refining step. In detail, in the various stages of pyrometallurgical processing the following technologies are used world-wide (Rentz et al., 1996):

Battery scrap preparation
For battery scrap preparation various processes are possible, which can be differentiated by the degree of separation of single battery components. On an industrial scale, the Penneroya process, the MA process, the Tonolli-CX, and Contibat process are used. Generally heavy metal emissions from battery scrap preparation play a minor role compared to the smelting operation. The Varta and the Bergsoe process are smelting processes carried out without an initial separation, so that the batteries are directly smelted in a furnace.

Smelting
For the industrial production of secondary lead, various kinds of smelting furnaces are employed. The short rotary furnace is the most extensively used furnace for smelting separated battery scrap materials, while long rotary kilns and reverberatory furnaces are only used in a few applications. In contrast to the short rotary kiln, the long rotary kiln is operated continuously. Reverberatory furnaces may also be used for smelting a lead-rich slag, which has been recovered in a primary furnace. Shaft furnaces are typically used for smelting unprepared battery scrap, together with lead cable scrap, furnace slag and filter dusts.

Refining
The lead bullion from secondary lead production contains various impurities, mainly copper, antimony, and tin, which may require elimination or adjustment by refining. Generally the operations necessary for secondary lead refining are limited compared to those necessary for primary lead refining. Pre-decopperising is not necessary and only final decopperising is carried out. In addition, a removal and adjustment of antimony and the elimination of tin may be necessary.

3.4 Emissions

In the secondary lead production process various direct and fugitive heavy metal emission sources are present (Rentz et al., 1996):

From *battery scrap preparation* only small amounts of particulate heavy metals are emitted as direct emissions if single preparation devices are equipped with a special waste gas cleaning facility.

For the *smelting process*, depending on the type of furnace various kinds of fuels are used. Generally short rotary furnaces and long rotary kilns are equipped with natural gas/air burners or sometimes with oxy-fuel burners, while shaft furnaces use coke as fuel. With the generated waste gas, irrespective of which kind of furnace is used, considerable amounts of heavy metals contained in the dust, as well as certain amounts of gaseous heavy metals are released, depending on the melting temperature and the vapour pressure.

For *refining and alloying*, several kettles are installed depending on the required lead quality. Because of the ongoing reactions in the waste gas from the refining and alloying kettles various amounts of heavy metals in particulate and gaseous form may be emitted.

Fugitive emissions from secondary lead smelting are released with almost all *stockpiling, transferring, charging,* and *discharging processes* The amount and composition greatly depends on the process configuration and operation mode. Values concerning the magnitude of unabated and abated emissions have not been revealed. The smelting furnaces are connected with fugitive emissions during the *charging* of raw materials and the *discharging* of slag and lead bullion. Also the *furnace openings* may be an emission source. Fugitive emissions from refining operations arise mainly during *charging, discharging* and *metal transfer* operations. Refining vessels not covered with primary hoods, may be a further emission source.

As in many plants, direct emission sources are preferably equipped with emission reduction measures, and the fugitive emissions released into ambient air in secondary lead production are generally much higher compared to direct emissions.

By far the most important *SO_2 and NO_x* emission source during secondary lead production is the operation of the smelting furnaces. The amount of SO_2 formed is mainly determined by the amount of sulphur contained in the raw materials and in the fuel used. Although a major part of the sulphur remains in the slag formed during the smelting process, a considerable share is also converted to SO_2.

SO_2 concentrations in the off-gas from reverberatory furnaces and blast furnaces are only available on a volume-percentage basis. During tests carried out at a reverberatory furnace using natural gas as a fuel, the concentration of SO_2 in the off-gas was measured at about 0.1 vol.-%. At a blast furnace using coke as fuel an even smaller off-gas concentration in the range of about 0.03 vol.-% was measured (Rentz et al., 1996b).

The formation of polychlorinated dioxins and furans depends on a number of factors such as scrap composition, process type, temperature, etc.

3.5 Controls

Most of the secondary lead smelters are equipped with dust-removing installations, such as baghouses for the control of direct emissions. The control efficiency of these installations is often very high and can reach 99.9 %. In secondary lead production for most processes it is possible to carry out final dedusting with fabric filters. In this way clean gas dust loads in general below 5 mg/m^3(STP) are achieved. For covering direct emissions from the refining and alloying kettles, primary suction hoods are arranged above the refining and melting kettles. These hoods are also linked to fabric filters. Waste gases from the furnace and the refining kettles may be dedusted together in one filter. Electrostatic precipitators or wet

scrubbers may be in use for special raw gas conditions. Wet scrubbers are sometimes in place for the control of SO_2. Fugitive particulate emissions can be collected by local systems like hoods and other suction facilities or by partial or complete enclosures (Rentz et al., 1996).
Primary measures for the control of SO_2 aim to reduce the sulphur content in the fuel and in the raw materials used. Accordingly lower SO_2 emissions occur when using natural gas instead of heavy fuel oil for short rotary, long rotary and reverberatory furnace firing. Within blast furnace operation, the use of coke with a low sulphur content reduces emissions.

Oxy-fuel burners have been used in short rotary furnaces resulting in a significant reduction of the fuel input. Accordingly, a smaller pollutant mass flow is observed, although the concentration in the off-gas may be higher than in conventional firing technologies.

Significantly lower emissions occur during secondary lead production if desulphurisation of the lead paste is carried out prior to thermal treating. Within the Engitec-CX process, for example, sulphur is removed from the electrode paste by adding NaOH or Na_2CO_3. According to an operator, a reduction of SO_2 emissions in excess of 90 % can be achieved by this measure (Rentz et al., 1996b).

4 SIMPLER METHODOLOGY

Application of general emission factors with appropriate activity statistics can be regarded as a simpler methodology for estimation of emissions from secondary lead production. However, it should be noted that the chemical composition of input scrap is one of the most important factors affecting the amount of emissions. The chemical composition of input scrap varies considerably from one plant to another and therefore emission factors also vary. Default emission factors in accordance with the simpler methodology are proposed in section 8.

5 DETAILED METHODOLOGY

In this case, different emission factors for various production technologies should be used. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of lead in secondary smelters is available from the United Nations Industrial commodity statistics yearbooks. This information is satisfactory to estimate emissions with the use of the simpler estimation methodology.

However, in most cases, no information is available from the statistical yearbooks on the quantities of the metal produced by various types of industrial technologies employed in the secondary lead industry. Therefore, the application of detailed estimation methodology may be complicated unless the statistical data are available directly from a given smelter. Some information in this respect is available from the International Lead and Zinc Study Group (ILZSG) (e.g. ILZSG, 1985).

7 POINT SOURCE CRITERIA

Secondary lead smelters should be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Information available from the sources cited below does not allow for further differentiation of emission factors with respect to either various industrial processes involved in the secondary lead production or different production technologies used at present. Therefore, the factors in table 8-1 can only be used in a simpler emission estimation methodology applied to the whole sector. As only limited background data are available on the emission factors, such as abatement type etc, a data quality E has been assigned.

The CORINAIR methodology requires the separate reporting of combustion related emissions (SNAP 030307) and process related emissions (SNAP 040300). Table 8-1 also gives emission factors related to the energy input in [g/GJ] based on CORINAIR90 data. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 values for the specific energy consumption were reported between 38.5 and 100 GJ/Mg product.

9 SPECIES PROFILES

At present no reliable information exists on physical and chemical species of trace elements emitted during the secondary lead production. It can be assumed that the majority of trace elements volatilised from scrap and other lead-containing materials enter the atmosphere on fine particles. Table 9-1 indicates the heavy metal composition of dust from various secondary lead furnaces (Rentz et al., 1996):

Table 9-1: Weight composition of dust from secondary lead furnaces

	Weight composition of dust [wt.-%]	
Short rotary furnace	As 0.002 - 0.4 Cd 0.07 - 0.7 Cr 0.01 Hg 0.01	Ni 0.002 - 0.01 Pb 20 - 54 Sb 0.011 - 1 Zn 0.5
Reverberatory furnace	As 0.1 - 10 Cd 0.01 - 0.5 Cu 0.001 - 0.005	Pb 30 - 50 Sb 0.1 - 40 Zn 0.01 - 1
Shaft furnace	As 0.01 - 3 Cd 0.5 - 10 Cu 0.01 - 0.04	Pb 30 - 55 Sb 0.1 - 3 Zn 1 - 10

Table 8-1: Emission Factor Table

Compound	**Plant type**	**Emission factor**	**Data Quality**	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Country or region**	**Ref.**
SO_2	*unknown*	0.85 - 8 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
SO_2	*reverberatory furnace*	40,000 g/Mg charged	*E*	*n. a.*	*n. a.*	*n. a.*	*U.S.A.*	*EPA 1990*
SO_2	*blast furnace (cupola)*	26,500 g/Mg charged	*E*	*n. a.*	*n. a.*	*n. a.*	*U.S.A.*	*EPA 1990*
SO_2	*pot furnace heater*	17.26 g/l burned	*E*	*n. a.*	*n. a.*	*NAPFUE 204*	*U.S.A.*	*EPA 1990*
SO_2	*pot furnace heater*	9,611 g/Mm^3 burned	*E*	*n. a.*	*n. a.*	*NAPFUE 301*	*U.S.A.*	*EPA 1990*
SO_2	*secondary metal production, process heaters*	17,209 S g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 204*	*U.S.A.*	*EPA 1990*
SO_2	*secondary metal production, process heaters*	19,006 S g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 203*	*U.S.A.*	*EPA 1990*
NO_x	*unknown*	60 - 110 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
NO_x	*reverberatory furnace*	150 g/Mg charged	*E*	*n. a.*	*n. a.*	*n. a.*	*U.S.A.*	*EPA 1990*
NO_x	*blast furnace (cupola)*	50 g/Mg charged	*E*	*n. a.*	*n. a.*	*n. a.*	*U.S.A.*	*EPA 1990*
NO_x	*pot furnace heater*	2.4 g/l burned	*E*	*n. a.*	*n. a.*	*NAPFUE 204*	*U.S.A.*	*EPA 1990*
NO_x	*pot furnace heater*	2,242,573 g/Mm^3 burned	*E*	*n. a.*	*n. a.*	*NAPFUE 301*	*U.S.A.*	*EPA 1990*
NO_x	*secondary metal production, process heaters*	2,396.78 g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 204*	*U.S.A.*	*EPA 1990*
NO_x	*secondary metal production, process heaters*	6,591.15 g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 203*	*U.S.A.*	*EPA 1990*
VOC	*pot furnace heater*	0.024 g/l burned	*E*	*n. a.*	*n. a.*	*NAPFUE 204*	*U.S.A.*	*EPA 1990*
VOC	*pot furnace heater*	44,851 g/Mm^3 burned	*E*	*n. a.*	*n. a.*	*NAPFUE 301*	*U.S.A..*	*EPA 1990*
VOC	*secondary metal production, process heaters*	23.97 g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 204*	*U.S.A.*	*EPA 1990*

Table 8-1 (continued)

Compound	**Plant type**	**Emission factor**	**Data Quality**	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Country or region**	**Ref.**
VOC	*secondary metal production, process heaters*	33.55 g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 203*	*U.S.A.*	*EPA 1990*
VOC	*secondary metal production, process heaters*	44,851 g/m^3 fuel	*E*	*n. a.*	*n. a.*	*NAPFUE 301, process gas*	*U.S.A.*	*EPA 1990*
NMVOC	*unknown*	10 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
CH_4	*unknown*	2 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
CO	*unknown*	7 - 30 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
CO_2	*unknown*	55 kg/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
N_2O	*unknown*	3 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
As	*unknown*	8 g/Mg Pb produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Austria*	*Schneider 1994*
Cd	*unknown*	2.5-3 g/Mg Pb produced	*E*	*ESP*	*ca. 99 %*	*n. a.*	*Europe*	*Pacyna 1986, Schneider 1994*
Cu	*unknown*	1.0 g/Mg Pb produced	*E*	*ESP*	*ca. 99 %*	*n. a.*	*Canada*	*Jacques 1987*
Pb	*unknown*	770 g/Mg Pb produced	*E*	*ESP*	*ca. 99 %*	*n. a.*	*Europe*	*Pacyna 1986*
Pb	*unknown*	100-300 g/Mg Pb produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Europe, Canada*	*PARCOM 1992, Schneider 1994, Env. Can. 1983*
Zn	*unknown*	150 g/Mg Pb produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Austria*	*Schneider 1994*
Zn	*unknown*	300 g/Mg Pb produced	*E*	*ESP*	*ca. 99 %*	*n. a.*	*Europe*	*Pacyna 1986*
PCDD/F	*unknown*	5-35 µg I-TEQ/Mg Pb produced	*E*	*fabric filter/ lime injection - limited abatement*	*range*	*n. a*	*Europe*	*Bremmer 1995 TNO 1995*

n. a.: not available

10 UNCERTAINTY ESTIMATES

It is difficult to assess current uncertainties of emission estimates for pollutants emitted during the secondary lead production. Recently it was concluded that up to 50 % of uncertainties can be assigned for the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Higher uncertainty can be assigned for emission estimates of these compounds from the secondary lead production. Information on emission factors and statistics is more limited for the secondary lead smelters than for major point sources, such as primary smelters and power plants.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for the secondary lead production. This improvement should focus on preparing individual emission factors for major industrial technologies currently employed in the lead industry. In this way a detailed approach methodology for emission estimates can be applied. It will be necessary to obtain relevant statistical data on the production of lead in various secondary lead furnaces.

The fuel-specific emission factors provided in table 8-1, are related to point sources and area sources without specification. CORINAIR90 data can only be used in order to give a range of values 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 FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The secondary lead production is a continuous process. No temporal disaggregation is needed.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

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16 VERIFICATION PROCEDURES

Estimated emission factors could be best verified by measurements at plants using different industrial technologies.

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19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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SNAP CODE: **030308**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Secondary Zinc Production

NOSE CODE: **104.12.09**

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

Zinc is produced from various primary and secondary raw materials. The primary processes use sulphidic and oxidic concentrates, while in secondary processes recycled oxidised and metallic products mostly from other metallurgical operations are employed. This chapter includes information on atmospheric emissions during the production of secondary zinc. In practice, a clear distinction of primary and secondary zinc production is often difficult, because many smelters use both primary and secondary raw materials.

Zinc production in the western world stood at about 5.2 million tonnes in 1990. Of this, 4.73 million tonnes originate from primary resources (ores), while the balance of 0.47 million tonnes is produced at the smelters from secondary raw materials (Metallgesellschaft 1994). The production of zinc in secondary smelters is increasing in various regions of the world. This increase can be as high as 5% per year in Eastern Europe. This chapter describes the methods to estimate both combustion and process emissions of atmospheric pollutants during the secondary zinc recovery from various types of zinc scrap (e.g. Barbour et al, 1978).

2 CONTRIBUTIONS TO TOTAL EMISSIONS

There are several trace metals as well as dioxins and furans which can be emitted during the secondary zinc production process. However, heavy metal emissions from this source category are not very significant on a global scale. Nriagu and Pacyna (1988) concluded that the secondary zinc production contributes well below 1 % of the total atmospheric emissions of lead, cadmium, antimony, selenium, and zinc. A similar contribution to European atmospheric emissions from secondary zinc production was estimated at the beginning of the 1980’s (Pacyna, 1983). The estimated contribution of both primary and secondary zinc production to European emissions is given in Table 2.1 (Berdowski 1997). However, a secondary zinc smelter can be an important emission source on a local scale.

The contribution of emissions released from secondary zinc production to total emissions of those pollutants covered by the CORINAIR90 inventory is negligible (see Table 2.2).

Table 2.1: Contribution to total heavy metal emissions of the OSPARCOM-HELCOM- UNECE inventory for 1990 (up to 38 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Total Zinc Production	0403zn	0	9.1	0	0	7.1	0	0.5	9.8

Table 2.2: Contribution to total emissions of the CORINAIR90 inventory (up to 28 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Secondary Zinc Production	030308	-	-	-	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Secondary zinc production is unlikely to be a significant source of sulphurhexafluoride (SF_6), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs), (ETC/AEM-CITEPA-RISOE 1997).

3 GENERAL

3.1 Description

A secondary zinc smelter is defined as any plant or factory in which zinc-bearing scrap or zinc-bearing materials, other than zinc-bearing concentrates (ores) derived from a mining operation, are processed (e.g. Barbour et al., 1978). In practice, primary smelters often also use zinc scrap or recycled dust as input material.

Zinc recovery involves three general operations performed on scrap, namely pre-treatment, melting, and refining. Scrap metal is delivered to the secondary zinc processor as ingots, rejected castings, flashing, and other mixed metal scrap containing zinc (US EPA, 1995).

Scrap *pre-treatment* includes sorting, cleaning, crushing and screening, sweating, and leaching. In the sorting operation, zinc scrap is manually separated according to zinc content and any subsequent processing requirements. Cleaning removes foreign materials to improve product quality and recovery efficiency. Crushing facilitates the ability to separate the zinc from the contaminants. Screening and pneumatic classification concentrates the zinc metal for further processing. Leaching with sodium carbonate solution converts dross and skimmings to zinc oxide, which can be reduced to zinc metal (US EPA, 1995).

Pure zinc scrap is *melted* in kettle, crucible, reverberatory, and electric induction furnaces. Flux is used in these furnaces to trap impurities from the molten zinc. Facilitated by agitation, flux and impurities float to the surface of the melt as dross, and are skimmed from the surface. The remaining molten zinc may be poured into moulds or transferred to the refining operation in a molten state (US EPA, 1995).

Refining processes remove further impurities from clean zinc alloy scrap and from zinc vaporised during the melt phase in retort furnaces. Molten zinc is heated until it vaporises. Zinc vapour is condensed and recovered in several forms, depending upon temperature, recovery time, absence or presence of oxygen, and equipment used during zinc vapour condensation. Final products from refining processes include zinc ingots, zinc dust, zinc oxide, and zinc alloys (US EPA, 1995).

Generally the processes used for the recycling of secondary zinc can be distinguished by the kind of raw materials employed (Rentz et al., 1996):

Very poor oxidic residues and oxidic dusts, e.g. from the steel industry, are treated in *rotary furnaces* (Waelz furnaces), producing metal oxides in a more concentrated form. These concentrated oxides (Waelz oxides) are processed together with oxidic ores in primary thermal zinc smelters, in particular Imperial Smelting furnaces which are in use for combined lead and zinc production. In this case, a clear discrimination between primary and secondary zinc production as well as between zinc and lead production is difficult.

Metallic products prior to smelting are comminuted and sieved to separate metal grains from the oxides. Afterwards the metallic products are melted in *melting furnaces*, mainly of the induction type or muffle furnaces. Finally the molten zinc is cast and in part refined to high-purity zinc in distillation columns.

In *New Jersey retorts* it is possible to process a large variety of oxidic secondary materials together with metallic materials simultaneously. For charge preparation the oxides are mixed with bituminous or gas coal, briquetted, and coked. The briquettes together with the metallic materials are charged into the retorts. The zinc vapours from the retorts are condensed by splash-condensing.

3.2 Definitions

Secondary zinc production: - production of zinc from materials other than ores.

Other definitions are covered in sections 3.1 and 3.3.

3.3 Techniques

A *sweating furnace* (rotary, reverberatory, or muffle furnace) slowly heats the scrap containing zinc and other metals to approximately 364°C. This temperature is sufficient to melt zinc but is still below the melting point of the remaining metals. Molten zinc collects at the bottom of the sweat furnace and is subsequently recovered. The remaining scrap metal is cooled and removed to be sold to other secondary processors (US EPA, 1995).

A more sophisticated type of sweating operation involves holding scrap in a basket and heating it in a molten salt bath to a closely controlled temperature. This yields a liquid metal, which separates downwards out of the salt, and a remaining solid of the other metals still free from oxidation. By arranging for heating to a sequence of temperatures, related to the melting point of the metals or alloys involved, a set of molten metal fractions with minimum intermixture can be obtained (e.g. Barbour et al., 1978).

For zinc production in *New Jersey retorts* the zinc containing raw materials are picked up from the stockpiling area. For some raw materials a *charge preparation* is carried out, including comminution, sieving, and magnetic separation, so that a metallic and a oxidic fraction is obtained. Furthermore, for some raw materials dechlorination is necessary. The oxidic raw materials, like dusts and zinc drosses are mixed with bituminous coal. Subsequently, the mixture which contains about 40 % zinc is briquetted together with a binding agent, coked at temperatures around 800°C in an autogenous coking furnace and then charged to the New Jersey retorts together with small amounts of pure metallic materials. By heating with natural gas and CO containing waste gases, in the retorts temperatures of around 1,100°C are achieved, so that the zinc is reduced and vaporised. Subsequently, the vaporised zinc is precipitated in splash-condensers and transferred to the foundry via a holding furnace. Here the so-called selected zinc is cast into ingots. The residues from the retorts are treated in a melting cyclone to produce lead-zinc-mix oxides and slag. Figure 3.1 shows a schematic diagram for secondary zinc production using New Jersey retorts. Potential sources of particulate and heavy metal emissions are indicated. The metallic fraction from charge preparation together with other metallic materials like galvanic drosses, scrap zinc, and scrap alloys are melted. The raw zinc is then sent to a *liquation furnace* where, in a first refining step, zinc contents from 97.5 to 98 % are achieved. The melted and refined zinc is also cast into ingots (Rentz et al., 1996).

The raw materials for *Waelz furnaces* are mainly dusts and slurry from electric arc furnaces used in the steel industry, together with other zinc and lead containing secondary materials. For transferring and charging, the dustlike secondary materials are generally pelletised at the steel plant.

After mixing, the zinc and lead containing pellets, coke as reducing agent, and fluxes are charged via a charging sluice at the upper end of the slightly sloped rotary kiln. The rotation and the slope lead to an overlaid translational and rotational movement of the charge. In a counter-current direction to the charge air as combustion gas is injected at the exit opening of the furnace. At temperatures of around 1,200°C and with residence times of around 4 hours zinc and lead are reduced and vaporised. The metal vapours are reoxidised in the gas filled space of the furnace and evacuated through the charge opening together with the waste gas. In a cleaning device, the metal oxides are collected again and as filter dust the so-called Waelz oxide with a zinc content of around 55 % and a lead content of around 10 % is generated. The Waelz oxide is subsequently charged into an Imperial Smelting furnace which is used for combined primary zinc/lead smelting. The slag from the Waelz furnace is cooled down and granulated in a water bath. Additional oil as fuel is only needed at the start-up of the furnace, while in stationary operation the combustion of the metal vapours and carbon monoxide covers the energy demand of the process (Rentz et al., 1996). A schematic representation of the Waelz process is depicted in Figure 3.2.

Secondary zinc is sometimes combined with primary material for refining. Various pyrometallurgical refining technologies can be applied, depending on the feed material and product specification. Thermal zinc refining by fractional distillation is possible in rectifying columns at temperatures around 950°C (Rentz et al., 1996).

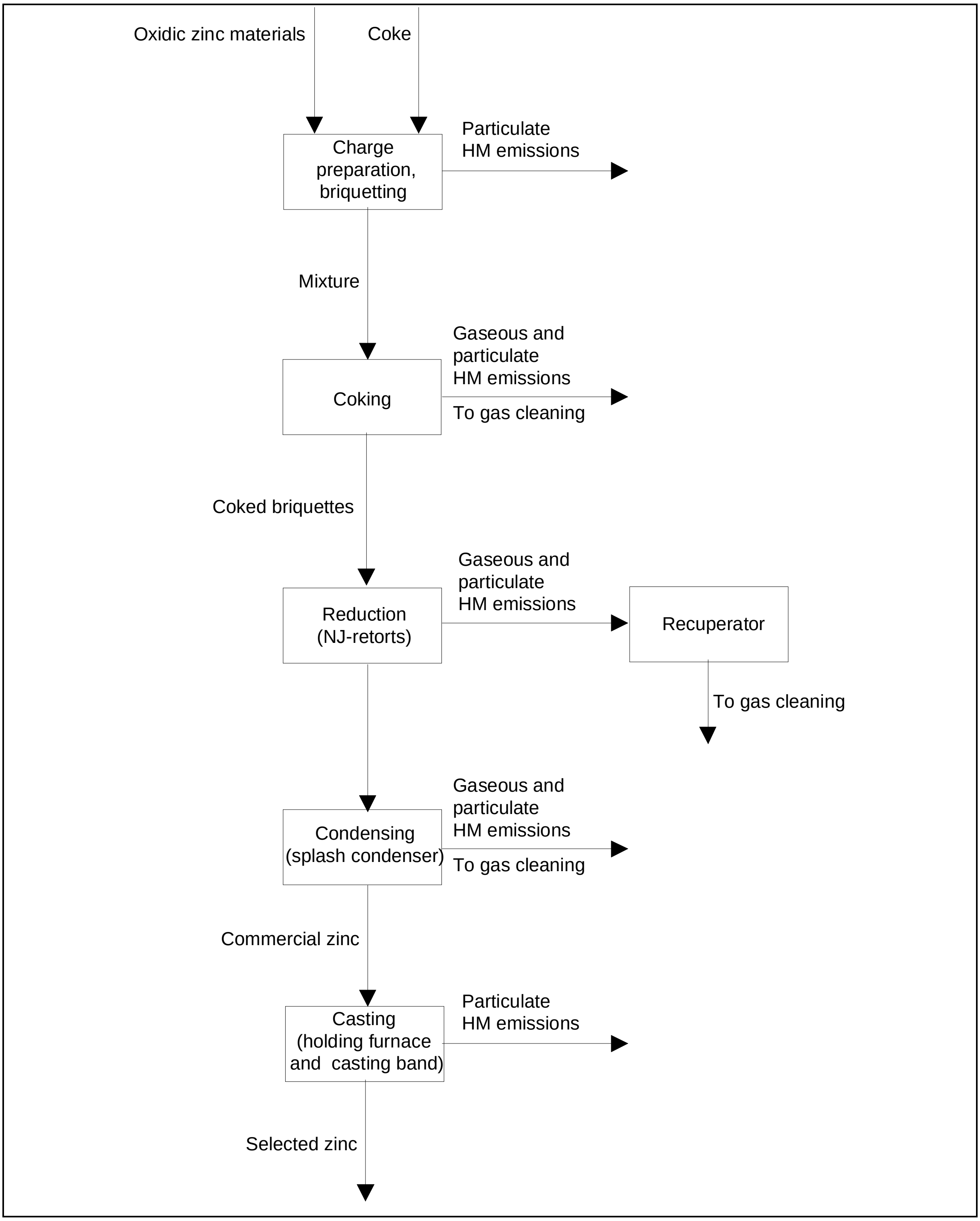

Figure 3.1: Secondary zinc production using New Jersey retorts with potential heavy metal emission sources (Rentz et al., 1996)

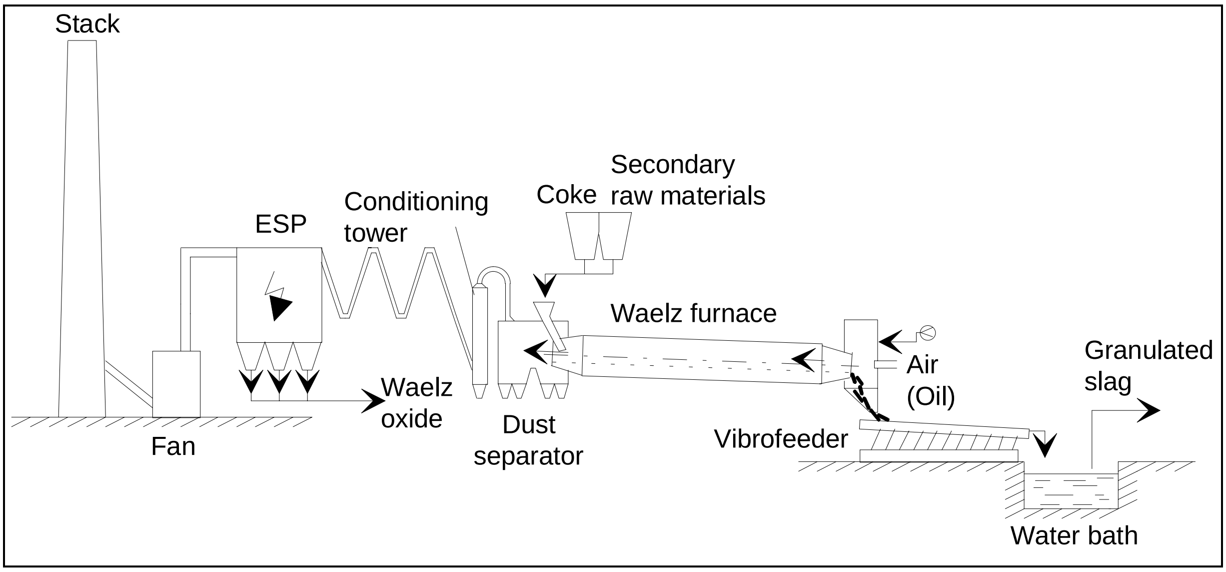

Figure 3.2: Waelz furnace with emission reduction installations (Rentz et al. 1995)

3.4 Emissions

Among the various process steps the melting furnace operation represents the most important source of atmospheric emissions. In general, continuous and periodical emissions can be distinguished. Continuous emissions are connected with the process as such, whereas periodical emissions occur e.g. during charging, heating, skimming, or cleaning operations. The most important factors influencing emissions from scrap pre-treatment and melting are:

- The composition of the raw material, in particular the content of organic and chlorinated compounds which affects the formation of dioxins and furans,
- the utilisation of flux powder ,
- the furnace type - direct heating with a mixture of process and combustion waste gases reduces the content of organic compounds released from the bath,
- the bath temperature - a temperature above 600°C creates significant emissions of zinc oxide,
- the fuel type - in general, natural gas or light fuel oil are used.

Continuous emissions from the melting furnace consist of combustion waste gases and gaseous effluents from the bath. The specific gas flow amounts to about 1,000 m^3 (STP)/Mg zinc produced.

Important periodical emissions often occur with charging and melting of the raw material. Emissions of organic compounds are mainly connected with charging operations. Furnace clearing, fluxing, ash drawing, and also cleaning operations are of minor relevance. Tapping is carried out at low temperature and therefore, no metal vapours are released.

In zinc distillation a high quality input material is used and therefore, emissions of carbon or chlorine containing compounds are low. Emissions mainly consist of zinc and zinc oxide containing particles and combustion waste gases (R. Bouscaren et. al., 1988).

3.5 Controls

Most of the secondary zinc smelters are equipped with dust removing installations, such as baghouses. In general, emission control systems vary depending on the type of scrap being processed and the products being obtained. A distinction can be made between purely oxidised, mixed oxidised/metallic and purely metallic products.

The control efficiency of dust removing installations is often very high reaching 99.9 %. Both, primary gases and fugitive dust emissions are reduced in baghouses to concentrations below 10 mg/m³.

Afterburners are reported for non-ferrous-metal industry in the USA. Also wet scrubbers may be used.

4 SIMPLER METHODOLOGY

Application of general emission factors with appropriate activity statistics can be regarded as a simple methodology for estimation of emissions from secondary zinc production. However, it should be noted that the chemical composition of input scrap is one of the most important factors affecting the amount of emissions. The chemical composition of input scrap varies considerably from one plant to another and so do emission factors. Default emission factors in accordance with the simpler methodology are proposed in section 8.

5 DETAILED METHODOLOGY

In this case, specific emission factors for the different process steps of the various production technologies should be used. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites. Currently, appropriate default emission factors are not available.

6 RELEVANT ACTIVITY STATISTICS

In many metal statistics secondary zinc production is not reported separately. The World Metal Statistics Year Book published by the World Bureau of Metal Statistics in Massachusetts, USA, reports total production of zinc without disaggregating it into primary and secondary production. The World Metal Statistics published monthly by the same organisation reports more detailed data which includes primary and secondary production for some countries and total production for others.

Information is also available from the UN statistical yearbooks (e.g. United Nations 1993). These data are satisfactory to estimate emissions using the simpler methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of the metal produced by various types of industrial technologies employed in the secondary zinc industry. Therefore, the application of a detailed estimation methodology may be complicated unless the statistical data are available directly from a given smelter. Some information in this respect is available from the International Lead and Zinc Study Group (ILZSG) (e.g. ILZSG, 1985).

7 POINT SOURCE CRITERIA

Secondary zinc smelters should be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

In the literature only emission factors for the simpler methodology are currently available. The CORINAIR methodology requires the separate reporting of combustion related emissions (SNAP 030308) and process related emissions (SNAP 040300). Table 8.1 also gives emission factors related to the energy input in [g/GJ] based on CORINAIR90 data. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR 90 a value for the specific energy consumption of 38.5 GJ/Mg product was reported.

Currently, a uniform emission factor for dioxin emissions from secondary zinc production cannot be given due to the enormous range of concentrations measured in the waste gases of 6 orders of magnitude. This is illustrated by results from measurements at German plants given in Tables 8.1 and 8.3 (Quaß 1997).

Table 8.1: Emission Factor Table

Compound	**Plant type**	**Emission factor**	**Data Quality**	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Country or region**	**Ref.**
SO_2	*unknown*	0.85 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
SO_2	Calcining kiln	9,150g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
SO_2	Retort distillation/ oxidation	10,000g/Mg zinc oxide produced	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
SO_2	Muffle distillation/ oxidation	20,000g/Mg zinc oxide produced	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
SO_2	Secondary metal production, process heaters	17,209 · S g/m^3 fuel	*E*	*n. a.*	*n. a.*	NAPFUE 204, S = sulphur content of fuel	*USA*	*US EPA (1990)*
SO_2	Secondary metal production, process heaters	19,006 · S g/m^3 fuel	*E*	*n. a.*	*n. a.*	NAPFUE 203, S = sulphur content of fuel	*USA*	*US EPA (1990)*
NO_x	*unknown*	27 g/GJ	*E*	*n. a.*	*n. a.*	*coke oven coke*	*Europe*	*CORINAIR90*
NO_x	*unknown*	60 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
NO_x	Pot furnace	950 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
NO_x	Galvanising kettle	200 g/Mg zinc used	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
NO_x	Rotary sweat furnace	100 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
NO_x	Retort distillation / oxidation	3,950 g/Mg zinc oxide produced	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
NO_x	Muffle distillation/ oxidation	55,000 g/Mg zinc oxide produced	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
NO_x	Process heaters in secondary metal production	2,397 g/m^3 fuel	*E*	*n. a.*	*n. a.*	NAPFUE 204	*USA*	*US EPA (1990)*
NO_x	Process heaters in secondary metal production	6,591 g/m^3 fuel	*E*	*n. a.*	*n. a.*	NAPFUE 203	*USA*	*US EPA (1990)*
VOC	Calcining kiln	30 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
VOC	Concentrate dryer	2 g/Mg processed	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
VOC	Sweating furnaces (general) Kettle (pot) melting furnace	1,200 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
VOC	Crucible melting furnace, scrap smelting	1,250 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
VOC	Reverberatory melting furnace, scrap smelting	2,600 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
VOC	Electric induction melting furnace, scrap melting	90 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*US EPA (1990)*
VOC	Process heaters in primary metal production	24 g/m^3 fuel	*E*	*n. a.*	*n. a.*	NAPFUE 204	*USA*	*US EPA (1990)*

Table 8.1: continued

VOC	Process heaters in primary metal production	34 g/m³ fuel	*E*	*n. a.*	*n. a.*	NAPFUE 203	*USA*	*US EPA (1990)*
VOC	Process heaters in primary metal production	44,851 g/m³ fuel	*E*	*n. a.*	*n. a.*	NAPFUE 301, process gas	*USA*	*US EPA (1990)*
CO	*unknown*	535 g/GJ	*E*	*n. a.*	*n. a.*	*coke oven coke*	*USA*	*US EPA (1990)*
CO	*unknown*	7 g/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
CO_2	*unknown*	105 kg/GJ	*E*	*n. a.*	*n. a.*	*coke oven coke*	*Europe*	*CORINAIR90*
CO_2	*unknown*	55 kg/GJ	*E*	*n. a.*	*n. a.*	*natural gas*	*Europe*	*CORINAIR90*
As	*unknown*	10 (1-20) g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany (1980s)*	PARCOM/ ATMOS (1992)
Cd	*unknown*	25 (2-50) g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany (1980s)*	PARCOM/ ATMOS (1992)
Cd	*unknown*	14 g/Mg zinc produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	S. Hlawiczka (1995)
Hg	*unknown*	0.02 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany (1980s)*	PARCOM/ ATMOS (1992)
Pb	*unknown*	85 g/Mg zinc produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	S. Hlawiczka (1995)
Pb	*unknown*	200 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany (1980s)*	PARCOM/ ATMOS (1992)
Zn	*unknown*	5,000 g/Mg product	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany (1980s)*	PARCOM/ ATMOS (1992)
Zn	*unknown*	9,000 g/Mg zinc produced	*E*	*uncontrolled*	*0 %*	*n. a.*	*Europe*	PARCOM/ ATMOS (1992)
Zn	*unknown*	1,089 g/Mg zinc produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	S. Hlawiczka (1995)
Zn	*unknown*	10,000 g/Mg zinc produced	*E*	*n. a.*	*n. a.*	*n. a.*	*Europe*	R. Bouscaren (1988)
PCDD/F	*Hot briquetting plant capacity 16.7 Mg Zn/h*	63.1-379 µg I-TEQ/Mg zinc produced	*E*	*controlled*	*n. a.*	*n. a.*	*Germany*	Quaß (1997)
PCDD/F	*Rotating cylinder (Waelz furnace), plant capacity 16.7 Mg Zn/h*	62.3 µg I-TEQ/Mg zinc produced	*E*	*controlled*	*n. a.*	*n. a.*	*Germany*	Quaß (1997)

n. a.: not available

Table 8.2: Heavy Metal Emission Measurements

Process type:	*New Jersey retorts* *Process waste gases*	Waelz furnace Process waste gases, metal oxide recovery	Waelz furnace Furnace mouth
Country or region:	Germany	Germany	Germany
Abatement:	*Recuperator, heat exchanger, cooler, flat bag filter (polyacrylonitrile)*	*Dust separator, conditioning tower, 3-field electrostat. precip.*	*Bag filter (Nomex needlefelt)*
Waste gas stream: [m^3(STP)/h]	*124,000*	*62,000*	*9,200*
Compound:	*Clean gas [mg/m^3(STP)]*	*Clean gas [mg/m^3(STP)]*	*Clean gas [mg/m^3(STP)]*
As	*0.0009*	n. a.	n. a.
Cd	0.02	0.014	< 0.001
Cr	n. a.	n. a.	n. a.
Cu	< 0.0009	n. a.	n. a.
Hg	< 0.0009	n. a.	n. a.
Ni	n. a.	n. a.	n. a.
Pb	0.11	0.4	1.3
Zn	n. a.	1.6	3.4
Particulates	6.3	5.7	8
Reference:	Steinmann (1984)	Kola (1991)	Kola (1991)

n. a.: not available

Table 8.3: PCDD/F Emission Measurements

Country or region:	Germany	
Process type	**PCDD/F concentration** waste gas [ng I-TEQ/m^3]	**Mass flow** [µg I-TEQ/h]
Hot briquetting	20 - 120	1054 - 6326
Rotating cylinder	20.8	1040
Ore roasting furnace	0.0018	
Zinc melting furnace	0.042 - 0.121	0.9 - 2.7
Zinc melting furnace	0.097	5.2
Zinc melting furnace	0.028	0.3
Reference:	Bröker (1995)	

9 SPECIES PROFILES

At present little information exists on physical and chemical species of trace metals and dioxins/furans emitted during the secondary zinc production. Atmospheric emissions of various pollutants depend greatly on the degree of pre-sorting and the type and homogeneity of the scrap charged. Particles emitted during the production process contain predominantly zinc oxide, some metallic zinc, chlorides of various compounds, as well as the impurities derived from other metals in the scrap charge (Rentz et al., 1996). $ZnCl_2$ containing particulates result from the use of fluxes and granulated metal recovered from galvanic processes as a raw material. ZnO is formed from the reaction of zinc vapour with oxides at the surface. (R. Bouscaren et al., 1988).

10 UNCERTAINTY ESTIMATES

It is difficult to assess current uncertainties of emission estimates for pollutants emitted during the secondary zinc production. Recently it was concluded that up to 50 % of uncertainties can be assigned for the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Much bigger uncertainty can be assigned for emission estimates of these compounds from the secondary zinc production. Information on emission factors and statistics is largely missing for the secondary zinc smelters; thus the accuracy of emission estimates for this category cannot even be compared with the accuracy of emission estimates for major point sources, such as primary smelters and power plants.

A key uncertainty is the type of abatement associated with the emission factors in section 8 which is currently not known.

Uncertainty is also increased by missing information on secondary zinc production in activity statistics. If activity rates related to the energy input are required a conversion of units is often necessary which may cause a further increase of uncertainty.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Development of emission factors for trace elements and dioxins/furanes and improvement of zinc emission factors given in section 8 is necessary in order to obtain emission estimates for the secondary zinc production. Further work is required to assess the missing parameters such as abatement type and efficiencies. The improvement should also focus on preparing individual emission factors for major industrial technologies and process units currently employed in the zinc industry. In this way a detailed methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data on the production of zinc in various secondary zinc furnaces.

In many cases, a clear distinction between primary and secondary zinc production is not possible due to the simultaneous use of primary and secondary raw materials. In addition, a combined production of lead and zinc may occur (e. g. in IS-furnaces). Here, a double counting of emissions has to be avoided. Therefore, emissions from smelters should be reported as point sources using plant specific activity data.

The fuel specific emission factors cited from the CORINAIR90 inventory in Table 8.1 are related to both point sources and area sources without specification. It is assumed that according to the CORINAIR methodology they only include emissions from combustion (SNAP 030308). Further investigations should cover the influence of fuel characteristics and process technology on these factors for an improved discrimination between combustion and process related emissions.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The secondary zinc production is a continuous process. No temporal disaggregation is needed.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

No supplementary documents are required.

16 VERIFICATION PROCEDURES

Estimated emission factors could be best verified by measurements at plants using different industrial technologies.

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19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **030309**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Secondary Copper Production

NOSE CODE: **104.12.10**

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions during the production of copper in secondary copper smelters. Secondary copper smelters produce about 40 % of the total copper production in the world (e.g. Pacyna, 1989). Pyrometallurgical processes are used to rework scrap and other secondary materials. As with primary copper production, final refining, where practised, is electrolytic. This chapter describes the methods to estimate emissions of atmospheric pollutants during the secondary copper recovery (e.g. Parker, 1978; UN ECE, 1994).

2 CONTRIBUTIONS TO TOTAL EMISSIONS

There are several trace elements which can be emitted during the secondary copper production. However, these emissions are not very significant on a global scale. Nriagu and Pacyna (1988) concluded that the secondary copper production contributes well below 1 % of the total atmospheric emissions of copper, lead, antimony, selenium, and zinc. Similar contribution of atmospheric emissions during the secondary copper production was estimated for the European emissions in the beginning of the 1980’s (Pacyna, 1983). However, a secondary copper smelter or refinery can be an important emission source of trace element contamination on a local scale.

The contribution of emissions released from secondary copper production to total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 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_2O	NH_3
Secondary Copper Production	030309	0	-	0	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

A secondary copper smelter is defined as any plant or factory in which copper-bearing scrap or copper-bearing materials, other than copper-bearing concentrates (ores) derived from a mining operation, is processed by metallurgical or chemical process into refined copper and copper powder (a premium product).

The recycling of copper is the most comprehensive among the non-ferrous metals. The copper metal scrap can be in the form of:

- copper scrap, such as fabrication rejects, wire scrap, plumbing scrap, apparatus, electrical systems, products from cable processing,
- alloy scrap, such as brass, gunmetal, bronze, in the form of radiators, fittings, machine parts, turnings, shreddar metals, and
- copper-iron scrap like electric motors or parts thereof, plated scrap, circuit elements and switchboard units, telephone scrap, transformers, and shreddar materials.

Another large group of copper-containing materials is composed of oxidised materials, including drosses, ashes, slags, scales, ball mill fines, catalysts as well as materials resulting from pollution control systems.

The copper content of scrap varies from 10 to nearly 100% (UN ECE, 1994). The associated metals which have to be removed are mainly zinc, lead, tin, iron, nickel and aluminium as well as certain amounts of precious metals.

Depending on their chemical composition, the raw materials of a secondary copper smelter are processed in different types of furnaces, including:

- blast furnaces (up to 30% of Cu in the average charge),
- converters (about 75% Cu), and
- anode furnaces (about 95% Cu).

The blast furnace metal (“black copper”) is treated in a converter, the converter metal is refined in an anode furnace. In each step additional raw material with corresponding copper content is added.

In the blast furnace , a mixture of raw materials, iron scrap, limestone and sand as well as coke is charged at the top. Air which can be enriched with oxygen is blown through the tuyeres, the coke is burnt and the charge materials are smelted under reducing conditions. Black copper and slag are discharged from tapholes.

The converters used in primary copper smelting, working on mattes containing iron sulfide, generate surplus heat and additions of scrap copper are often used to control temperature. The converter provides a convenient and cheap form of scrap treatment, but often with only moderately efficient gas cleaning. Alternatively, hydrometallurgical treatment of scrap, using ammonia leaching, yields to solutions which can be reduced by hydrogen to obtain copper powder (e.g. Barbour et al., 1978). Alternatively, these solutions can be treated by solvent extraction to produce feed to a copper-winning cell.

Converter copper is charged together with copper raw materials in anode furnace operation. For smelting the charge, oil or coal dust is used , mainly in reverberatory furnaces. After smelting, air is blown on the bath to oxidise the remaining impurities.

Leaded brasses, containing as much as 3% of lead, are widely used in various applications and recycling of their scrap waste is an important activity. Such scrap contains usually much swarf and turnings coated with lubricant and cutting oils. Copper-containing cables and motors contain plastic or rubber insulants, varnishes, and lacquers. In such cases, scrap needs pre-treatment to remove these non-metallics. The smaller sizes of scrap can be pre-treated termally in a rotary kiln provided with an after-burner to consume smoke and oil vapors (so-called Intal process). There are also various techniques available to remove rubber and plastic insulations of cables (e.g. Barbour et al., 1978; UN ECE, 1994).

Atmospheric emissions of various pollutants are generated during all three types of processes employed in the secondary copper industry.

3.2 Definitions

Secondary copper production: - production of copper from materials other than ores.

3.3 Controls

Controls in secondary copper production should include effective dust collecting arrangements for dust from both primary exhaust gases and fugitive dust emissions. Fabric filters can be used reducing the dust emissions to below 10 mg/ m³ (UN ECE, 1994).

4 SIMPLER METHODOLOGY

Application of general emission factors with appropriate activity statistics can be regarded as a simpler methodology for estimation of emissions from secondary copper production. However, it should be noted that the chemical composition of input scrap is one of the most important factors affecting the amount of emissions. The chemical composition of input scrap varies considerably from one plant to another and so do emission factors.

5 DETAILED METHODOLOGY

In this case, different emission factors for various production technologies should be used. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of copper in secondary smelters is available from the UN statistical yearbooks. This information is satisfactory to estimate emissions with the use of the simpler estimation methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of the metal produced by various types of industrial technologies employed in the secondary copper industry. Therefore, the application of detailed estimation methodology may be complicated unless the statistical data are availbale directly from a given smelter.

7 POINT SOURCE CRITERIA

Secondary copper smelters should be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 2 contains fuel related emission factors for secondary copper production based on CORINAIR90 data [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/m^3), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 38.5 up to 100 GJ/Mg product has been reported.

Table 2: Emission factors for secondary copper production[7)]

		Type of fuel	NAPFUE code	Emission factors SO_2[2)] [g/GJ]	NO_x[3)] [g/GJ]	NMVOC[4)] [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
l	oil	residual	203	495-1,470[1)]	150[1)]	30[1)]	30[1)]	15[1)]	76-78[1)]	2[2)]
l	oil	gas	204	94-1,410[1)]	100[1)]	1.5[1)]	1.5[1)]	12[1)]	73-74[1)]	2[1)]
g	gas	natural	301	0.28[1)]	100[1)]	4[1)]	4[1)]	13[1)]	57[1)], 60[5)], 59[6)]	1[1)]
g	gas	liquified petroleum gas	303	0.04[1)]	100[1)]	2.1[1)]	0.9[1)]	13[1)]	65[1)]	1[1)]

[1)] CORINAIR90 data, point sources

2)	SO_x: (EPA, 1990)	750	g/Mg charged	Scrap dryer (rotary)
		6,400	g/Mg charged	Wire burning, incinerator
		250	g/Mg charged	Crucible and pot furnace, charged with brass and bronze
		15	g/Mg charged	Electric arc furnace, charged with brass and bronze
		15	g/Mg charged	Electric induction furnace, charged with brass and bronze
		2,182	g/Mg product	Refining
		17,209 · S	g/m³ fuel	Secondary metal production, process heaters NAPFUE 204, S = sulphur content of fuel
		19,006 · S	g/m³ fuel	Secondary metal production, process heaters NAPFUE 203, S = sulphur content of fuel
3)	NO_x: (EPA, 1990)	850	g/Mg charged	Wire burning, incinerator
		40	g/Mg charged	Reverberatory furnace, charged with brass and bronze
		300	g/mg charged	Rotary furnace, charged with brass and bronze
		2,397	g/m³ fuel	Secondary metal production, process heaters, NAPFUE 204
		6,591	g/m³ fuel	Secondary metal production, process heaters, NAPFUE 203
4)	VOC: (EPA, 1990)	2	g/Mg charged	Scrap dryer (rotary)
		300	g/Mg charged	Wire burning, incinerator
		60	g/Mg charged	Sweating furnace
		223,500	g/Mg coke free charge	Cupola, charged with insulated copper or brass and scrap copper
		90	g/Mg charged	Cupola, charged with scrap copper or brass and scrap copper
		2,600	g/Mg charged	Reverberatory furnace, charged with copper / charged with brass and bronze
		1,200	g/Mg charged	Rotary furnace, charged with brass and bronze
		3,350	g/Mg charged	Crucible and pot furnace, charged with brass and bronze
		1,950	g/Mg charged	Electric arc furnace, charged with copper
		0	g/Mg charged	Electric arc furnace, charged with brass and bronze
		0	g/Mg charged	Electric induction furnace, charged with copper or brass and bronze
		24	g/m³ fuel	Secondary metal production, process heaters, NAPFUE 204
		34	g/m³ fuel	Secondary metal production, process heaters, NAPFUE 203
		44,851	g/Mm³ fuel	Secondary metal production, process heaters, NAPFUE 301

[5)] CO_2: Locally contaminated scrap input, brass production (Bremmer, 1995)

[6)] CO_2: Strongly contaminated scrap input, brass production (Bremmer, 1995)

[7)] It is assumed, that emission factors cited within the table are related to combustion sources in secondary copper production. Footnotes may contain emission factors for total emissions (fuel and process related).

A list of emission factors for several trace elements emitted from secondary copper smelters is presented in Table 3. Results of measurements and estimates carried out in various countries are presented. However, in some cases the factors originate from the same sources.

Information available from the above mentioned measurements and estimates does not allow for further differentiation of emission factors with respect to neither various industrial processes involved in the secondary copper production or different production technologies used at present. Therefore, the factors in Table 3 can only be used in a simpler emission estimation methodology.

Table 3: Compilation of emission factors for secondary copper production (in g/tonne Cu produced)

Element	Estimates by Pacyna (1986)	Estimates in Canada (Jacques, 1987)	PARCOM program (PARCOM, 1992)	Estimates in the U.K. (Leech, 1993)	Estimates in Austria (Schneider, 1994)	Suggested
Arsenic					2	2
Antimony	3					3
Cadmium	4		5	5	2	2-4
Copper	150	200-400			20	20-150
Lead	50-200	230	130	130	50	50-130
Nickel		1				1
Zinc	500-1600		500	500	250	250-500
Control	ESP, ca. 99% efficiency	Based on questionnaires. Most plants use ESPs with 99% efficiency	Unspecified	Based on emission factors by Pacyna and PARCOM	Unspecified	Common ESPs with 99% efficiency

9 SPECIES PROFILES

At present no reliable information exist on physical and chemical species of trace elements emitted during the secondary copper production. It can be assumed that the majority of trace elements volatilized from scrap and other copper-containing materials enter the atmosphere on fine particles.

10 UNCERTAINTY ESTIMATES

It is difficult to assess current uncertainties of emission estimates for pollutants emitted during the secondary copper production. Recently it was concluded that up to 50 % of uncertainties can be assigned for the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Even bigger uncertainty can be assigned for emission estimates of these compounds from the secondary copper production. Information on emission factors and statistics is more limited for the secondary copper smelters than for major point sources, such as primary smelters and power plants.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for the secondary copper production. This improvement should focus on preparing individual emission factors for major industrial technologies currently employed in the copper industry. In this way, a detailed methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data on the production of copper in various secondary copper furnaces.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not applicable.

13 TEMPORAL DISAGGREGATION CRITERIA

The secondary copper production is a continuous process. No temporal disaggregation is needed.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

The following supplementary document can be suggested:
UN ECE State-of-the-Art Report on the Heavy Metals Emissions, the UN ECE Task Force on Heavy Metals Emissions, Prague, the Czech Republic, June 1994.

16 VERIFICATION PROCEDURES

At present no specific verification procedures are available for estimation of atmospheric emissions from the secondary copper production. Estimated emission factors could be best verified by measurements at plants using different industrial technologies.

17 REFERENCES

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18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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SNAP CODE: **030310**

SOURCE ACTIVITY TITLE: **PROCESSES WITHOUT CONTACT**
Secondary Aluminium Production

NOSE CODE: **104.12.11**
104.12.12

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions during the production of Aluminium in secondary Aluminium smelters. Secondary Aluminium smelters produce about 50 % of the total Aluminium production in the United States (e.g. UN, 1994). Similar Aluminium production proportion is found in the Netherlands, France, Austria, and Italy. The secondary Aluminium industry is characterised by a large number of relatively small plants treating mostly so-called new scrap. This chapter describes the methods to estimate emissions of atmospheric pollutants during the secondary Aluminium operations (e.g. Parker, 1978).

2 CONTRIBUTIONS TO TOTAL EMISSIONS

There are various pollutants which can be emitted during the secondary Aluminium production, including smoke, acids, and particles. Major problems may arise due to emissions of Aluminium chloride and its hydrolysis product, hydrochloric acid. These emissions are not very significant on a global scale. However, a secondary Aluminium smelter can be an important emission source of pollution on a local scale.

The contribution of emissions released from secondary Aluminium 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_2O	NH_3
Secondary Aluminium Production	030310	0	0	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Secondary Aluminium production plant have the potential to emit cadmium, hexachlorobenzene, dioxins and furans, PAHs and sulphurhexafluoride (ETC/AEM-CITEPA-RISOE 1997).

3 GENERAL

3.1 Description

A secondary Aluminium smelter is defined as any plant or factory in which Aluminium-bearing scrap or Aluminium-bearing materials, other than Aluminium-bearing concentrates (ores) derived from a mining operation, is processed into Aluminium Alloys for industrial castings and ingots. Energy for secondary refining consumes only about 5% of that required for primary Aluminium production.

In most cases, the first step in the secondary Aluminium production is removal of magnesium from the scrap charge in order to prevent off-grade castings when the refined Aluminium is cast. As much as 1% of magnesium can be found in the scrap charge and its reduction to 0.1% is necessary. This reduction can be achieved by lancing the molten charge with chlorine gas during and after the melting cycle (Barbour et al., 1978).

After pre-treatment the scrap charge is subjected to melting and demagging (chlorination). Small crucible furnaces are used to produce Aluminium Alloys for casting. Larger melting operations use reverberatory furnaces.

The final step in the production process is chlorination to obtain a high quality Aluminium product.

3.2 Definitions

Secondary Aluminium production: - production of Aluminium from materials other than ores.

3.3 Controls

Secondary Aluminium processing faces the difficult problem of suppressing emissions of corrosive Aluminium chloride associated with hydrogen chloride. Two approaches have been employed for some time to deal with the problem (Barbour et al., 1978). The Derham process uses proprietary fluxes. It claims more than 97% magnesium-chlorine efficiency for the chlorination stage at magnesium levels of less than 0.1%.

The Alcoa fumeless process depends on effecting a stoichiometric chlorination of magnesium in a multi-stage enclosed settler-reactor tank after melting and prior to casting (Barbour et al., 1978). Efficient gas-liquid contact gives a selective magnesium chlorination reaction (99% efficiency).

Afterburners are used generally to convert unburned VOC to CO_2 and H_2O. Wet scrubbers are sometimes used.

Controls in secondary Aluminium production should also include effective dust collecting arrangements for dust from both primary exhaust gases and fugitive dust emissions. Fabric filters can be used reducing the dust emissions to below 10 mg/ m^3.

4 SIMPLER METHODOLOGY

Application of general emission factors with appropriate activity statistics can be regarded as a simpler methodology for estimation of emissions from secondary Aluminium production. However, it should be admitted that the chemical composition of input scrap is one of the most important factors affecting the amount of emissions. The chemical composition of input scrap can vary considerably from one plant to another and so do emission factors.

5 DETAILED METHODOLOGY

In this case, different emission factors for various production technologies should be used. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of Aluminium in secondary smelters is available from the UN statistical yearbooks (e.g. UN, 1994). This information is satisfactory to estimate emissions with the use of the simpler estimation methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of the metal produced by various types of industrial technologies employed in the secondary Aluminium industry. Therefore, the application of detailed estimation methodology may be complicated unless the statistical data are available directly from a given smelter.

7 POINT SOURCE CRITERIA

Secondary Aluminium smelters should be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Emissions from secondary Aluminium operations include fine particles, gaseous chlorine, and selected persistent organic pollutants.

Table 8.1 contains fuel related emission factors for secondary Aluminium production based on CORINAIR90 data in [g/GJ]. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 1.7 up to 3.5 GJ/Mg product has been reported.

Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/m^3), are presented in Tables 8.2 through 8.4 for SO_x, NO_x and NMVOC, respectively. No information exists on the type and efficiency of abatement techniques, but the factors in these tables seem to be valid for emissions from uncontrolled processes.

Table 8.1: Emission factors for secondary Aluminium production (based on CORINAIR)

	Type of fuel		NAPFUE code	Emission factors SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
l	oil	residual	203	143	100	3	5	12	73	10
l	oil	gas	204	1,410	100			12	75	
g	gas	natural	301						87-100	54-58

Table 8.2: Emission factors for SO_2 from secondary Aluminium production.

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country of origin
Sweating furnace	N/A	N/A	N/A	kg/tonne Al	1.75	E	USA
Smelting Furnace:							
-crucible	N/A	N/A	N/A	kg/tonne Al	1.25	E	USA
-reverberatory	N/A	N/A	N/A	kg/tonne Al	0.45	E	USA
Burning, drying	N/A	N/A	N/A	kg/tonne Al	0.15	E	USA
Heavily contaminated scrap input	N/A	N/A	N/A	kg/tonne Al	0.54	E	USA
Pouring, casting	N/A	N/A	N/A	kg/tonne charged	0.01	E	USA
Process heaters	N/A	N/A	gas oil	kg/m^3 fuel	17.2 x S	E	USA
	N/A	N/A	residual oil	kg/m^3 fuel	19.0 x S	E	USA

N/A = Data not available
S = sulphur content of fuel

Table 8.3: Emission factors for NO_x from secondary aluminium production

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Sweating furnace	N/A	N/A	N/A	kg/tonne Al	0.3	E	USA
Smelting furnace							
-crucible	N/A	N/A	N/A	kg/tonne Al	0.85	E	USA
-reverberatory	N/A	N/A	N/A	kg/tonne Al	0.38	E	USA
Burning, drying	N/A	N/A	N/A	kg/tonne Al	0.25	E	USA
Annealing furnace	N/A	N/A	N/A	kg/tonne Al	0.75	E	USA
Pouring, casting	N/A	N/A	N/A	kg/tonne Al	0.005	E	USA
Slab furnace	N/A	N/A	N/A	kg/tonne Al	0.75	E	USA
Can manufacture	N/A	N/A	N/A	kg/tonne Al	0.35	E	USA
Rolling, drawing, extruding	N/A	N/A	N/A	kg/tonne Al	0.35	E	USA
Process heaters	N/A	N/A	gas oil	kg/m^3 fuel	2.4	E	USA
	N/A	N/A	residual oil	kg/m^3 fuel	6.6	E	USA

N/A = Data not available

Table 8.4: Emission factors for NMVOCs from secondary aluminium production

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Sweating furnace	N/A	N/A	N/A	kg/tonne Al	1.20	E	USA
Smelting furnace							
-crucible	N/A	N/A	N/A	kg/tonne Al	1.25	E	USA
-reverberatory	N/A	N/A	N/A	kg/tonne Al	0.10	E	USA
Burning, drying	N/A	N/A	N/A	kg/tonne Al	16.00	E	USA
Foil rolling	N/A	N/A	N/A	kg/tonne Al	0.65	E	USA
Foil converting	N/A	N/A	N/A	kg/tonne Al	1.20	E	USA
Annealing furnace	N/A	N/A	N/A	kg/tonne Al	0.002	E	USA
Slab furnace	N/A	N/A	N/A	kg/tonne Al	0.002	E	USA
Pouring, casting	N/A	N/A	N/A	kg/tonne Al	0.07	E	USA
Can manufacture	N/A	N/A	N/A	kg/tonne Al	150.0	E	USA
Rolling, drawing, extruding	N/A	N/A	N/A	kg/tonne Al	0.045	E	USA
Process heaters	N/A	N/A	gas oil	kg/m^3 fuel	0.024	E	USA
	N/A	N/A	residual oil	kg/m^3 fuel	0.034	E	USA
	N/A	N/A	natural gas	kg/m^3 fuel	44.85	E	USA
	N/A	N/A	process gas	kg/m^3 fuel	44.85	E	USA

N/A = Data not available

Fine particle emission factors cited in US EPA (1973) and Economopoulos (1993) are presented in Table 8.5.

Table 8.5. Emission factors for fine particles from secondary aluminium production (US EPA, 1973)

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Sweating furnace	Uncontrolled	O	N/A	kg/tonne Al	7.25	D	USA
	Baghouse	N/A	N/A	kg/tonne Al	1.65	D	USA
Smelting furnace							
-crucible	Uncontrolled	O	N/A	kg/tonne Al	0.95	D	USA
-reverberatory	Uncontrolled	O	N/A	kg/tonne Al	2.15	D	USA
	Baghouse	N/A	N/A	kg/tonne Al	0.65	D	USA
	Electrostatic precipitator	N/A	N/A	kg/tonne Al	0.65	D	USA
Chlorination	Uncontrolled	O	N/A	kg/tonne chlorine used	500.0	D	USA
	Baghouse	N/A	N/A	kg/tonne chlorine used	25.0	D	USA

N/A = Data not available

Hexachloroethane has been used in the secondary Aluminium industry and in Aluminium foundries in the form of tablets for degassing purposes in refining operations, resulting in hexachlorobenzene (HCB) emissions. An emission factor of 5 g HCB/ tonne Aluminium produced has been reported (in PARCOM, 1992).

Concentrations of dioxins and furans in the flue gas passing the control equipment in the secondary Aluminium production are presented in Table 8.6 after a compilation of data by the Working Group of the Subcommittee on Air/Technology of the Federal Government /Federal States Emission Control Committee in Germany (Umweltbundesamt, 1996).

Table 8.6: Concentrations of dioxins and furans in the flue gas after passing the control devices, in ng TEQ/m^{3} *1

Process	Emission Control Device	PCDD/F Concentration	Data Quality Code
Drum furnace with convertors	Hydrated lime fabric filters	0.1 - 13.7	D
Hearth trough kiln	Hydrated lime fabric filter	0.01 - 0.7	D
Smelting and casting furnace	No treatment	0.06 - 0.09	D
Induction furnace	Fabric filters	0.01 - 0.3	D
Al smelting plant	Fabric filters	0.02 - 0.23	D

*1 TEQ = toxic equivalency factor established by NATO/CCMS

In general, concentrations of dioxins and furans in the flue gas after the control device vary substantially due to differences in operational processes employed.

Secondary Aluminium Also generates so called climate gases, including CF_4, C_2F_6, and SF_6. A temporal increase of about 2% per year in CF_4 has been measured in the global atmosphere (in Stordal and Myhre, 1991). The current concentration of SF_6 in the atmosphere is 1 to 2 ppt, and the rate of increase has recently been estimated to be 7.4 % per year in the period from 1979 to 1989 (Rinsland et Al., 1990). However, no data are available to the authors of this chapter regarding emission factors of these gases for the secondary Aluminium production.

9 SPECIES PROFILES

Not applicable.

10 UNCERTAINTY ESTIMATES

It is rather difficult to assess current uncertainties of emission estimates for pollutants emitted during the secondary Aluminium production. The uncertainties of SO2 emission estimates can be assessed in a similar way as the uncertainties of the estimates for the fossil fuel combustion (see chapter B 111).

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for the secondary aluminium production. This improvement should focus on preparing individual emission factors for major production techniques, currently employed in the secondary aluminium industry. In this way, a detailed approach methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data on the production of aluminium in various secondary melting furnaces.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The secondary Aluminium production is a continuous process. No temporal disaggregation is needed.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

Barbour A.K., Castle J.F. and Woods S.E. (1978) Production of non-ferrous metals. In: Industrial Air Pollution Handbook, A. Parker (ed.), Mc Graw-Hill Book Comp. Ltd., London.

16 VERIFICATION PROCEDURES

Estimated emission factors could be best verified by measurements at plants using different industrial technologies.

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18 BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP42 or the PARCOM-ATMOS Manual can be used.

19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **030311**
040612

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Cement
Cement (decarbonizing)

NOSE CODE: **104.11.02**
105.11.21

NFR CODE: **1 A 2 f**
2 A 1

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion and technological processes within cement production. Therefore, also non-combustion emissions are mentioned in this chapter where appropriate.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of gaseous emissions released from the production of cement to total emissions in countries of the CORINAIR90 inventory is presented in Table 2.1.

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_2O	NH_3
Cement	030311	0.8	2.3	0	0	0.2	2.1	0.3	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

The emission of dust containing heavy metals is also relevant, particularly in the case when wastes are burnt as fuel. Europe-wide data on dust emissions is not readily available, but the contribution of cement production to the UK's National Atmospheric Emissions Inventory of PM10 is given in Table 2.2. Because of its distribution costs, cement tends to be produced relatively near to its point of use, so other countries might be expected to have comparable levels of cement production and emissions.

Table 2.2 Contribution of cement production to the total emission of PM10 in the UK

Compound	**Contribution (%)**
PM10	1.7

For heavy metal emissions, specific figures for this source activity are available from Baart *et al.* (1995). The average relative contribution from the cement production industry to the total emission of heavy metals has been presented for European countries in Table 2.3.

Table 2.3 Average relative contribution of the production of cement to the total emission of heavy metals in European countries (Baart et al., 1995)

Compound	**Contribution (%)**
Cadmium	1.2
Chromium	1.5
Nickel	1.7
Lead	0.23

In addition to the metals presented in Table 2.3, cement production may be an important source of mercury. It was estimated that on a global scale cement contributes with about 1.0 % to the total emissions of the element emitted from anthropogenic sources (Pacyna and Pacyna, 1996). However, Table 2.4 gives the contribution of cement to total emissions of heavy metals and POPs from the OSPARCOM-HELCOM-UNECE emission inventory, and the estimate for mercury is a 15 % contribution.

Table 2.4 Contribution to total POP and heavy metal emissions of the OSPARCOM-HELCOM-UNECE emission inventory (up to 39 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions (including emissions from nature) [%]**										
		As	Cr	Cu	Pb	Cd	Hg	Ni	Zn	PCBs	PCDD/Fs	PAH
Cement	040612	0.5	1.2	0	0.1	0.5	15	0.3	0.3	0	0.2	0

3 GENERAL

3.1 Description

The “standard” cement is Portland cement, which accounts for about half of the EU/EEA consumption (European IPPC Bureau, 2000). The raw materials for Portland cement clinker are limestone, sand, shale, clay and iron oxide. Other cements are composite cements and blast furnace cement, which substitute blast furnace slag or other materials for a portion of the raw materials. In each case, the processing is largely the same, and the clinker is later combined with gypsum to create the final cement. The main process stages are:

- Handling of raw materials, intermediate products and final product;
- Fuel grinding if solid fuel is used;
- Kiln feed preparation;
- Pyroprocessing in a rotary kiln to form clinker;
- Clinker cooling;
- Milling (grinding and blending with gypsum).

Types of fuels used vary across the industry. Cement kilns are highly energy-intensive and fuel costs have a critical effect on profitability. Historically, some combination of coal, oil, and natural gas was used, but over the last 15 years, most plants have switched to coal. However, in recent years a number of plants have switched to systems that burn a combination of coal and waste fuel. (IPCC, 1995).

3.2 Definitions

Portland cement	a type of hydraulic cement usually made by burning a mixture of limestone and clay in a kiln
Kiln	a furnace for burning fuel and cement clinker

3.3 Techniques

Portland cement can either be produced by dry or wet milling. In the case of wet milling the raw cement clinker is first mixed with water; this mixture is fired into a rotary kiln and finally milled. In the dry process the mixing with water is omitted. The dry process requires less energy than the wet process.

The raw materials are first brought to site; some will normally be conveyed from nearby quarries or open pits. The materials are then mixed, crushed and ground to produce a raw mix (raw meal) of the correct particle size and chemical properties. The raw meal is converted into cement clinker by pyroprocessing in rotary kilns. These consist of a refractory lined cylindrical steel shell slightly inclined to the horizontal and rotating at 1 – 3 rpm. Raw material is fed in at the upper end and gradually moves downward towards the lower end where there is a burner providing counter-current heating.

Most cement kilns now use the dry process, in which raw mill material is fed into the rotary kiln dry. Before passing into the kiln the material may be preheated in a vertically arrayed multi-cyclonic preheater, in which the rising hot gases exiting the kiln contact the downward flowing raw materials. Some dry processes also employ a precalciner stage beneath the preheater, just before the raw material enters the kiln. Preheaters and precalciners often have an alkali bypass between the feed end of the rotary kiln and the preheater to remove undesirable volatile components.

The use of the wet process, where the ground meal is mixed with water and fed into the kiln as a slurry, is now less common. The wet process uses about 40% more energy than the dry process.

The last stage involves cooling the clinker. As the hot clinker comes off the lower end of the kiln it is rapidly cooled by ambient air in a clinker cooler. There are many different designs of cooler, the most common of which is a travelling grate with under-grate fans that blow cool air through the clinker. Some of this air can be used for combustion, but some is vented to atmosphere or used for drying solid fuels and raw materials.

Finally, the cooled clinker is then mixed with gypsum and, for composite cements, other materials such as blast furnace slag, and ground to a fine homogeneous powder to produce the final product, which is then stored in silos prior to bulk transportation or bagging.

3.4 Emissions

Dust emissions result from activities such as handling raw materials; on site transportation; firing of clinker; milling; and shipment. The largest emission sources are the three units of kiln operation: the feed system, the fuel firing system, and the clinker cooling and handling system. The most desirable method of disposing of the collected dust is injection into the kiln burning zone and production of clinkers from the dust. If the alkali content of raw materials is too high, however, some of the dust is discarded and leached before returning to the kiln. In many instances, the maximum allowable cement alkali content of 0.6 % (calculated as sodium oxide) restricts the amount of dust that can be recycled.

Nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon monoxide (CO), and carbon dioxide (CO_2) are the primary emissions in the manufacture of portland cement. Small quantities of volatile organic compounds (NMVOC, methane (CH_4)), nitrous oxide (N_2O), and ammonia (NH_3) also may be emitted (see also Table 8.1). Emissions may also include residual materials from the fuel and raw materials or products of incomplete combustion that are considered to be hazardous. Because some facilities burn waste fuels, particularly spent solvents, in the kiln, these systems also may emit small quantities of additional hazardous organic pollutants (IPCC, 1995).

Oxides of nitrogen are generated during fuel combustion by oxidation of chemically-bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. As flame temperature increases, the amount of thermally generated NO_x increases. The amount of NO_x generated from fuel increases with the quantity of nitrogen in the fuel. In the cement manufacturing process, NO_x is generated in both the burning zone of the kiln and the burning zone of a precalcining vessel. Fuel use affects the quantity and type of NO_x generated. There is a marked increase in the amount of oxides of nitrogen (mainly nitric oxide) which is formed at temperatures above 1,400 °C. The formation of nitric oxide is also a function of the excess air (IPCC, 1995; EPA, 1995).

Sulphur dioxide may be generated both from the sulphur compounds in the raw materials and from sulphur in the fuel. Here only emissions from combustion are taken into account originating from the sulphur in the fuel. The sulphur content of both raw materials and fuels varies from plant to plant and with geographic location. Sulphur is normally present in the form of metal sulphide and sulphates. The amount of sulphur present will vary widely according to the nature of the deposits used. During the calcining operation, sulphur dioxide is released.

Compounds of sulphur are common constituents of most fuels and levels of sulphur may be as high as 5 wt%. Sulphides and organic sulphur compounds in the raw materials will normally be oxidised to sulphur dioxide and pass through the burning zone of the kiln with the process gases. For practical purposes sulphur in the kiln exhaust may be assumed to be emitted as sulphur dioxide, although there is usually some sulphur trioxide formed. Where this sulphur dioxide is formed at temperatures lower than the calcium carbonate calcination, it will be emitted from the kiln and preheater system to a significant extent. Some absorption may take place in the precipitator or raw mill. In most circumstances, only a small fraction of the sulphur dioxide generated within the kiln from the fuel is released to atmosphere, since it is mainly incorporated into the cement clinker by chemical combination. (IPCC, 1995; EPA, 1995).

The CO_2 emissions from portland cement manufacturing are generated by two process steps: As with most high-temperature, energy-intensive industrial processes, combusting fuels to generate process energy releases substantial quantities of CO_2. Substantial quantities of CO_2 are also generated through calcining of limestone or other calcareous material. This calcining process thermally decomposes $CaCO_3$ to CaO and CO_2. The amount of CO_2 released in the calcining process is about 500 kilograms (kg) per Mg of portland cement produced. Total CO_2 emissions from the pyroprocess depend on energy consumption and generally fall in the range of 0.85 to 1.35 Mg of CO_2 per Mg of clinker. Carbon dioxide comprises at least 20 % of the dry combustion gases and is produced from the carbon content of fuels and from calcination of the calcium carbonate (IPCC, 1995; EPA, 1995).

Fuel combustion at portland cement plants can emit a wide range of pollutants in smaller quantities. If the combustion reactions do not reach completion, CO and volatile organic pollutants (VOC) can be emitted. Incomplete combustion also can lead to emissions of specific hazardous organic air pollutants, although these pollutants are generally emitted at substantially lower levels than CO or VOC (IPCC, 1995).

Carbon monoxide is formed by the incomplete combustion of carbonaceous fuels and even with good combustion control small amounts of carbon monoxide will be present in combustion gases. When operating near to stoichiometric conditions in the kiln, there is localised generation of carbon monoxide (HMIP, 1992).

Heavy metal emissions from cement plants depend on their content in fuels and raw materials, industrial technology (e.g. combustion temperature), and emission control measures. During the cement production process at high temperatures many heavy metals present in the fuel and the raw materials evaporate and then condense on the clinker and partly on fine particles in the flue gas. The latter portion of the metals finds its way to the atmosphere after passing through the emission control equipment.

Fluorine compounds in the feed constituents are partly volatised into gaseous acidic fluorides at the high temperatures in the kiln. However, such acidic compounds are immediately neutralised (in the form of solid calcium fluoride) by the alkaline constituents in both the clinker and the feed. Thus, 88 - 98 % of the fluoride content of the feed materials is trapped in the clinker and the remainder deposits on dust particles and is mainly removed by the dust control devices. Chlorine compounds behave in a similar manner to those of fluorine.
Some kilns do burn hazardous waste as supplemental fuel. Other types of non-hazardous liquid and solid wastes used as supplemental fuels include tyres, waste oil, and wood chips. Dioxins (PCDDs) and furans (PCDFs) were first detected in stack emissions from portland cement kilns in the early 1980s (e.g. EPA, 1994). They were detected at low concentrations and were thought to be caused by the co-firing of liquid hazardous waste with conventional

fossil fuels. Recently more information has become available on the possible formation mechanisms of dioxins in the portland cement kilns. The following mechanisms have been suggested:

- some primary combustion fuels and fuel supplements used to sustain elevated temperatures in the kiln to form clinker may also produce aromatic hydrocarbon compounds that can later become chlorinated ring structures. The oxidation of HCl gas has been shown to provide chlorine available for ring substitution;
- the chlorinated aromatic compounds may act as precursor molecules to the thermalytic formation of CDD/CDFs on the active surface of carbonaceous particles;
- de novo synthesis of CDD/CDFs on the active surface of carbonaceous particles in the presence of a catalytic agent (e.g. metal ions);
- post-kiln temperatures of the combustion gases are often within the range of temperatures that promote the continued formation of CDD/CDFs;
- co-firing of liquid hazardous organic wastes with coal and petroleum coke may lead to an increase in the amount of CDD/CDFs formed in the post-combustion zone.

3.5 Controls

Emission reduction is usually obtained by reducing the dust emissions. Electrostatic precipitators (ESPs) and fabric filters (FFs) are most widely used on both kilns and clinker coolers. For electrostatic precipitation dust concentrations of 30 - 40 mg/m^3 can be achieved. For fabric filters a value of 20 to 50 mg/m^3 is common. A few gravel bed filters have also been used to control clinker cooler emissions. Fugitive emission sources are normally captured by a ventilation system and the dust is collected by fabric filters.

A portion of heavy metals in the flue gas will also be removed with particles. However, the most volatile heavy metals are present on very fine particles, often penetrating both ESPs and FFs. It is proposed that further reduction of dust concentrations in the flue gas to 10 mg/m^3 should be achieved in order to obtain reasonable reduction of heavy metals.

Emissions of sulphur dioxide are best reduced by use of low sulphur raw materials. Removal of sulphur dioxide from the exhaust gases is possible using injection of calcium hydroxide into the air stream - after the preheater for minor reductions, or by a separate fluid bed absorber for significant reductions. However, the alkaline nature of the cement provides for direct absorption of SO_2 into the product, thereby mitigating the quantity of SO_2 emissions in the exhaust stream. Depending on the process and the source of the sulphur, SO_2 absorption ranges from about 70 percent to more than 95 percent. However, in systems that have sulphide sulphur (pyrites) in the kiln feed, the sulphur absorption rate may be as low as 70 percent without unique design considerations or changes in raw materials. Fabric filters on cement kilns are also reported to absorb SO_2 (IPCC, 1995; EPA, 1995).

Flue gas desulphurisation equipment also reduces the concentration of gaseous mercury present in the flue gas. This reduction can be as high as 50 %. Further reduction of up to 85 % can be achieved through the application of very expensive measures such as injection of activated carbon or application of activated carbon beds.
Oxides of nitrogen can be reduced by applying the following techniques (EPA, 1995):

- Use of low-NO_x-burners where practicable, the principle of which is the avoidance of localised hot spots.
- Avoidance of over-burning of the clinker. The temperature in the burning zone can be limited to that necessary to produce a free lime content which gives acceptable clinker quality. Cements kilns can be fitted with on-line oxides of nitrogen sensors which form the basis of an automatic kiln control system. The prevention of over-burning not only gives reduced oxides of nitrogen levels but also provides some worthwhile energy savings.

The formation of carbon dioxide should be minimised by the use of energy efficient systems and techniques (HMIP, 1992).

4 SIMPLER METHODOLOGY

For the simpler methodology, where limited information is available, a default emission factor can be used together with information on cement production in a given country or region without further specification on the type of industrial technology or the type and efficiency of control equipment. Default emission factors for this purpose are provided in Section 8.1.

5 DETAILED METHODOLOGY

The detailed methodology to estimate emissions of gaseous pollutants from the cement production is based on measurements or estimations using emission factors. The measurement and estimation approaches described for “Combustion plants as point sources” chapter B111 can also be used for assessing emissions from combustion sources within the cement production.

The detailed methodology to estimate emissions of trace elements from the cement production is similar to the simpler one. However, more information on the type of the process, e.g. wet and dry kilns, as well as on the type of the industrial technology should be made available. This information shall be used to estimate specific emissions for at least a specific industrial technology.

Measurements of the emission rate and chemical composition of fine particles with $< 1.0\ \mu m$ diameter are often carried out at major cement kilns world-wide. The results of these measurements are then used to estimate atmospheric emissions of several trace elements contained as impurities in the raw materials and fuel.

Reference emission factors for comparison with users own data are provided in Section 8.2.

6 ACTIVITY STATISTICS

Information on the production of cement is widely available from the UN statistical yearbooks. This information is satisfactory to estimate emissions with the use of the simpler estimation methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of cement produced by various types of industrial technologies employed in the cement industry. Therefore, the application of the detailed estimation methodology may be complicated unless the statistical data are available directly from a given cement plant.

No information is easily available on the content of impurities in the copper ores from different mines or even mining regions.

7 POINT SOURCE CRITERIA

The cement production plants are regarded 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

Pollutant	**Emission factor**	**Units**
Particulate matter		
Total suspended particulate	400	g/tonne cement
PM10	110	g/tonne cement
PM2.5	40	g/tonne cement
Arsenic	0.2	g/tonne cement
Cadmium	0.01	g/tonne cement
Chromium	1	g/tonne cement
Copper	0.4	g/tonne cement
Mercury	0.1	g/tonne cement
Nickel	0.1	g/tonne cement
Lead	0.2	g/tonne cement
Selenium	0.002	g/tonne cement
Zinc	2	g/tonne cement
Dioxins and furans	0.2	µg TEQ/tonne cement
Hexachlorobenzene	11	µg TEQ/tonne cement
Polyaromatic hydrocarbons	3	mg/tonne cement

Polychlorinated biphenyls	1	µg/tonne cement

8.2 Reference Emission Factors For Use With Detailed Methodology

Table 8.2a contains reference emission factors for the production of cement based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg clinker), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a value for the specific energy consumption of 13 GJ/Mg product has been reported.

Table 8.2a Emission factors for the production of cement (fuel related)

Type of fuel				**NAPFUE code**	**Emission factors**						
					SO_2 [g/GJ]	**NO_x [g/GJ]**	**NMVOC [g/GJ]**	**CH_4 [g/GJ]**	**CO [g/GJ]**	**CO_2 [kg/GJ]**	**N_2O [g/GJ]**
s	coal	hc	coking	101	569[1], 85-165[2]	701[1], 450-709[2]		1[1][2]		86[1][2]	
s	coal	hc	steam	102	44-880[1], 35-600[2]	150-170[1], 0.4-575[2]	15[1], 15-33[2]	14.7-15[1], 0.3-15[2]	10-110[1], 18-100[2]	93-94[1], 78-101[2]	12[1], 3-12[2]
s	coal	hc	sub-bituminous	103	134-154[1], 1,260[2]	57[1] 820-1,300[2]			22[1]	99[1], 320-420[2]	8[2]
s	coal	hc	brown coal/lignite	105	25[2]	575[2]	15[2]	15[2]		100-113[2]	3.5[2]
s	coal	hc	briquettes	106	11[2]	575[2]	15[2]	15[2]	100-260[2]	97-98[2]	3.5[2]
s	coke	hc	coke oven	107	25[2]	575[2]	15[1], 0.5[2]	15[1], 0.5[2]	110[1], 100[2]	108[1], 100-105[2]	14[1], 4[2]
s	coke		petroleum	110	355-511[1], 85-1,200[2]	300-568[1], 0.4-575[2]	1.5[1], 1.5-15[2]	1.5[1], 1-15[2]	10-70[1], 15-100[2]	99-102[1], 97-102[2]	14[1], 3-14[2]
s	waste		municipal	115	161[1]	200[1]	15-40[1]	15-40[1]	70[1]	100-121[1]	5-12[1]
s	waste		industrial	116	135[2]	0.4-568[2]		0.2[2]	1429[2]	83[2]	4[2]
l	oil		residual	203	131-1,030[1], 16-1,079[2]	150-220[1], 0.4-575[2]	3[1], 3-10[2]	1-3[1], 1-5[2]	15-20[1], 8-79[2]	76-79[1] [2]	2-15[1] [2]
l	oil		gas	204	4-1,410[2]	0.4-575[2]	1.5[1], 1.5-2.5[2]	1-5[1], 1-8[2]	12[1], 12-79[2]	74[1], 73-74[2]	12[1], 2-14[2]
l	gasoline		motor	208			2.5[1]	2.5[1]	12[1]	72[1]	12[1]
l	oil		shale-oil	211						78[1]	
g	gas		natural	301	0.1-135[2]	175[1], 60-560[2]	2.5[1], 2.5-18.4[2]	2.5[1], 0.4-5[2]	20[1], 10-120[2]	53-56[1], 55-69[2]	3[1] , 1-3.7[2]
g	gas		liquified petroleum gas	303	0.04[2]	100[2]	2.5[1], 2.1[2]	2.5[1], 0.9[2]	20[1], 13[2]	65[1][2]	3[1], 1[2]
g	gas		coke oven	304	0.6[2]	575[2]	2.5[2]	2.5[2]	10[2]	44[2]	1.5[2]
Data quality rating					B	B	D	D	C	C	D

1) CORINAIR90 data, area sources

2) CORINAIR90 data, point sources

Technique related emission factors are listed in Tables 8.2b through 8.2g for sulphur dioxide, nitrogen oxides, non-methane VOCs, CO, methane, and particulate matter. No information exists on the type and efficiency of abatement techniques, but the factors in these tables seem to be valid for emissions from uncontrolled processes.

Table 8.2b Emission factors for SO_2 from cement production.

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Dry process kiln	N/A	N/A	N/A	kg/tonne	5.1	E	USA
Wet process kiln	N/A	N/A	N/A	kg/tonne product	5.1	E	USA
Cement production	N/A	N/A	N/A	kg/tonne cement	0.2-0.3	E	USA
Clinker production	N/A	N/A	N/A	g/gJ	0.02-50.0	E	USA

Table 8.2c Emission factors for NO_x from cement production.

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Dry process kiln	N/A	N/A	N/A	kg/tonne product	1.4-2.1	E	USA
Wet process kiln	N/A	N/A	N/A	kg/tonne product	1.1-1.4	E	USA
Semi-wet process kiln	N/A	N/A	N/A	kg/tonne product	1.8	E	USA
Clinker production	N/A	N/A	N/A	g/GJ	1.2	E	USA
Clinker production (80% NO_x reduction, 20% energy saving)	N/A	N/A	N/A	kg/tonne clinker	0.6	E	USA
Cement production	N/A	N/A	N/A	g/GJ	130-220	E	USA
Cement production	N/A	N/A	N/A	kg/tonne cement	1.3-1.4	E	USA
Cement/lime industry, kiln	N/A	N/A	Natural gas	kg/GJ	1.1	E	USA
Cement/lime industry, kiln	N/A	N/A	Oil	kg/GJ	0.5	E	USA
Cement/lime industry, kiln	N/A	N/A	Coal	kg/GJ	0.5	E	USA

N/A - Data not available

Table 8.2d Emission factors for NMVOC from cement production.

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Dry process kiln	N/A	N/A	N/A	g/tonne product	10.0	E	USA
Cement production	N/A	N/A	N/A	kg/tonne cement	50.0	E	USA

N/A - Data not available

Table 8.2e Emission factors for CO from cement production.

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Cement/lime industry, kiln	N/A	N/A	Natural gas	g/GJ	83.0	E	USA
Cement/lime industry, kiln	N/A	N/A	Oil	g/GJ	79.0	E	USA
Cement/lime industry, kiln	N/A	N/A	Coal	g/GJ	79.0	E	USA

N/A - Data not available

Table 8.2f Emission factors for CH_4 from cement production.

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Cement/lime industry, kiln	N/A	N/A	Natural gas	g/GJ	1.1	E	USA
Cement/lime industry, kiln	N/A	N/A	Oil	g/GJ	1.0	E	USA
Cement/lime industry, kiln	N/A	N/A	Coal	g/GJ	1.0	E	USA

N/A - Data not available

Table 8.2g Emission factors for particles from cement production.

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Kilns	"In operation"	N/A	N/A	g/tonne clinker	10 – 400	E	EU (EIPPC, 2000)
Cement production	"In operation"	N/A	N/A	g/tonne clinker	236	E	UK (Passant et al, 2000)
Clinker production	N/A	N/A	N/A	g/tonne product	212.0	E	USA
Cement production	N/A	N/A	N/A	g/tonne product	29.0-46.0	E	USA
Portland cement prod., dry process, fuel preparation	N/A	N/A	N/A	g/tonne product	20.0	E	USA
Portland cement prod., dry process, clinker firing	N/A	N/A	N/A	g/tonne product	100.0	E	USA
Portland cement prod., dry process, cement milling	N/A	N/A	N/A	g/tonne product	100.0	E	USA
Portland cement prod., dry process, cement shipping	N/A	N/A		g/tonne product	30.0	E	USA
Blast furnace cement, raw materials transport	N/A	N/A		g/tonne product	55.0	E	USA
Blast furnace cement, cement drying, milling, shipping	N/A	N/A		g/tonne product	60.0	E	USA

N/A - Data not available

The emission factors for heavy metals are determined by the composition of the raw material and the type of fuels used for firing. An illustration of the range of emission factors to be expected is given in Table 8.2h. This table is derived from the PARCOM-ATMOS Emission Factors Manual (van der Most and Veldt, 1992). Unfortunately, no information is available on the abatement efficiency for these data.

Table 8.2h Examples of emission factors for heavy metals from cement production in g/Mg cement (van der Most and Veldt, 1992)

Substance	Coal and oil fired	Proportion of waste oil	Fuel unknown	Fuel unknown	Fuel unknown
Arsenic	-	-	-	0.012	-
Cadmium	-	-	0.04	0.008	< 0.001
Chromium	0.006-0.02	0.02-0.3	-	0.105	-
Lead	0.006	0.012-0.2	1.1	0.216	<0.033
Mercury	-	-	-	0.275	-
Nickel	-	-	-	0.111	-
Selenium	-	-	-	0.002	-
Zinc	-	-	-	0.293	0.003-0.47

- Data not available

Similar results were reported for the UK cement industry (Salway, 1997).

In the CIS countries cement plants operate mostly using the wet process, and in this way 83 % of cement is produced. Some preliminary emission factors suggested for these countries are within the ranges presented in the above tables (EMEP-MSC-E, 1997). The same can be concluded for the emission factors developed in the Netherlands.

Concentrations of dioxins and furans in the flue gas after passing the control equipment in the cement production are presented in Table 11 after a compilation of data by the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Emission Control Committee in Germany (Umweltbundesamt, 1996) and information obtained from Schreiber et al. (1995), EPA (1994), and (Quass, 1997).

9 SPECIES PROFILES

An analysis of dust emissions from clinker firing in the Netherlands gave results presented in Table 9.1. The composition is given in mg per tonne cement:

Table 9.1 Composition of dust from clinker firing

Substance	Concentration in dust (g/tonne of cement)
Antimony	6
Arsenic	4
Cadmium	6
Chromium	5
Copper	8
Lead	6.5
Mercury	9
Nickel	4
Selenium	3
Tellurium	5
Thallium	3
Uranium	3
Vanadium	5
Zinc	4

EPA (1995) gives size distributions for particulate matter emitted from various cement production processes. These are reproduced in Table 9.2. The profiles for controlled dry process kilns and controlled clinker coolers seem most appropriate for the EU and suggest that particulate matter emissions comprises about 80% PM10.

Table 9.2 Particle size distributions and size-specific emission factors (EPA 1995)

Process	**Abatement technology**	**Particle size (µm)**	**Cumulative mass % less than stated size**
Kilns, wet process	Uncontrolled	2.5	7
		5	20
		10	24
		15	35
		20	57
		total	100
Kilns, wet process	ESP	2.5	64
		5	83
		10	58
		15	91
		20	98
		total	100
Kilns, dry process	Uncontrolled	2.5	18
		10	42
		15	44
		total	100
Kilns, dry process	Fabric filter	2.5	45
		5	77
		10	84
		15	89
		20	100
		total	100
Clinker coolers	Uncontrolled	2.5	0.54
		5	1.5
		10	8.6
		15	21
		20	34
		total	100
Clinker coolers	Gravel bed filter	2.5	40
		5	64
		10	76
		15	84
		20	89
		total	100

In general, no reliable information exists at present on physical and chemical species of trace elements emitted during the cement production. It can be assumed that the majority of trace elements volatilised from the raw material and fuel enter the atmosphere on fine particles.

Very general information collected by Pacyna (1987) appears to indicate that elemental forms, oxides and sulphates are the major chemical forms of atmospheric trace elements from the cement production.

10 UNCERTAINTY ESTIMATES

It is rather difficult to assess current uncertainties of emission estimates for pollutants emitted during the cement production. The uncertainties of sulphur dioxide emission estimates can be assessed in a similar way as the uncertainties of the estimates for the fossil fuel combustion (see chapter B111).

Recently it was concluded that up to 50% of uncertainties can be assigned to the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Similar uncertainty can be assigned for emission estimates of these compounds from the cement production.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge of abatement techniques, dust removal efficiencies and operating techniques is limited; measurement data of composition of dust is poor.

The fuel specific emission factors provided in Table 8.1 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. Emission factors also need to be generated, which specifically relate to different levels of abatement on different types of plant.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Cement production plants should be considered as point sources if plant specific data are available. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Cement production can be considered as a continuous process.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

Emission inventory in The Netherlands, 1992. Emission to air and water

Personal information and experience during emission inventories 1975 - 1995

Emission factors to be used for the building industry, TNO report 89/091

Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP 42

PARCOM-ATMOS Emission Factors Manual

16 VERIFICATION PROCESSES

Verification of the emissions can be done for metal emissions by calculating the emissions using the factors from the PARCOM ATMOS manual and comparing the results with a mean profile.

17 REFERENCES

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18 BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP 42 or the PARCOM-ATMOS Manual can be used.

19 RELEASE VERSION, DATE AND SOURCE

Version: 2.3

Date: April 2000

Source: J.J.M. Berdowski, P.F.J.van der Most, R.Wessels Boer
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SNAP CODE: **030312**
040614

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Lime
Lime (decarbonizing)

NOSE CODE: **104.01.02**

NFR CODE: **1 A 2 f**
2 A 2

1 ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions during lime work operations. Lime (CaO) is the high-temperature product of the calcination of limestone. The production occurs in vertical and rotary kilns fired by coal, oil or natural gas. Calcium limestone contains between 97 and 98 % of calcium carbonate on a dry basis. The rest includes magnesium carbonate, aluminium oxide, iron oxide and silica. However, some limestones contain as much as 35 to 45 % magnesium carbonate and are classified as dolomite.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Atmospheric emissions in the lime manufacturing industry include particulate emissions from the mining, handling, crushing, screening, and calcining of the limestone and emissions of air pollutants generated during fuel combustion in kilns. These emissions are not very significant on global or even regional scale. However, lime works can be an important emission source of air pollutants on a local scale.

Table 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_2O	NH_3
Lime	030312	0.1	0.2	0	0	0.3	0.3	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

Two major types of processes can be considered within the lime work operations: quarrying, crushing, and size grading of minerals and then combustion of fuels in lime kilns. Limestone quarries are usually developed in a number of benches or lifts. For primary blasting of the limestone, holes are made by drills operated by compressed air (Parker, 1978). The excavated limestone is transferred for crushing and grinding. There are several types of crushing and grinding machines to produce limestone of sizes suitable for several designs of kilns.

During the kiln operations the limestone reaches temperatures as high as 900° C, and carbon dioxide is driven off limestone to leave so-called quicklime. The quicklime descends through the cooling zone and is discharged at the base of the kiln. Obviously, various air pollutants are generated during combustion of fuels in the kiln. At present two major types of kilns are in use: vertical and rotary kilns.

The vertical kilns, because of larger size of charge material, lower air velocities, and less agitation emit lower amounts of particles but higher amounts of sulfur dioxide and carbon monoxide. However, in recent years there have been important developments in the design and use of rotary kilns. They require a more carefully classified and smaller size of limestone than for the vertical kilns.

Hydrated lime is made by adding water to crushed or ground quicklime and thoroughly mixing the quicklime and the water.

Milk of lime can be produced either by slaking quicklime with an excess of water or by mixing hydrated lime with water.

3.2 Definitions

Lime: - the high-temperature product of the calcination of limestone.

3.3 Emissions

Pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), and nitrous oxide (N_2O). According to CORINAIR90 the main relevant pollutants are SO_2, NO_x, CO and CO_2 (see also table 1).

Sulphur dioxide emissions are influenced by several factors, including the sulphur content of the fuel, the sulphur content and mineralogical form (metal sulphide like pyrite, or sulphates like gypsum) of the stone feed, the quality of lime being produced, and the type of kiln. Due to variations in these factors, plant-specific SO_2 emission factors are likely to vary significantly from the average emission factors presented here. The dominant source of sulphur emissions is the kiln’s fuel, particularly coal and petroleum derived coke, where the levels of sulphur may be as high as 5 % by weight. The amount of sulphur present will vary widely according to the nature of the deposits used. During the calcining operation, sulphide and sulphates are decomposed to yield sulphur dioxide. On combustion of the fuel, the sulphur compounds present in the fuel are oxidised to sulphur dioxide, and pass through the burning zone of the kiln with the exhaust gases (EPA, 1995; HSMO, 1992).

When sulphur containing fuels are burnt, for practical purposes sulphur in the kiln exhaust may be assumed to be emitted as sulphur dioxide, although there is usually some sulphur trioxide formed. In the case of lime manufacture in shaft kilns, much of the sulphur re-combines with the burnt lime and the emissions of sulphur dioxide are subsequently reduced. In the case of rotary and rotating hearth kilns, combinations of process design and combustion conditions can be selected to ensure that most of the sulphur is expelled as sulphur dioxide in the kiln gases (HSMO, 1992).

The oxides of nitrogen are produced through the reaction of the nitrogen and oxygen in the air and through the oxidation of the nitrogen compounds contained in the fuel. There is a significant increase in the amount of oxides of nitrogen (mainly nitric oxide) which is formed at temperatures above 1,400 °C. The formation of nitric oxide is also a function of the excess air. When operating near to stoichiometric conditions in the kiln, there is localised generation of carbon monoxide. This acts as a reducing agent so that any nitric oxide which may be present is converted to nitrogen. Some oxides of nitrogen are also formed in electrostatic precipitators (HSMO, 1992).

Carbon dioxide and carbon monoxide are formed as main products of the combustion process. Carbon monoxide is formed by the incomplete combustion of carbonaceous fuels and even with good combustion control small amounts of carbon monoxide will be present in combustion gases.

3.4 Controls

Emissions of sulphur oxide can be reduced by using low sulphur fuels and by limiting the sulphur contents of the fuel and raw materials. Sulphur dioxide emissions may be further reduced if the polluting equipment is fitted to desulphurise the exhaust gases (e.g. by using a wet process) (EPA, 1995; HMSO, 1992).

The design of kiln and combustion conditions may be selected to ensure that most of the sulphur is retained in the burnt lime. In most circumstances, especially in shaft kilns, only a small fraction of the sulphur dioxide generated within the kiln (whether originating from the raw materials or from the fuel) is released to atmosphere, since it is mainly incorporated into the lime by chemical combination (HSMO, 1992).

The following techniques can be reasonably applied to reduce oxides of nitrogen discharges to the atmosphere:

- the use of low-NO_x-burners where practicable, the principle of which is the avoidance of localised hot spots, and
- the use of very finely pulverised coal so that complete combustion can be achieved with low excess air.

Modern lime works are equipped with electrostatic precipitators that remove at least 98 % of the particulate matter from exhaust gases. Other control devices are also used including multiple cyclones, wet scrubbers, and baghouses.

4 SIMPLER METHODOLOGY

Application of emission factors with appropriate activity statistics can be regarded as a simpler methodology for estimation of emissions from lime work operations. However, it should be admitted that the chemical composition of fuel used in kilns is one of the factors affecting the amount of these emissions.

5 DETAILED METHODOLOGY

In this case, different emission factors for different types of kilns should be used. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of lime is available from the UN statistical yearbooks (e.g. UN, 1994). This information is satisfactory to estimate emissions with the use of the simpler estimation methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of lime produced in vertical and rotary kilns. Therefore, the application of detailed estimation methodology is much more complicated.

7 POINT SOURCE CRITERIA

Lime works should be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Limited information is available on emission factors for various air pollutants emitted from lime works. Old data from the U.S. Environmental Protection Agency (U.S. EPA, 1973) are available for primary and secondary crushing and calcining in both vertical and rotary kilns.
Very recently a collection of emission factors was performed for World Health Organization (Economopoulos, 1993). The results of this work are presented in table 2.

Table 2: Emission factors for selected air pollutants emitted during lime production, in kg/tonne of lime produced, after Economopoulos (1993)

Operation	**Total suspended particles**	**SO_2**	**NO_X**	**CO**
Coal Storage and Processing (If Coal is used as fuel)				
Coal Storage				
Open Piles	0.5			
Semi-Enclosed Piles	0.25			
Compartments	0.1			
Silos	0.1			
Coal Crushing and Screening				
Uncontrolled	0.18			
Fabric Filter	0.002			
Coal Grinding				
(Semi) Direct Fired System	0.0			
Indirect Fired System				
Uncontrolled	10.0			
Fabric Filter	0.1			
Raw Material Storage	0.16			
Crushing & Screening				
Uncontrolled	1.5			
Fabric Filter	0.0005			
Crushed Material Storage				
Open Piles	1.0			
Semi-Enclosed Piles	0.5			
Compartments	0.2			
Silos	0.2			
Raw Material Conveying				
Uncontrolled	1.2			
Fabric Filter	0.01			
Raw Material Calcining				
Vertical Shaft Kiln				
Uncontrolled	3.0	0.9S	0.1	2.0
Cyclone	1.0	0.9S	0.1	2.0
Multicyclones	0.75	0.9S	0.1	2.0
Vertical Double Inclined Kilns				
Uncontrolled	10.5	0.9S	0.1	2.0
Cyclone	3.6	0.9S	0.1	2.0
Multicyclones	2.6	0.9S	0.1	2.0
Parallel Flow/Counterflow Regenerative Kilns				
Uncontrolled	8.0	0.9S	0.1	2.0
Cyclone	2.8	0.9S	0.1	2.0
Multicyclones	2.0	0.9S	0.1	2.0
Annular Kilns				
Uncontrolled	12.0	0.9S	0.1	2.0
Cyclone	4.2	0.9S	0.1	2.0
Multicyclones	3.0	0.9S	0.1	2.0

Operation	**Total suspended particles**	**SO_2**	**NO_X**	**CO**
Rotary Short Kiln/Air Suspension Preheater				
Uncontrolled	40.0	0.36S	1.5	1.0
Cyclone	14.0	0.36S	1.5	1.0
Multicyclones	9.0	0.36S	1.5	1.0
ESP	0.6	0.36S	1.5	1.0
Fabric Filter	0.2	0.36S	1.5	1.0
Rotary Long Kiln				
Uncontrolled	140.0	0.36S	1.5	1.0
Cyclone	49.0	0.36S	1.5	1.0
Multicyclones	35.0	0.36S	1.5	1.0
ESP	2.0	0.36S	1.5	1.0
Fabric Filter	0.4	0.36S	1.5	1.0
Calcimatic Kiln				
Uncontrolled	25.0	0.9S	0.1	1.0
Cyclone	8.7	0.9S	0.1	1.0
Multicyclones	6.2	0.9S	0.1	1.0
Lime Cooling				
Grate Cooler				
Uncontrolled	20.0			
Cyclone	4.0			
Multicyclones	2.0			
Fabric Filters	0.1			
Planetary, Rotary, or Vertical Shaft Coolers	0.0			
Lime Packaging/Shipping	0.12			
Lime Hydration				
Uncontrolled	35.0			
Scrubber	0.04			

“S” is the sulfur percent in the fuel.

Table 3 contains fuel related emission factors for lime works based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 3 up to 4.7 GJ/Mg product has been reported.

Table 3: Emission factors for lime works[8]

					8.1.1.1.1	**Emission factors**					
	Type of fuel			NAPFUE code	SO_2[3] [g/GJ]	NO_x[4] [g/GJ]	NMVOC[5] [g/GJ]	CH_4[6] [g/GJ]	CO[7] [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
s	coal	Hc	steam	102	33-786[1]	150-340[1]	15-40[1]	0.3-15[1]	10-6000[1]	92-98[1]	4-14[1]
s	coal	Hc	brown coal/lignite	105	25[1], 80[2]	140[1], 300[2]	15[1][2]	15[1][2]	100[1], 15[2]	113[1], 100[2]	3.5[1], 3[2]
s	coal	Hc	briquettes	106	11[1]	140[1]	15[1]	15[1]	6000[1]	95-981)	3.5[1]
s	coke	Hc	coke oven	107	25-400[1]	40-300[1]	0.5-15[1]	0.5-15[1]	70-6000[1]	45-200[1]	4-12[1]
s	coke	Bc	coke oven	108	650[1]	220[1]	5[1]	15[1]	90[1]	86[1]	3[1]
s	coke		petroleum	110	275[1] 120-2,852[2]	300[1] 200-300[2]	1.5[1] 1.5-112[2]	1.51) 1.5-15[2]	70-75[1] 10-133[2]	97-99[1] 95-105[2]	10-14[1] 3-14[2]
s	biomass		wood	111	5.2[1]	103-200[1]	48-50[1]	30-32[1]	1430-6772[1]	92[1]	4-14[1]
s	waste		industrial	116	5.2[1]	115[1]	48[1]	32[1]	1430[1], 15[2]	83[1] 76-92[2]	4[1] 6-14[2]
l	oil		residual	203	47-1,470[1] 94-1,712[2]	100-310[1] 170-215[2]	3-4[1] 3-46[2]	3-8[1] 1-3[2]	12-6000[1] 7-94[2]	73-78[1] 75-78[2]	2-14[1] 2.5-14[2]
l	oil		gas	204	85-305[1] 26[2]	70-310[1] 313[2]	1.5-2.5[1]	1-8[1]	10-20[1], 76[2]	72-74[1]	2-14[1]
g	gas		natural	301	0.1-8[1] 0.9[2]	50-1111[1] 14-100[2]	2.5-10[1] 2.5[2]	0.4-4[1]	20-6000[1] 13-17[2]	55-56[1] 53[2]	1-3.7[1] 1.5[2]
g	gas		coke oven	304	15[2]	83[2]			84[2]		
g	gas		blast furnace	305	63[2]	286[2]		2.5[3]	286[2]		
g	gas		coke oven and blast furnace gas	306	328[2]	250[2]	0.8[2]	0.8[3]	15[2]	205[2]	3[2]

[1] CORINAIR90 data, area sources

[2] CORINAIR90 data, point sources

[3]	SO_x:	4,100	g/Mg product	Calcining, vertical kiln (EPA, 1990)
		2,550	g/Mg product	Calcining, rotary kiln (EPA, 1990)
		4,100	g/Mg product	multiple hearth calciner (EPA, 1990)
[4]	NO_x:	1,500	g/Mg product	General (Bouscaren, 1992)
		1,400	g/Mg product	Calcining: vertical kiln, rotary kiln and multiple hearth calciner
		1,111	g/GJ	Cement/lime industry, kilns: natural gas (IPCC, 1995)
		527	g/GJ	Cement/lime industry, kilns: oil (IPCC, 1995)
		527	g/GJ	Cement/lime industry, kilns: coal (IPCC, 1995)
[5]	VOC:	10	g/Mg product	Calcining,: vertical kiln (EPA, 1990)
		30	g/Mg product	Calcining: rotary kiln (EPA, 1990)
		10	g/Mg product	Calcining: multiple hearth calciner (EPA, 1990)
[6]	CH_4:	1.1	g/GJ	Cement/lime industry, kilns: natural gas (IPCC, 1995)
		1.0	g/GJ	Cement/lime industry, kilns: oil (IPCC, 1995)
		1.0	g/GJ	Cement/lime industry, kilns: coal (IPCC, 1995)
[7]	CO:	83	g/GJ	Cement/lime industry, kilns: natural gas (IPCC, 1995)
		79	g/GJ	Cement/lime industry, kilns: oil (IPCC, 1995)
		79	g/GJ	Cement/lime industry, kilns: coal (IPCC, 1995)

[8] It is assumed, that emission factors cited within the table are related to combustion sources in lime works. Footnotes may also include emission factors for other process emissions (e.g. calcination).

9 SPECIES PROFILES

Not applicable.

10 UNCERTAINTY ESTIMATES

It is difficult to assess current uncertainties of emission estimates for lime works operations. The difficulty results from a lack of emission measurements in these plants and thus the uncertainty of emission factors based on limited information.

11 WEAKEST ASPECTS/ PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for lime works operations. This improvement should focus on preparing individual emission factors for different types of kiln operations. In this way, a detailed methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data.

The fuel specific emission factors provided in Table 3 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 FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The production process in lime works is continuous.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Parker A. (1978) Lime works. In: Industrial Air Pollution Handbook, A. Parker (ed.), Mc Graw-Hill Book Comp. Ltd., London.

16 VERIFICATION PROCEDURES

Estimated emission factors could be best verified by measurements at respective plants.

17 REFERENCES

Bouscaren M. R. (1992) CORINAIR Inventory, Default Emission Factors Handbook,; second Edition, Comission of the European Communities, Paris.

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SNAP CODE: **030313**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Asphalt Concrete Plants

NOSE CODE: **104.11.04**

NFR CODE: **1 A 2 f**

1 ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions of particulate matter during the production of asphaltic concrete, a paving substance composed of a combination of aggregates uniformly mixed and coated with asphalt cement.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

During the production of asphalt concrete considerable amounts of fine particles can be generated. These emissions are not very significant on global or even regional scale. However, asphalt concrete plants can be an important emission source of particles on a local scale.

Table 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_2O	NH_3
Asphalt Concrete Plants	030313	0.1	0	0	-	0	0.1	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

There are various steps in the production of asphaltic concrete. Selecting and handling the raw material is the first step in which the raw aggregates are crushed and screened at the quarries to obtain the required size distributions. The coarse aggregate usually consists of crushed stone and gravel, but waste materials, such as slag from steel mills or crushed glass, can also be used as raw material (U.S. EPA, 1973).

Plants produce finished asphaltic concrete through either batch or continuous aggregate operations. In either operation the aggregate is transported first to a gas- or oil-fired rotary dryer and then to a set of vibrating screens.

In the final operation, the aggregate and the asphalt are brought together and mixed in a batch or a special mixer.

3.2 Definitions

3.3 Controls

Rotary dryer, hot aggregate elevators, vibrating screens, as well as various hoppers, mixers and transfer points are the major sources of particulate emissions in the asphaltic concrete plants. Most of these emissions are fugitive, however, the rotary dryer is often considered as a separate source for emission control.

Various types of control installations have been used in asphaltic concrete plants, including mechanical collectors, scrubbers, and fabric filters. In many cases dual dust collection systems are used with primary and secondary collectors in order to improve the collection efficiency. In some plants even a tertiary collection devices are employed (U.S. EPA, 1973).

4 SIMPLER METHODOLOGY

The application of general emission factors with appropriate activity statistics can be regarded as a simple approach methodology for estimation of emissions from the asphaltic concrete production.

5 DETAILED METHODOLOGY

In this case, different emission factors for various production steps in the asphaltic concrete plants should be used, particularly for the rotary dryer. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of asphaltic concrete is largely missing in the international statistical yearbooks. This information should be obtained at a national or a country district level.

7 POINT SOURCE CRITERIA

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Very limited information is available on emission factors for asphaltic concrete plants. Old data from the U.S. Environmental Protection Agency indicate (U.S. EPA, 1973) that an uncontrolled emission factor for particulate matter should not exceed 22.5 kg/tonne asphaltic concrete, assuming that at least a precleaner is installed following the rotary dryer.

Various controlled emission factors are listed in the EPA emission factor handbook (U.S. EPA, 1973) for different types of control devices including:

- 850 g particulate matter/ tonne of asphaltic concrete produced for a high-efficiency cyclone,
- 200 g particulate matter/ tonne of asphaltic concrete produced for a spray tower,
- 150 g particulate matter/ tonne of asphaltic concrete produced for a multiple centrifugal scrubber,
- 150 g particulate matter/ tonne of asphaltic concrete produced for a baffle spray tower,
- 20 g particulate matter/ tonne of asphaltic concrete produced for an orifice-type scrubber, and
- 50 g particulate matter/ tonne of asphaltic concrete produced for a baghouse.

It was also suggested that emissions from a properly designed, installed, operated, and maintained collector can be as low as 2.5 to 10 g particulate matter/ tonne of asphaltic concrete produced.

9 SPECIES PROFILES

10 CURRENT UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for asphaltic concrete plants. This improvement should focus on preparing individual emission factors for individual steps in the asphaltic concrete production. In this way, a detailed approach methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

U.S. EPA (1973) Compilation of air pollutant emission factors. 2nd edition. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

16 VERIFICATION PROCEDURES

At present no specific verification procedures are available for estimation of atmospheric emissions from the production of asphaltic concrete. Estimated emission factors could be best verified by measurements at respective plants which are often equipped with different emission control devices.

17 REFERENCES

U.S. EPA (1973) Compilation of air pollutant emission factors. 2nd edition. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

18 BIBLIOGRAPHY

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NFR CODE:	**1 A 2 f** **2 A 7**

1 ACTIVITIES INCLUDED

The activities described under chapter 040613 regard the process emissions during the production of different types of glass (flat glass, container glass, glass wool and other glass {including special glass}). The activities concerned with the combustion and the resulting emissions are described in the chapters 030314, 030315, 030316 and 030317. The emissions treated in this chapter are carbon dioxide emissions from the carbonisation process and emissions of micropollutants, heavy metals and dust, partly resulting from the combustion of fossil fuels, partly from the basic materials. For micropollutants, heavy metals and dust separate emission factors for combustion and process emissions are not available. The factors given are to be used as default values for the whole process.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of emissions released from the production of glass to total emissions to air in countries of the CORINAIR90 inventory is given as follows:

Table 1: Contribution to total emissions to air of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]						
		SO_2	NO_x	NMVOC	CH_4	CO	N_2O	NH_3
Flat Glass	030314	0.1	0.3	0	-	0	-	-
Container Glass	030315	0.1	0.2	0	-	0	-	-
Glass Wool	030316	0	0	-	-	-	-	-
Other Glass	030317	0	0.1	-	-	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Table 2: Contribution to total emissions to air (OSPAR-HELCOM-UNECE Emission Inventory)

Source-activity	Contribution to total emissions [%]							
	Arsenic	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
Glass industry	1.3	1.3	0.9	0.1	0.1	0.1	0.9	0.2

Table 3: Contribution from the carbonisation process

Source-activity	Contribution of carbon dioxide to total emissions [%]
Glass industry	

The emission of fluorides and dust are also important.

3 GENERAL

In the production of glass products can be distinguished, for instance flat glass, container glass, special glass, glass wool, continuous filament fibres, water glass and tableware. The smelting process for the different product groups is similar.

The production of flat glass, container glass, glass fibres and commodity glass is dominated by large multinational companies, whereas domestic glass production (manufacture of table and decorative ware) take place in small- and medium-sized enterprises. Unlike technical glass production, domestic glass production is characterised by a great diversity of products and processes, including hand forming of glass. /11, 12/

3.1 Description of Activities

The manufacturing process of glass consists of the following steps /5, 11, 12/:

- *Selection and controlling of raw materials.*
- *Preparation of raw materials:* preparation consists essentially of a weighing and mixing operation.
- *Melting:* the raw materials undergo fusion at high temperature in a furnace.
- *Forming:* the molten glass is given a shape and allowed to solidify (production of flat and container glass); the formation of fibres into glasswool mats is carried out (production of glasswool).
- *Curing:* the binder-coated fibreglass mat is allowed to cure (production of glasswool).
- *Annealing:* internal stresses are removed by heat treatment.
- *Finishing:* finishing includes in particular quality control and cutting (production of flat and container glass); finishing includes cooling the mat, and backing, cutting, and packaging the insulation, as well as quality control (production of glasswool); finishing includes quality control, cutting, and for hand-shaped glass, further decorative treatment such as engraving or polishing (special glass).

A large variety of glass with differing chemical composition is produced, and therefore a great diversity of raw materials is used in glass manufacturing /15/. Main raw materials are silica sand, lime, dolomite and soda for the production of soda lime glass, as well as lead oxide, potash and zinc oxide for the production of special glass /11, 13/. Glass wool is a boro-silicate glass, which is manufactured from sand, limestone, dolomite, boric-oxide and other oxides. Refining agents such as antimony oxide, nitrates, sulphates, and colouring agents like metal oxides and sulphides enter also in the composition of special glass, e.g. TV glass, crystal glass, etc. /15/.

Nowadays, approximately 85 % of the glass produced in Europe is made up of soda lime, and consists principally of flat and container glass. The remaining 15 % of the European glass production include glass wool and special glass such as hand-shaped glassware, lighting, TV-screen, optical glasses. /14/

Recycled glass is also largely used in the manufacturing of glass and represents typically between 20 and 25 % of the quantity of melted flat glass and up to 80 % of the quantity of melted container glass. Throughout the industry, virtually all internally generated cullet is reused. The poor quality and contamination of external cullet virtually eliminates its use for flat, commodity and domestic glassware, but much external cullet (with treatment) can be used in the container glass industry. /14/

Currently, the majority of raw material is delivered to the glass production site in a prepared form; only broken glass pieces from recycling undergo processing steps such as sieving. The different materials are weighed and mixed, and the mixed batch is transferred to the melting furnace. /11/

3.2 Definitions

Borosilicate glass:	a silicate glass that is composed of at least five percent oxide of boron and is used especially in heat-resistant glassware.
Crown glass:	alkali-lime silicate optical glass having relatively low index of refraction and low dispersion value.
Fibreglass:	glass in fibrous form used in making various products (as glass wool for insulation).
Flint glass:	heavy brilliant glass that contains lead oxide, has a relatively high index of refraction, and is used in lenses and prisms.
Float glass:	flat glass produced by solidifying molten glass on the surface of a bath of molten tin.
Glass wool:	there exist two types of glass fibre products, textile and wool, which are manufactured by similar processes. Here only glasswool is taken into account: glass fibres in a mass resembling wool and being used especially for thermal insulation and air filters.
Lead glass:	glass containing a high proportion of lead oxide and having extraordinary clarity and brilliance.
Optical glass:	flint or crown glass of well-defined characteristics used especially for making lenses.

3.3 Techniques

For container glass production, the melting stage can be preceded by a pre-heating of the mixed batch /11/; however, this is not commonly done: around 10 batch preheaters are currently in operation world wide /14/.

The melting process is the most important step with regard to quality and quantity of glass, which depend on the furnace design /12/. In the melting furnaces, the glass is melted at temperatures ranging from 1,500 °C to 1,600 °C (the flame temperature achieving more than 2,000 °C) and are transformed through a sequence of chemical reactions to molten glass. Although there are many furnace designs, furnaces are generally large, shallow, and well-insulated vessels that are heated from above. In operation, raw materials are introduced continuously on top of a bed of molten glass, where they slowly mix and dissolve. Mixing is effected by natural convection, gases rising from chemical reactions, and, in some operations, by air injection into the bottom of the bed. /6/ In the glass production, both continuously and batch-wise operated melting furnaces are in use. In large glass manufacturing installations as it is the case for flat and container glass production, and where the forming processes are fully automated, refractory lined tank furnaces are operated in the continuous mode. For the production of smaller quantities of glass, especially for hand-shaped glassware, the batch operating mode is preferred since molten glass has to be removed from the pot furnace by hand. /12, 15/

Some characteristics of the above mentioned furnaces are summarised in the following table.

Table 4: Some characteristics of furnaces used in glass production /15, 34/

Type of Furnace	Type of Firing	Energy Source	Operating Mode	Capacity [Mg/d]
Single or multi-pot	flame or electrically heated	gas, oil, electricity	batch	0.1 – 35
Day tank	flame or electrically heated	gas, oil, electricity	batch	0.1 – 3
Tank furnace	flame or electrically heated	gas, oil, electricity	continuous	2 - 900

In order to achieve a higher energy efficiency and a higher flame temperature, the combustion air is preheated. Air preheaters in use are recuperative or regenerative. /11, 16, 17/ Glass melting furnaces use natural gas and/or oil as a fuel, since the use of hard coal or lignite would result into an import of molten ash in the glass phase, and would subsequently lead to a lower product quality and would block the refractory lattice of the regenerators or the recuperators /11, 14/. For the production of container glass, approximately 70 % of the furnaces are operating with oil and 30 % with natural gas. City gas or liquified gas are used in isolated cases. /7/

The furnace most commonly used within flat glass production is a cross-fired furnace with regenerative preheating working in the continuous mode; very few exception with end-fired furnaces do exist in the production of printed glass /14/. In container glass production, mostly regeneratively heated furnaces are in use /14/.

Additional electric heating is frequently employed to increase output and to cope with peak-load demands. Between 5 to 30 % of the total energy is passed in the form of electrical energy directly into the glass batch through electrodes. /7/

Table 5: Specific energy demand for the production of glass

Type of Glass	Specific Energy Demand [GJ/Mg glass]
Flat glass	7
Container glass	6
Glass wool	12
Special glass	25

However, more advanced glass furnaces do exist with lower specific energy demands (for example around 4 GJ/Mg /7/ in the production of flat glass).

Glass Wool Manufacturing Process

In the “indirect” melting process, molten glass passes to a forehearth, where it is drawn off, sheared into globs, and formed into marbles by roll-forming. The marbles are then stress-relieved in annealing ovens, cooled, and conveyed to storage or to further processing in other plants. In the “direct” glass fibre process, molten glass passes from the furnace into a refining unit, where bubbles and particles are removed by settling, and the melt is allowed to cool to the proper viscosity for the fibre forming operation. /cf. 35/

During the formation of fibres into a wool fibreglass mat (the process is known as “forming” in the industry), glass fibres are made from molten glass, and a chemical binder is simultaneously sprayed on the fibres as they are created. Although the binder composition varies with product type, typically the binder consists of a solution of phenol-formaldehyde resin, water, urea, lignin, silane, and ammonia. Colouring agents may also be added to the binder. Two methods of creating fibres are used by the industry. In the rotary spin process, centrifugal force causes molten glass to flow through small holes in the wall of a rapidly rotating cylinder to create fibres that are broken into pieces by an air stream. This is the newer of the two processes and dominates the industry today. In the flame attenuation process, molten glass flows by gravity from a furnace through numerous small orifices to create threads that are then attenuated (stretched to the point of breaking) by high velocity, hot air, and/or a flame. /35/

3.3.1 Gas- and Oil-Fired Glass Melting Furnaces with Regenerative Air Preheating

The common feature of all tank furnaces is a large ceramic tank which serves as a melting container. In general, tank furnaces are operated by alternating flame-heating based on the regenerative principle. /cf 7/

Regenerative air preheaters use a lattice of brickwork to recover waste heat from the exhaust gas. The regenerators are made up of two chambers, each of them consisting of a refractory lattice; the chamber walls and the mentioned lattice represent the heat storing material, which transfers the heat from the waste gas to the combustion air. The waste gas is lead from the furnace to one of these chambers, whereby the lattice is warmed up. The combustion air enters the furnace via the other chamber. The combustion air flow and the waste gas flow are then reversed: the combustion air flows then through the hot chamber and is heated there, while the waste gas flows through the second chamber, reheating the refractory lattice. The temperature of the incoming air achieves up to 1,350 °C, and the waste gas leaves the regenerative chambers with a temperature of about 500 – 550 °C. /11, 15, 18/

Depending on the arrangement of the burners and the position of the flames, one differentiates between cross-fired and end-fired tanks. /cf 7/ Because of the higher number of burner necks and the larger regenerator chambers, the specific energy consumption is higher for cross-fired furnaces than for comparable end-fired furnaces. /15/ Small and medium-sized tanks are built as end-fired tanks, larger ones as cross-fired burner tanks. In both arrangements, the flames flow closely over the molten glass surface and transmit heat to it, primarily by radiation. /cf 7/

Cross-fired furnaces give better control of melting chamber temperatures and oxidation state and therefore predominate in the larger throughput and ”quality glass” furnaces. Cross-fired furnaces are used exclusively in float glass furnaces and in the larger container furnaces, whereas for melting surfaces up to 120 m^2 more and more are laid down as end-fired furnaces, since they show a simpler arrangement, a lower price and a higher energy efficiency than comparable cross-fired furnaces. /15/

3.3.2 Gas- and Oil-Fired Glass Melting Furnaces with Recuperative Air Preheating

Another configuration of the tank furnace is the recuperatively heated glass melting tank. Recuperative air preheaters use most commonly a steel heat exchanger, recovering heat from the exhaust gas by exchange with the combustion air; the preheating temperature can reach up to 800 °C /15/. Here, the hot waste gas and the cold combustion air flow through two parallel, but separated ducts, and the heat exchange is performed via the separation wall. Unlike regenerative heating furnaces, the combustion is not interrupted and the waste gas is continuously recuperated via the heat exchanger. In order to achieve an optimal energy use, the recuperators are often connected to waste heat boilers for steam or hot water generation. /11, 18/ The lower flame temperatures achieved (compared with those from regenerative systems) eliminates them from use in the higher quality glasses (e. g. float glass) or high specific pull (many container glasses). Recuperatively heated furnaces are generally of cross-fired configuration. /14/

3.3.3 Pot Furnaces

The use of pot furnaces is confined to manually worked specialty glasses, with intermittently operation and melting temperatures under 1,460 °C. One furnace usually is comprised of several pots permitting simultaneous melting of several types of glass. Flame-heated regeneratively and recuperatively-operated furnaces as well as electrically heated furnaces, are put to use here. City gas, natural gas, liquefied gases and light oil as well as electricity are used as heat energy. The specific heat consumption (relative to glass production) of pot furnaces is comparatively high and averages 30 GJ/Mg glass produced. /cf. 10/

3.3.4 Electric Furnaces

Electric furnaces melt glass by passing an electric current through the melt. Electric furnaces are either hot-top or cold-top. The former use gas for auxiliary heating, and the latter use only the electric current. /6/ Electric heating is used either for additional heating (electric boost) or almost exclusively in small- and medium-sized furnaces for the manufacturing of special glass such as lighting glass, glass fibres, crystal glass. /11, 16, 17/ One case of soda lime glass manufacturing via electric heating is currently known, but is restricted to low furnace outputs and special composition glasses /14/. Further information on electric heating is given later in this chapter.

3.4 Emissions

3.4.1 Combustion-related Emissions

Pollutants released during the manufacture of glass are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2) and nitrous oxide (N_2O). Also emissions of hydrogen chloride, hydrogen fluoride, particulate matter and heavy metals are produced by the melting process. Emissions of particulate matter can also result from handling raw materials. Heavy metals will be present in the particulate matter. According to CORINAIR90 of these, the main relevant pollutants are SO_2, NO_x, and CO_2 (see also Table 1).

The waste gases released from melting furnaces consist mainly of combustion gases generated by fuels and of gases arising from the melting of the batch, which in turn depends on chemical reactions taking place within this time. The proportion of batch gases from exclusively flame-heated furnaces represents 3 to 5 % of the total gas volume. /7/

Sulphur Oxides

The amount of SO_2 released during glass manufacturing is mainly determined by the sulphur content of the fuel, the sulphate content of the molten batch and the sulphur absorption ability of the glass produced /7, 22/.

The sulphur contained in the batch is partly bound in the glass as SO_3. Glass contains up to 0.4 wt.-% SO_3 /7/. The SO_3-content is 5 to 10 % of the SO_2-content. The amount of SO_3 depends on the excess air and the combustion temperature. /cf. 7/

The SO_2 content in the off-gas is also determined by the operating conditions of the glass melting tank. With tank furnaces operated by alternating flame heating, based on the regenerative principle, an increase of the SO_2 content in the off-gas during the firing interval is observed. This is most likely due to a decrease in the sulphur absorption ability of the molten glass with an increasing temperature in the upper zone of the furnace, and evaporation of already condensed sulphurous species in the air preheater /22/. The oxygen content in the upper zone of the furnace also has an impact on the SO_2 content of the off-gas: if the amount of excess air is decreased, in order to minimise fuel input and to suppress NO_x formation, an increase in the SO_2 content of the off-gas is observed. This is due to the fact that the sulphur absorption ability of the molten glass decreases with a decreasing oxygen content in the upper furnace zone /22/.

Since natural gas and city gas contain only trace amounts of sulphur, a lower SO_2 content in the off-gas of glass melting tanks fired with gaseous fuels is observed compared to oil fired glass melting tanks. /11/

Nitrogen Oxides

The relevant NO_x emission process step within the production of glass is the melting stage. NO_x emissions released by glass furnaces are nitric oxides (NO to about 90 % due to the near stoichiometric operation of the furnaces, the remainder being nitrogen dioxide NO_2). The concentrations of nitrous oxide in glass furnace waste gases are in general below the detection limit. /19/

Four main NO_x formation mechanisms exist: three of them are combustion related and include thermal, fuel and prompt NO_x formation; the fourth mechanism (the 'batch' NO_x formation) results from the use of nitrates in the raw materials for certain glasses. /19/ In the glass melting furnace, the temperature ranges from 1,500 °C to 1,600 °C /15/, leading to flame temperatures above 2,000 °C /14/. This explains the presence of high NO_x concentrations, almost exclusively due to thermal NO_x formation (according to the Zeldovich mechanism). Several parameters influence the mechanism of thermal NO_x formation: flame temperature, oxygen content in the reaction zone, and retention time of the combustion gas in high temperature zones of the flame. These parameters are in direct relation with operating parameters as for example burner and melting furnace design, amount of excess air, mixing of fuel and combustion air, etc. /18, 20, 21/ Prompt NO_x is relatively small, and when firing natural gas, fuel NO_x is sensibly zero. /19/

The conversion of nitrogen compounds contained in the raw materials and in the refining agents contributes also to NO_x emissions due to the batch NO_x formation. The quantity of nitrogen oxides arising from the feed material (see also chapter B4614) will be affected by the concentration and composition of the nitrates in the feed. /8/ For example, certain tinted glasses in the flat glass sector require the use of nitrates, which produce additional NO_x-emissions almost as great as uncontrolled emissions from a clear flat glass operation: typical emissions might be 2,500 mg/Nm^3 for clear glass, 4,000 mg/Nm^3 for tint glass /33/. It must be acknowledged that such tints are only occasionally manufactured.

When using gas fired glass melting tanks, the achieved flame temperature is higher compared to oil. As a consequence, oil fired tanks emit less NO_x than gas fired tanks. Moreover, as end-fired furnaces allow a more favourable flame characteristic than cross-fired glass melting furnaces, the first show lower NO_x emissions. Recuperative furnaces induce lower NO_x emissions than regenerative furnaces, due to their lower preheating temperature. /11, 18/
Following table gives the NO_x-concentrations for some types of furnaces.

Table 6: NO_x-emissions for some types of furnaces /11, 23/

Type of Furnace / Fuel	NO_x-Emission* [mg/Nm^3]
Oil fired recuperatively heated furnace	400 – 1,400
Gas fired recuperatively heated furnace	400 – 1,600
Oil fired regeneratively heated furnace	
• end-fired furnace	1,000 – 2,400
• cross-fired furnace	1,600 – 3,600
Gas fired regeneratively heated furnace	
• end-fired furnace	1,400 – 3,000
• cross-fired furnace	1,600 – 4,000

* These values refer to an O_2-content in the waste gas of 8 vol.-%.

3.4.2 Process-related Emissions

The most important source of atmospheric emissions is the hot furnace. The heavy metals from the raw materials or the fuel partly vaporize in the hot furnace. The heavy metals which are emitted to air are mainly arsenic, cadmium, chromium, lead, tin, and selenium.

If fuel oil is used in the combustion process also nickel and vanadium may be found. In south and eastern Europe fluorspar is often used in the melting process. If recycled glass originating from these countries some fluorine may be emitted.

Basic materials for glass production are silicium oxide and oxides of alkalimetals. The alcali metal oxides are produced during the process from dissociation of carbonates. The emission factors given under /38/ are calculated from the amount of carbonates added in general in the production process of the different types of glass, assuming that all metal oxides have their origin in carbonates and that no recycled glass is added. If however oxides, hydrocarbonates, sulfates, or a relevant amount of recycled glass are used corrections must be made.

3.5 Controls

3.5.1 NO_x-Emission Reduction Measures

3.5.1.1 Primary Emission Reduction Measures

3.5.1.1.1 Lowering the Amount of Excess Air

Technical Aspects

This relatively simple measure aims at achieving near stoichiometric combustion, resulting in a lower oxygen concentration in the reaction zone, and consequently in a reduction of nitrogen oxides. Sealing of the furnace against inleaked (false) air is an additional measure to lowering the amount of excess air. NO_x emission reduction efficiencies between 30 and 70 % (depending on the initial level) are achievable /18/. Further a slight decrease in specific energy consumption is observed /14/.

However, it may be noted that a move to near stoichiometric combustion can give a significant reduction in NO_x, but may lead on the other hand to an increase of the emissions of other pollutants (e. g. CO, dust) as well as to a slight increase of energy demand. Furthermore, the quality of the product and the furnace lifetime can both be influenced by the O_2-content in the upper zone of the glass melting furnace. /11/

Side-Effects

Near stoichiometric combustion (as performed when lowering the amount of excess air) lowers the nitrogen oxides formation, but in the same time induces slightly increased emissions of measured SO_2.

3.5.1.1.2 Reduced Air Preheating

Preheaters have originally been used to improve the heat transfer from flame to batch, and have proved to lead to savings in energy consumption /14/.

Technical Aspects

By reducing the air preheating temperature, the flame temperature is reduced and consequently the formation of nitrogen oxides. Reduction of the preheating temperature can be carried out by using recuperative air preheaters instead of regenerative air preheaters /11/. However, when switching from a regenerative to a recuperative preheater, the melting capacity is reduced, inducing the need of larger facilities and thus higher costs. Furthermore, recuperative air preheaters achieve lower energy efficiencies. /14/

Side-Effects

The use of recuperative air preheaters instead of regenerative ones results in a reduction of flame temperature and hence glass quality, pull rate and energy efficiency /14/.

3.5.1.1.3 Staged Combustion

In a classical combustion facility, the totality of fuel and air/oxygen is injected at the same place. The resulting flame is then composed of a hot and oxidising primary zone located at the flame root and a colder secondary zone located at the flame end. The primary zone generates most of the NO-emissions, which increase exponentially with the temperature, whereas the contribution of the secondary zone is rather modest. Staged combustion aims at decreasing the temperature in the primary zone. Therefore, only a part of the fuel or of the air/oxygen is injected at the burner, the rest being injected downstream of the main combustion zone.

Emission reduction rates in the range of 50 to 70 % can be achieved by combining staged combustion with other primary measures. It is estimated that about 30 to 50 % of the reduction may originate from staged combustion alone. Concentrations around 700 mg/Nm^3 may be reached in the best cases. /24/

Air/Oxygen Staging

The KORTING air staging process /25/ has been tested at three furnaces in Germany at the beginning of the 90s, but has been abandoned meanwhile. Maintenance problems have appeared on the air ejector at high temperatures, and anyway this technique does not allow as good reduction efficiencies as do state-of-the-art low-NO$_x$ burners. /24, 27/

Oxygen staging with the Oxygen Enriched Air Staging (O.E.A.S.) process /26/ is still in a state of development (three test furnaces are running in the USA) and it is therefore impossible to conclude about efficiency and applicability. /24/ Due to the high costs of oxygen, this technique will most probably not be generally applied /14/.

Fuel Staging

A lack of fuel in the primary zone decreases the flame temperature. The fuel-rich secondary zone becomes reducing, generating hydrocarbon radicals reducing NO into molecular nitrogen. About 8 to 10 % of the fuel is injected into the combustion air in the port neck, resulting in sub-stoichiometric conditions in the main flame, and therefore leading to reduced NO$_x$ formation. The remaining fuel is injected within the furnace and ensures complete burnout. NO$_x$ concentrations below 800 mg/m^3 have been reported with initial values between 1,800 and 2,200 mg/m^3. /11/

Fuel staging has proven to be rather attractive: it has been implemented at 12 German glass melting tanks for nitrogen oxides abatement /11/; however, this measure is expected to be phased out with the installation of new low-NO$_x$ burners /14/.

Side-Effects

No side-effects have been observed.

3.5.1.1.4 Flue Gas Recirculation

Technical Aspects

This technology is in principle similar to staged combustion: NO_x-emissions are reduced by lowering the flame temperature. Secondary air is mixed with a part of the flue gas, and this oxygen lacking air is injected as combustive agent in the furnace.

Three tests of flue gas recirculation have been performed in the glass production sector /14/. NO_x emission abatement rates between 16 and 44 % could be achieved, but this technology proved to be difficult to be implemented, and has meanwhile been abandoned. /24/

Side-Effects

No side-effects have been observed, but it must be acknowledged that the experience is very limited.

3.5.1.1.5 Reburning / 3R Process

The reburning process and the 3R process are similar technologies, based on the same principle. In the literature, both processes are either considered as primary NO_x-emission reduction measures or as secondary NO_x-removal options. In the framework of this report, the reburning / 3R process will be presented as a primary measure, since it can be compared to the fuel-staging process.

Technical Aspects

In both the reburning and 3R processes, NO or its precursors (HCN, NH_y) formed in the combustion zone undergo reduction by injection of natural gas or fuel as the waste gases enter the regenerators from the melting chamber. In the 3R process, hydrocarbon fuel is injected into the waste gas downstream of the glass melting furnace tank. /28/ The added fuel does not burn, but pyrolyses to form radicals converting the nitrogen oxides in the waste gas into nitrogen and water. A major advantage of this process is the possibility of using all kinds of hydrocarbon fuels (natural gas, fuel oil...) /14, 19/. Air is added downstream of the denitrification zone to ensure burnout of residual ”fuel” fragments.

Reburning is at an experimental stage, whereas the 3R process has been installed at one German float glass production site, achieving nitrogen oxides concentrations below 500 mg/m^3 /27/. According to /29, 30/, 3R has been successfully operated on float furnaces in Finland and California, and demonstrated on furnaces in the TV glass production (in Korea /14/), container, and shaped glass. In all cases, a nitrogen oxides abatement up to 85 % could be achieved. One further furnace has been equipped with 3R at a float glass production site in the UK. This technology is now applied by two float glass companies in the USA /14/.

Side-Effects

As this process is based on hydrocarbon fuel injection, an increased energy consumption is to be expected. Nevertheless, this technology ensures burnout of residual fuel fragments; subsequently, achievable levels of CO may be lower than with conventional combustion.

Moreover, if supplementary heat recovery is available, the additional CO_2 originating from the increased use of fuel can be compensated by the reduction that would have arisen from fossil fuel boilers or from the power station. /19/

3.5.1.1.6 Low-NO_x Glass Melting Furnaces

Technical Aspects

In recent years, new melting furnaces have been developed achieving low NO_x emissions: the FlexMelter® and the LoNOx® melter /28, 31/.

The LoNOx® melter is a combined electrical/fossil fuel fired melting tank with recuperative air preheating, including a batch preheating step. For this melting furnace, energy efficiency has been increased to compensate for the lower thermal efficiency of the air preheater compared with the regenerator and so the heat consumption of this modified recuperatively fired furnace can be compared to conventional regeneratively fired furnaces: waste gas from the melting furnace is first fed to the recuperative air preheater and afterwards used to preheat the cullet. Air temperatures of about 750 °C are reached /22/. This melting furnace allows to achieve NO_x concentrations below 500 mg/m^3 in the waste gas. /21, 27, 28, 31/ This type of low NO_x melter is exclusively used in the container glass manufacturing at about 70 – 80 % cullets undergoing preheating /14/.

The FlexMelter® has originally been developed for discontinuous production, but is operated nowadays both in the continuous and discontinuous mode. Typical applications are glass fibres for insulation, automobile lighting, and other special glass such as crystal glass. The relatively low flame temperatures from recuperative air preheaters precludes their use for typical flat glass and most container glass production /14/.

Currently, three low-NO_x melting furnaces with a total capacity of approximately 800 Mg/d glass are operated in Germany. /14/

Side-Effects

No side-effects have been observed.

3.5.1.1.7 Oxy-Fuel Firing

Technical Aspects

By this very effective, but also very expensive technology, preheated combustion air is replaced by high purity oxygen and there is thus no need for regenerators. Even though the resulting nitrogen oxide concentration in the flue gas is higher with oxy-fuel firing, mass emissions of NO_x are lower. Therefore, the actual mass flow has to be considered. Oxy-fuel firing can be applied to pot furnaces and day tanks /33/. The conversion from air to 100 % oxygen may result in a 50 - 60 % reduction of energy consumption /33/. As regards the achievable NO_x reduction rate, /9/ quotes a 80 to 95 %-reduction for oxy-fuel firing over 100%-air firing (50 % in the worst case of existing furnaces with poor sealing conditions /33/).

About one hundred furnaces are run world-wide on the oxy-fuel mode, representing approximately 4 % of the whole glass production. Since the beginning of the 90s, oxy-fuel combustion has gained importance mainly in the USA, where it represents nowadays about

10 % of the number of glass melting furnaces. The reason why oxycombustion is so popular in the USA is mainly due to economical reasons: sometimes nitrogen can be used for non-melting applications in the factory or associated products and then the overall cost of the oxygen is reduced. Furthermore, when applying this technology, an increase in capacity can be observed as well as an improvement of the product quality /33/. In Germany, two container glass melting furnaces are operated in the oxy-fuel mode, and several others are planned, among which two special glass production sites /11, 27, 14/. The application fields of oxy-combustion are basically the glass fibre, TV glass, container and special glass industries /8/.

Besides the environmental aspect, since regenerators and recuperators can be omitted, low investment is a further advantage increasing the interest of glass producers in oxy-fuel firing. Moreover, the change from a recuperatively heated furnace to oxy-fuel firing is very easy /14/. For an energy balance, production of oxygen has to be considered, and energy savings can be achieved in the case of an effective heat recovery. It should however be mentioned that the related operating costs are higher compared to 100% air firing, due to the high price of oxygen and that this technology is not yet applicable to every field of glass production /24, 28/. Furthermore, oxy-fuel firing is not effective when nitrate containing batches are melted, since only thermal NO_x is being reduced by oxy-combustion /29/. Another problem which had been reported several times is the corrosion of the furnace superstructure and crown due to higher concentration of volatiles in the furnace. /14/

Side-Effects

Besides NO_x, other pollutants can be abated via oxy-fuel firing: volatile components allowing substantial savings in batch materials and particulates in special glass (e. g. borosilicates). Energy savings can be expected when no consideration of the oxygen production is made. However, since electricity is required for the production of oxygen, the total energy consumption is the same as with conventional fired furnaces. /10, 14, 24/ Furthermore, it must be mentioned that a transfer of pollution occurs upstream towards electricity production, therefore not solving the pollution problem.

3.5.1.1.8 Electric Melting

Technical Aspects

Molten glass is an electricity conductor and thus can be heated via electrodes immersed in the bath of glass. These electrodes are generally made up of molybdenum or platinum, and are located either at the top, at the bottom or at the walls of the furnace tank. In electrically heated furnaces, no direct emissions are released. Furthermore, compared to conventional regeneratively fired furnaces, electric melting furnaces show several advantages such as good temperature control and preheating of the batch inherent to the system, but the following drawbacks should be mentioned:

- the pollution is transferred upstream, towards electricity production;
- the lifetime of an electric melting furnace is reduced compared to a conventionally fired one;
- the furnace size is limited;
- an incompatibility between glass and electrodes occur for some glass compositions;
- high operating costs related to energy costs may be expected. /15/

Electric melting is currently limited to production of special glass, especially crystal glass, and to glass fibre production /13, 24/. Very small units have been constructed in the float industry for specially formulated glasses only /14/.

Side-Effects

Via electric melting, pollution is transferred upstream towards electricity production.

3.5.1.2 Secondary Emission Reduction Measures

Even though high NO_x emission reduction can be achieved by primary measures, especially via combustion modifications and the reburning/3R process, secondary measures can be used in some cases to meet more stringent standards. Proven NO_x-abatement measures in the glass industry are the selective non-catalytic (SNCR) and catalytic (SCR) reduction processes.

3.5.1.2.1 Selective Non Catalytic Reduction (SNCR)

Technical Aspects

Ammonia is injected at an over-stoichiometric ratio into the waste gas stream of the glass melting furnace within a temperature window ranging from 850 to 1,100 °C. This temperature window is the most important parameter with regard to satisfactory NO_x conversion, in parallel with avoiding an increased ammonia slip. In regenerative glass melting furnaces, the above given temperature window can generally not be met. Therefore, this secondary measure is rather suitable for recuperatively heated furnaces, although SNCR technology can be found also in regeneratively fired glass melting furnaces. /18, 27/

The NO_2 conversion and the NH_3 slip are function of the amount of NH_3 injected: an appropriate NH_3 distribution in the waste gas is required to obtain a satisfactory conversion rate and ammonia slip. /11/

The SNCR process is characterised by relatively high costs with regard to a rather low NO_x-removal efficiency, typically around 50 % /14, 19/, which is not sufficient as regards European regulations.
Today in Germany, 6 glass melting plants are equipped with SNCR technology, and three further installations are planned /27/. Two further installations are located in the USA, and one in Switzerland /24/. Operational parameters of the six German plants are given in Table 7.

Table 7: Operational parameters of 6 SNCR installations in the European glass production sector /27/

Plant	1	2	3	4	5	6
Furnace	Recuperative	recuperative	recuperative	regenerative	recuperative	regenerative
Technical / Experimental	Technical	technical	technical	technical	technical	technical
Fuel	Natural gas	natural gas	heavy oil	natural gas / heavy oil	natural gas	natural gas
Glass	Special	special	container	water	special	soda lime
Waste gas flow rate	10,000 m^3/h	10,000 m^3/h	25,000 m^3/h	25,000 m^3/h	10,000 m^3/h	20,000 m^3/h
Ammonia feeding	Downstream Recuperator	downstream recuperator	between two recuperators	downstream first regenerator	downstream recuperator	middle of regenerator
Dissolved / gaseous NH_3	Gaseous	gaseous	gaseous	solution	gaseous	gaseous
Start of operation	1989	1992	1992	1989 / 1990	1994	1994
Efficieny	84 %	86 %	75 %	50 – 60 %	ca. 80 %	50 – 60 %
Ammonia slip	6 mg/m^3	23 mg/m^3	< 30 mg/m^3	< 30 mg/m^3	< 30 mg/m^3	< 30 mg/m^3
NO_x content in the cleaned gas*	180 mg/m^3	470 mg/m^3	<500 mg/m^3	<800 mg/m^3	350 mg/m^3	650 mg/m^3

* These values refer to an O_2-content in the waste gas of 8 vol.-%.

Side-Effects

Neither emissions to water, nor solid waste occur. But an increase in energy consumption and an ammonia slippage can be observed. The use of ammonia on-site is a potential safety hazard.

3.5.1.2.2 Selective Catalytic Reduction (SCR)

Technical Aspects

Here, the reduction of nitrogen oxides is based on the injection of gaseous or aqueous ammonia in a near stoichiometric ratio into the waste gas of the glass melting furnace in the presence of a catalyst and within a temperature window between 300 and 400 °C. A NO_x-abatement up to 90 % can be achieved. Some years ago, in glass production, catalyst lifetime was reduced by the presence of sodium sulphate in the waste gas which blocks and poisons the catalyst, but nowadays a catalyst can already achieve up to 4 years lifetime, and therefore, SCR has reached the status of a proven technology. /27/ However, the SCR applied in the glass manufacturing industry is always operated with an electrostatic precipitator, in order to achieve concentrations of soda dust below 10 mg/m^3, which may be a poison to the catalyst. For the same reason of catalyst poisoning, natural gas is preferred over oil as a fuel. /14/

Six SCR installations at glass melting plants are implemented in Germany, mainly in the field of special glass production (e. g. TV screen glass) /14/. In Hombourg (France), a SCR facility has been started in 1997 in the float glass production /19, 32/. Table 8 gives an overview of the operational parameters of SCR at six German glass production plants.

Table 8: Operational parameters of 6 SCR installations in the German glass production sector /5, 27, 33/

Plant	**1**	**2**	**3**	**4**	**5**	**6**
Furnace	Regenerative	regenerative	regenerative	regenerative	regenerative	regenerative
Fuel	Natural gas	natural gas	natural gas	natural gas	natural gas	natural gas
Type of Glass	Container	special	special	container	special	special
Waste gas flow rate	50,000 m^3/h	50,000 m^3/h	40,000 m^3/h	60,000 m^3/h	40,000 m^3/h	40,000 m^3/h
Dissolved / gaseous NH_3	Solution	solution	gaseous	solution	solution	gaseous
Catalyst	Zeolithe	V_2O_5/TiO_2	V_2O_5/TiO_2	V_2O_5/TiO_2	V_2O_5/TiO_2	V_2O_5/TiO_2
Number of layers	1	1	1	2	2	1
Start of operation	1987	1989	1991	1994	1994	1994
Efficiency	55 %	75 %	70 %	76 %	n. a.	75 %
Ammonia slip	28 mg/m^3	< 30 mg/m^3	< 30 mg/m^3	2 mg/m^3	< 30 mg/m^3	< 30 mg/m^3
NO_x content in the cleaned gas	480 mg/m^3	1,000 mg/m^3	1,350 mg/m^3	500 mg/m^3	< 1,500 mg/m^3	< 1,000 mg/m^3

n. a. = data is not available

The installation at plant 1 was stopped in June 1997 in favour of primary measures /14/. The only SCR installed at a container glass production plant is currently running at PLM Glashütte Münder, where clean gas concentrations of 500 mg/Nm^3 are achieved (low NO_x burners are already installed) /5, 33/.

Side-Effects

SCR generates solid waste via deactivated catalyst, but it can often be reprocessed by the manufacturer or be used as combustion material. As for SNCR, the increased energy consumption and ammonia slippage have to be accounted for. The use of ammonia on-site is a potential safety hazard.

3.5.2 SO_x-Emission Reduction Measures

3.5.2.1 Primary Emission Reduction Measures

The most important option for the reduction of SO_2 emissions from glass melting furnaces is the use of fuels with a lower sulphur content. SO_2 emissions from gas fired glass melting tanks are lower than the emissions from oil fired furnaces, since gaseous fuels have a lower sulphur content than liquid fuels. /11/ However, the selection of fuels depends on their availability and on the furnace design in place. /7/

Furthermore, the melting furnace should be operated in such a way that the sulphur absorption ability of the melt is not decreased: it it thus necessary to obtain a certain oxygen concentration in the upper zone of the furnace. /11/

3.5.2.2 Secondary Emission Reduction Measures

Emissions of sulphur oxide from the off-gases of glass melting furnaces can be removed via sorption, e.g. by supply of appropriate sorbents (dry sorbent, or calcium and sodium based sorbents). Besides sulphurous compounds, hydrogen chloride, hydrogen fluoride, and gaseous heavy metals are also removed by this process. Removal efficiency for the different compounds is mainly determined by the amount of sorbent used and by the temperature at which the reaction takes place. A higher temperature leads to higher removal rates for SO_2 and hydrogen chloride. The removal of hydrogen fluoride is slightly lower at higher temperatures. /22/

3.5.3 Emission Reduction Measures for Other Pollutants

Measures for decreasing air emissions from the combustion process will also result in a reduction of the heavy metal and dust emissions. Dust emissions from handling raw materials can be reduced using fabric filters or using different improved handling techniques. The emissions of carbon dioxide from the carbonisation process can be reduced by adding more recycled glass or using non-carbonate basic materials.

4 SIMPLER METHODOLOGY

An estimation of the emissions can be calculated by using production statistics and generalised default emission factors as presented in /38/. The values given for the carbonisation process are very much dependant on the local situation and can only be used if no information is available.

5 DETAILED METHODOLOGY

A detailed calculation should be based on individual plant information about the amounts of substances added. Also the amount of recycled glass used should be available. However these data are often confidential. Also fuel information and information about local abatement methods should be available.

6 RELEVANT ACTIVITY STATISTICS

Glass production statistics are available from several national and international sources.

7 POINT SOURCE CRITERIA

The production of glass is usually connected to medium size stacks that may be regarded as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 9: Emission factors to air in [g/Mg glass] for heavy metals and micropollutants for glass production in general

Substance	Default value	Range
Arsenic	0.10	0.1 - 0.25
Cadmium	0.15	0.05 - 0.25
Chromium	2.5	0.5 - 5
Copper	0.5	0.4 - 1.1
Lead (1)	10	2 - 24
Mercury	0.05	0.04 - 0.07
Nickel	2	1.2 - 2.6
Selenium	20	2.5 - 24
Zinc	10	5 - 24
Dichloromethane	5	0 - 11
Fluorine	30	5 - 70
Dust	400	3 - 800

The emission of lead is mainly determined by the amount of recycled glass used. /37/

Table 10: Theoretical process emission factors for carbon dioxide from the carbonisation process in [kg/Mg product] in relation to the alcaline content of the product

Glass type	sodium oxide (wt %)	potassium oxide (wt %)	Magnesium oxide (wt %)	calcium oxide (wt %)	barium oxide (wt %)	Carbon dioxide
Container glass	12-14	0.3-0.5	0.5-3	10-12	-	171-229
Flat glass	13.6	0.3	4.1	8.6	-	210
Continuous filament fibres						
E-fibres	< 2	< 2	20-24	20-24	-	157-203
AR-fibres	13-15	13-15	4-6	4-6	-	92-172
R/S-fibres	< 1	< 1	9-16	9-16	-	71-182
D-fibres	< 4	< 4	0	0	-	0-28
C-fibres	15-20	15-20	10-30	10-30		149-470
ECR-fibres	< 1	< 1	22-27	22-27	-	173-302
A-fibres	12-15	12-15	10-15	10-15		135-270
Special glass						
CRT panel	6.6-9.4	6.6-8.4	0-1.2	0-3.2	0	78-144
CRT tube	5.8-6.7	7.8-8.1	0.6-2.2	0.9-3.8	0	91-139
Glass tube, earth alk	12.5	2.5	2	4	0	154
Glass tube, borosilicate	3.5-6.5	0.5-1.5	0.01-0.5	0.01-1	0	27-66
Borosilicateglass	3.5-6.5	0.5-1.5	0.01-0.5	0.01-1	0	27-66
Opaque lighting glass	13.6	1.8	0	9.4	0	178
Lamb bulb	3-4	1.5-2.5	0.5	0.5	0	38-49
Glass ceramic	0.5-10	0	0-1	0.5-7	0	7.5-137
Quartz	0	0	0	0	0	0
Boron crown optical	0-5	12-18	0	0-0.3	0	56-122
Fluorine crown optical	0	0	0	0	20	57
Waterglass sodium sil.	22.5-24	0	0.008	0/008	0	160-171
Waterglass potassium silicate	0	27-32	0.008	0.008	0	126-150
Glass wool	12-18	12-18	8-15	8-15	0	119-292
Stone wool	0.5-5	0.5-5	30-45	30-45	0	238-527

The emission factors in Table 10 only give the theoretical amount of carbon dioxide emitted. Especially for container glass the amount of recycled glass may be up to 85 %.

8.1 Production of Flat Glass

For the situation in the Netherlands, the following can be proposed:

Emission factors for flat glass are given in kg/Mg glass.

handling/shipping:

dust:	0.15 kg/Mg

melting oven:

SO_2	3.0 kg/Mg
CO_2	140 kg/Mg
F_g	0.055 kg/Mg
Cl_g	0.06 kg/Mg
dust	0.37 kg/Mg

fuel:

SO_2	3.0 (fuel oil) kg/Mg
CO_2	530 kg/Mg
NO_x	5.5 kg/Mg
CO	0.09 kg/Mg

Heavy metals are incorporated in the dust emissions. The available information about compositions is scarce. The only consistent information is based on the work of Jockel and Hartje /10/, also incorporated in the PARCOM-ATMOS Manual. This information, based on the situation in Germany, is given in Table 11.

Table 11: Emission factors for glass production in [g/Mg glass] generalised for the situation in Germany.

Substance	Emission factor [g/Mg glass]	Range [g/Mg glass]
Arsenic	0.12	0.1-0.24
Cadmium	0.15	0.06-0.24
Chromium	2.4	0.5-5
Copper	0.6	0.4-1.1
Lead	12	2-24
Mercury	0.05	0.036-0.072
Nickel	1.9	1.2-2.6
Selenium	18	2.4-24
Zinc	11	4.8-24

Table 12: Emission factors for flat glass production$^{6)}$

Type of fuel				NAPFUE code	Emission factors						
					$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_2O [g/GJ]
s	Coal	hc	steam	102	650$^{1)}$	300$^{1)}$	15$^{1)}$	15$^{1)}$	100$^{1)}$	93$^{1)}$	4$^{1)}$
s	Coal	bc	brown coal/lignite	105	500$^{1)}$	300$^{1)}$	15$^{1)}$	15$^{1)}$	100$^{1)}$	113$^{1)}$	3.5$^{1)}$
s	Coal	bc	briquettes	106	220$^{1)}$	300$^{1)}$	15$^{1)}$	15$^{1)}$	100$^{1)}$	98$^{1)}$	3.5$^{1)}$
s	Biomass		wood	111	25$^{1)}$	130$^{1)}$	48$^{1)}$	32$^{1)}$	160$^{1)}$	105$^{1)}$	4$^{1)}$
l	Oil		residual	203	930-1,470 1,400$^{2)}$	98-1,800$^{1)}$ 180$^{2)}$	3-4$^{1)}$ 3$^{2)}$	3-4$^{1)}$ 3$^{2)}$	10-320$^{1)}$ 15$^{2)}$	72-78$^{1)}$ 78$^{2)}$	2-14$^{1)}$ 14$^{2)}$
l	Oil		gas	204	85-1,410$^{1)}$ 600$^{2)}$	100-450$^{1)}$ 180$^{2)}$	1.5-4$^{1)}$ 1.5$^{2)}$	1.5-4$^{1)}$ 1.5$^{2)}$	10-12$^{1)}$ 12$^{2)}$	73-74$^{1)}$ 74$^{2)}$	2-12$^{1)}$ 12$^{2)}$
g	Gas		natural	301	0.5-8$^{1)}$	60-570$^{1)}$ 100$^{2)}$	2.5-10$^{1)}$ 2.5$^{2)}$	2-3$^{1)}$ 2.5$^{2)}$	10-120$^{1)}$ 13$^{2)}$	53-56$^{1)}$ 53$^{2)}$	1-3$^{1)}$ 3$^{2)}$
g	Gas		coke oven	304	12$^{1)}$	400-450$^{1)}$	2.5$^{1)}$	2.5$^{1)}$	10$^{1)}$	44-49$^{1)}$	1.5$^{1)}$

1) CORINAIR90 data, area sources

2) CORINAIR90 data, point sources

3)	SO_x:	1,500	g/Mg product	Melting furnace /1/
		2,246	g/Mg product	General /2/
		1,675	g/Mg product	General, with venturi scrubber /2/
		1,182	g/Mg product	General, with low energy scrubber /2/
		2,800	g/Mg beaded glass	Ground cutlet beading furnace /1/
4)	NO_x:	8.6-10	kg/Mg product	General /3/
		2,920	g/Mg product	General /2/
		4,000	g/Mg product	Melting furnace /1/
		4,250	g/Mg product	Ground cutlet beading furnace
		800	g/Mg product	General, (FRG, GDR, 1990) /4/
5)	VOC:	50	g/Mg product	Melting furnace /1/
		150	g/Mg beaded glass	Ground cutlet beading furnace /1/

6) It is assumed, that emission factors cited within the table are related to combustion sources in flat glass production. Footnotes may also include emission factors for other process emissions.

8.2 Production of Container Glass

For the situation in the Netherlands, the following can be proposed:

Emission factors for container glass are as follows:

handling/shipping:

dust:	0.03 - 0.15 kg/Mg glass

melting oven:

SO_2	1.2 kg/Mg glass
CO_2	150 kg/Mg glass
F_g	0.014 kg/Mg glass
Cl_g	0.05 kg/Mg glass
dust	0.30 kg/Mg glass

fuel:

SO_2	3.0 (fuel oil) kg/Mg glass
CO_2	265 kg/Mg glass
NO_x	3.8 kg/Mg glass

The dust is the main source of heavy metals. The emissions are largely determined by the composition of the basic materials and the product. Jockel and Hartje /10/ produced some generalised emission factors for the situation in Germany. These factors, also used in the PARCOM-ATMOS Manual are given in Table 13 in g/Mg glass:

Table 13: Emission factors for glass production in [g/Mg glass] generalised for the situation in Germany

Substance	Emission Factor [g/Mg glass]	Range [g/Mg glass]
Arsenic	0.12	0.1-0.24
Cadmium	0.15	0.06-0.24
Chromium	2.4	0.4-1.1
Copper	0.6	0.4-1.1
Lead	12	2-24
Mercury	0.05	0.036-0.072
Nickel	1.9	1.2-2.6
Selenium	18	2.4-24
Zinc	11	4.8-24

The following Table 14 contains fuel related emission factors for container glass production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product) are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 6 - 100 GJ/Mg product has been reported.

Table 14: Emission factors for container glass production[7)]

Type of fuel			**NAPFUE code**	**Emission factors**						
				SO_2[2)] [g/GJ]	**NO_x[3)] [g/GJ]**	**NMVOC[4)] [g/GJ]**	**CH_4[4)] [g/GJ]**	**CO[5)] [g/GJ]**	**CO_2[6)] [kg/GJ]**	**N_2O [g/GJ]**
l	oil	residual	203	143-1,470[1)]	100-570[1)]	3[1)]	3-8[1)]	12-20[1)]	73-78[1)]	2-10[1)]
l	oil	gas	204	55-1,410[1)]	100-570[1)]	1.5[1)]	1.5-8[1)]	12-20[1)]	73-74[1)]	2[1)]
g	gas	natural	301	0.3[1)]	80-570[1)]	2.5-4[1)]	2.5-4[1)]	13-176[1)]	53-57[1)]	1[1)]
g	gas	Liquified petroleum gas	303	0.04[1)]	100[1)]	2.1[1)]	0.9[1)]	13[1)]	65[1)]	1[1)]

[1)] CORINAIR90 data, area sources

[2)]	SO_x:	2,246	g/Mg product	General /2/
		1,700	g/Mg product	Melting furnace /1/
[3)]	NO_x:	4.3-5	kg/Mg product	General /3/ (spec. fuel consumption 7.5 GJ/Mg glass)
		2,920	kg/Mg product	General /1/
		3,100	kg/Mg product	Melting furnace /1/
[4)]	VOC:	100	g/Mg product	Melting furnace /1/
[5)]	CO:	100	g/Mg product	Melting furnace /1/
[6)]	CO_2:	423	g/Mg product	General /2/

[7)] It is assumed, that emission factors cited within the table are related to combustion sources in container glass production. Footnotes may also include emission factors for other process emissions.

8.3 Production of Glass wool

For the situation in the Netherlands, the following can be proposed:

Emission factors for several compounds in kg/Mg glass wool are:

handling/shipping:

dust: 0.03 - 0.15 kg/Mg glass

melting oven:

SO_2	0.5 kg/Mg glass
CO_2	450 kg/Mg glass
F_g	0.006 kg/Mg glass
Cl_g	0.01 kg/Mg glass
dust	0.04 (after dust collector) kg/Mg glass

spinning/wool manufacturing:

formaldehyde	0.9 kg/Mg glass
phenol(s)	0.3 kg/Mg glass
ammonia	4.5 kg/Mg glass
VOS	0.6 kg/Mg glass

fuel:

SO_2	5.0 (fuel oil) kg/Mg glass
CO_2	670 kg/Mg glass
NO_x	2.8 kg/Mg glass

Emissions of heavy metals may be contained in the dust. No specific information for glass wool production is available. For a first estimation the factors referred to above for flat glass and container glass may be used.

The following Table 15 contains fuel related emission factors for the production of glass wool based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg material), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 4.3 - 100 GJ/Mg product has been reported.

Table 15: Emission factors for the production of glass wool$^{7)}$

				Emission factors						
	Type of fuel		NAPFUE code	$SO_2$$^{2)}$ [g/GJ]	$NO_x$$^{3)}$ [g/GJ]	NMVOC$^{4)5)}$ [g/GJ]	$CH_4$$^{5)}$ [g/GJ]	CO$^{6)}$ [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
l	oil	Residual	203	840-1470$^{1)}$	150-450$^{1)}$		8$^{1)}$	20$^{1)}$	76-77$^{1)}$	2$^{1)}$
l	oil	Gas	204	55-1410$^{1)}$	50-100$^{1)}$		81)	20$^{1)}$	73-74$^{1)}$	2$^{1)}$
g	gas	Natural	301	8$^{1)}$	60-150$^{1)}$	10$^{1)}$	2-3$^{1)}$	20-30$^{1)}$	53-55$^{1)}$	1-3$^{1)}$

[1)] CORINAIR90 data, area sources (preliminary data)

2)	SO_x:	2,246	g/Mg product	General /2/
		5,000	g/Mg material processed	Regenerative furnace and recuperative furnace /3/
		20	g/Mg material processed	Electric furnace
		300	g/Mg material processed	Unit smelter furnace
3)	NO_x:	5,400-6,000	g/Mg product	General /3/
		2,500	g/Mg material processed	Regenerative furnace /3/
		850	g/Mg material processed	Recuperative furnace /3/
		135	g/Mg material processed	Electric furnace /3/
		245	g/Mg material processed	Forming, rotary spin /3/
		550	g/Mg material processed	Alting oven: rotary spin /3/
		150	g/Mg material processed	Cooling /3/
		150	g/Mg material processed	Unit smelter furnace /3/
		1,000	g/Mg material processed	Cursing: flame attenuation /3/

[4]	NMVOC:	5,000	g/Mg product	/1/
[5]	VOC:	100	g/Mg material processed	Regenerative furnace, recuperative furnace and electric furnace /3/
		3,500	g/Mg material processed	Forming: rotary spin /3/
		1,500	g/Mg material processed	Cursing oven: rotary spin /3/
		150	g/Mg material processed	Forming: flame attenuation /3/
		3,500	g/Mg material processed	Cursing: Flame attenuation /3/
[6]	CO:	0-500	g/Mg glass	For electric melting /1/
		100-600	g/Mg glass	For other furnaces /3/
		125	g/Mg material processed	Regenerative furnace /3/ and recuperative furnace /3/
		25	g/Mg material processed	Electric furnace /3/
		850	g/Mg material processed	Cursing oven: rotary spin /3/
		125	g/Mg material processed	Unit melter furnace /3/
		1,750	g/Mg material processed	Cursing: flame attenuation /3/

[7] It is assumed, that emission factors cited within the table are related to combustion sources in glasswool production. Footnotes may also include emission factors for other process emissions.

8.4 Production of Other Glass

For the production of special glass the emission factors for general glass production as given flat glass and container glass can be used. For emissions of heavy metals some specific information is available. Emission factors are derived from the PARCOM-ATMOS Emission Factors Manual and the literature mentioned there:

- For the production of lead crystal glass an emission factor of 60 g lead/Mg product is mentioned, using bag filters as abatement method. Without abatement the emission factor is estimated to be 1% of the lead content of the glass. cf. /36/
- For coloured glass an emission factor of 0.11-0.15 g cadmium/g glass is mentioned.
- For the situation in Germany some specific information is given by Jockel and Hartje /10/. This information is given in Table 16.

Table 16: Emission factors for heavy metals from special glass production in Germany in [g/Mg product]

Substance	Emission Factor [g/Mg product]	Range [g/Mg product]
Arsenic (lead crystal glass)	140	22-310
Arsenic (crystal glass)	96	-
Cadmium	0.15	0.06-0.24
Chromium	2.4	0.5-5
Copper	0.6	0.4-1.1
Lead (lead crystal glass)	2700	2200-3200
Lead (crystal glass)	480	-
Mercury	0.05	0.036-0.072
Nickel	1.9	1.2-2.6
Selenium	18	2.4-24
Zinc	11	4.8-24

The following Table 17 contains fuel related emission factors for the production of other glass based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg material processed), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 25 - 6.000 GJ/Mg product has been reported.

Table 17: Emission factors for the production of other glass[6]

	Type of fuel			NAPFUE code	Emission factors SO_2[2] [g/GJ]	NO_x[3] [g/GJ]	NMVOC[4] [g/GJ]	CH_4[4] [g/GJ]	CO[5] [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
s	Coal	hc	steam	102	787[1]	150[1]	15[1]	15[1]	10[1]	94[1]	14[1]
s	Biomass		wood	111		200[1]	50[1]	30[1]		92[1]	14[1]
l	Oil		residual	203	960-1,470[1]	132-370[1]	3-19[1]	0.1-3[1]	15-19[1]	76[1]	14[1]
l	Oil		gas	204	138-1,410[1]	80-100[1]	2[1]	1[1]	12[1]	73[1]	14[1]
l	Kerosene			206	69[1]	80[1]	2[1]	1[1]	12[1]	71[1]	14[1]
l	Gasoline		motor	208	45[1]	80[1]	2[1]	11)	12[1]	71[1]	14[1]
g	Gas		natural	301	8-260[1]	32-622[1]	10-26[1]	0.4-3[1]	8.5-95[1]	53-56[1]	1-3.7[1]
g	Gas		liquified petroleum gas	303	2[1]	20-40[1]	1-4[1]	1-4[1]	13[1]	60-65[1]	3[1]

[1] CORINAIR90 data, area sources

[2]	SO_x:	2,246	g/Mg product	General /1/
		1,500	g/Mg material processed	Textile fiber, regenerative furnace and recuperative furnace /2/
		2,800	g/Mg product	Pressed and blown glass, melting furnace /2/
		2,800	g/Mg beaded glass	Ground cullet beading furnace /2/
[3]	NO_x:	3,500-6,000	g/Mg product	General /3/
		10,000	g/Mg material processed	Textile fiber; regenerative furnace, recuperative furnace and unit smelter furnace /2/
		1,300	g/Mg material processed	Textile fiber; curing oven /2/
		4,250	g/Mg product	Pressed and blown glass, melting furnace /2/
		4,250	g/Mg beaded glass	Ground cullet beading furnace /2/
[4]	VOC:	100	g/Mg material processed	Textile fiber: regenerative furnace and recuperative furnace /2/
		0	g/Mg material processed	Textile fiber: unit smelter furnace /2/
		150	g/mg product	Pressed and blown glass, melting furnace /2/
		150	g/Mg beaded glass	Ground cullet beading furnace /2/
[5]	CO:	100	g/Mg product	Pressed and blown glass, average /3/
		100	g/Mg product	Pressed and blown glass, melting furnace /2/

[6] It is assumed, that emission factors cited within the table are related to combustion sources in other glass production. Footnotes may also include emission factors for other process emissions.

9 SPECIES PROFILES

An analysis of dust emissions from a melting oven in the Netherlands is available. The major constituents from this analysis are given in g/Mg glass:

Substance	**Concentration [g/Mg glass]**
Aluminium	1.3
Chromium	0.15
Cobalt	0.05
Copper	0.15
Iron	2.4
Lead	0.30
Manganese	0.05
Nickel	1.0
Titanium	0.08
Vanadium	1.90
Zinc	0.25

These components are present as sulphates.

10 UNCERTAINTY ESTIMATES

If the simplified approach is used the results may differ very much from the real situation. A classification C-D is appropriate in this case. If more detail about the individual plant are available the factors should be corrected e in classifications in the B to C range.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The default calculation could be very much improved if information about the basic materials used is available.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant if treated as point source. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment or population statistics.

Production of special glass is usually done in small plants. They may be treated as an area source by disaggregating national emission estimates on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The production of flat glass, container glass, and glass wool can be considered as a continuous process. The production of special glass is usually a discontinuous process but no information is available on temporal profile.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

- Emission inventory in The Netherlands, 1992. Emission to air and water
- Personal information and experience during emission inventories 1975 - 1995
- Emission factors to be used for the building industry, TNO report 89/091
- Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP-42
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16 VERIFICATION PROCESSES

Verification should be applied by comparing calculated emissions with measured emissions at an individual plant.

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18 BIBLIOGRAPHY

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19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **030318**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Mineral Wool

NOSE CODE: **104.11.09**

NFR CODE: **1 A 2 f**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within mineral wool production.
A mixture of minerals and coke is heated until it is molten and can be spun into fibres. The fibres are treated with resins to form a wool-like product.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of fuel use related emissions released from the production of mineral wool to total emissions in countries of the CORINAIR90 inventory is minor, as indicated in table 1.

Table 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_2O	NH_3
Mineral Wool	0303018	0	0	-	-	0	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

The emissions of phenol(s) is also relevant but no estimates are available at the European level.

3 GENERAL

3.1 Description of activities

Products manufactured from man-made mineral fibres (MMMF) generally consist of inorganic fibres produced from a silicate melt, and, depending on their application and use, contain binding agents, additives and filters. /3/

Whilst basically the melting technology closely resembles the technology commonly used in glass-works, there are considerable differences in the composition of the glass types which have to be adapted to meet the special demands made on the man-made mineral fibres with respect to processability, viscosity, melting range, hydrolytic class, heat resistance etc. In particular, special glasses containing boron and glasses with additives of volcanic rock (phonolite, basalt, diabase) are used. /3/

3.2 Definitions

3.3 Techniques

Cupola furnaces are used for the production of silicate melts. The starting materials for the production of MMMF are silicate rocks (e.g. basalt, diabase) or metallurgical slags with alkaline or acid additives (e.g. limestone, dolomite, sandstone). Coke, fuel oil or gas are used as fuels. /3/

In electric melting units, the mineral raw materials are melted by electric resistance heating. Units of fireproof (refractory) materials and water-cooled metal containers are in use. /3/

The silicate melt is fed either in covered or open channels (feeders, troughs) or directly to the processing units in which the fibres are produced. The most commonly employed processes are the bushing blowing process, the centrifugal process and the bushing drawing process. /3/

Man-made mineral fibres are generally processed by impregnation, soaking or coating and possibly with subsequent drying processes to form a wide range of finished products. /3/

The impregnated or coated semi-finished product is dried by intensive contact with hot air. Continuous pass driers, single or multi-layer and chamber drying kilns are used. The hot air temperature can be up to 300 °C. The hot air is generally circulated (circulation air process), whereby both direct and indirect heating (e.g. by means of heat transfer oil) processes are in use. /3/ Hot pressing is commonly used for the manufacture of certain products, whereby the drying and hardening is performed by warming between heated moulds. /3/

Energy consumption is typically around 6 -10 GJ per ton produced.

3.4 Emissions

Dust emission can result from handling raw materials as well as from the melting process.

Other emissions result from the melting process, the spinning process as well as finishing the wool. Pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), and nitrous oxide (N_2O). According to CORINAIR90 the main relevant pollutants are SO_2, No_x, CO and CO_2 (see also table 1).

The cupola is a source of CO, CO_2 and NO_x emissions; SO_2 and H_2S emissions also occur, because blast furnace slags contain sulphur /cf 4/.

Emissions of organic and inorganic substances arise from manufacturing products of man-made mineral fibres. The raw gas contents of the melting facilities are generally of a purely inorganic nature and free from fibrous constituents. Emissions of organic substances can arise preparating the binding agent. /cf. 3/

Where binding agents containing nitrogen (ammonia, aminoplasts) are processed, ammonia and/or organic compounds containing nitrogen may occur in the waste gases, depending on the operating conditions. /cf. 3/

No gaseous or particulate emissions arise during the actual production of the fibres /3/.

3.5 Controls

Dust emissions from handling raw materials can be reduced using fabric filters or using different handling techniques.

Extraction systems and driers (hardening kilns, presses) should be designed with respect to the product throughput in such a way that overloading of the facilities by increased temperatures and excessive flow velocities or increased evaporation of constituents of the binding agents or the transport in the air current of droplets and fibrous dusts is prevented. /3/

The malodorous and organically contaminated waste gases from the drying and hardening kilns are transfered to waste gas treatment plants. Multistage wet separator systems (washers) can be used in conjunction with wet electrostatic precipitators or aerosol separators as well as catalytic and thermal post-combustion. Processes employing high-frequency drying result in neither malodorous or organic emissions. No significant dust emissions occur during the process stages drying and hardening. Waste gases are released by stack. /cf 3/

4 SIMPLER METHODOLOGY

The simpler methodology involves applying an appropriate emission factor to either production or energy consumption statistics.

5 DETAILED METHODOLOGY

If an extensive measuring programme is available the emissions can be calculated on for an individual plant.

6 ACTIVITY STATISTICS

Standard production and energy statistics from national or international statistical publications.

7 POINT SOURCE CRITERIA

The production of mineral wool is a minor source of emissions and hence can be treated on an area basis. However, production usually connected to high chimneys can be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

For the situation in the Netherlands, the following can be proposed:

Emission factors in kg per ton wool are as follows:

handling/shipping:

dust:	0.5 kg per ton wool

melting oven:

SO_2	1.5 kg per ton wool
CO_2	115 kg per ton wool
CO	3.2 kg per ton wool
F_g	0.008 kg per ton wool
dust	0.06 kg per ton wool (after dust collector)

spinning/wool manufacturing:

formaldehyde	0.2 kg per ton wool
phenol(s)	0.7 kg per ton wool
ammonia	1.8 kg per ton wool
VOS	1.0 kg per ton wool

fuel:

NO_x	1.1 kg per ton wool
CO_2	450 kg per ton wool

The following Table 2 contains fuel related emission factors for the production of mineral wool based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg charged), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 7 - 5.000 GJ/Mg product has been reported.

Table 2: Emission factors for the production of mineral wool 7)

Type of fuel				NAPFUE code	Emission factors							
					SO_2 2) [g/GJ]	NO_x 3) [g/GJ]	NMVOC 4) [g/GJ]	CH_4 4) [g/GJ]	CO 5) [g/GJ]	CO_2 6) [kg/GJ]	N_2O [g/GJ]	NH_3 [g/GJ]
s	coal	hc	steam	102	584-610 1)	150-200 1)	15 1)	5-15 1)	20-97 1)	93-95 1)	3-5 1)	
s	coke	hc	coke oven	107	138-584 1)	90-100 1)	1.5-83 1)	1.5 1)	97 1)	101-110 1)	3 1)	
s	coke	bc	coke oven	108	650 1)	220 1)	5 1)	15 1)	90 1)	86 1)	3 1)	
s	biomass		wood	111	130 1)	130 1)	48 1)	32 1)	160 1)	102 1)	4 1)	
l	oil		residual	203	143-1,030 1)	100-330 1)	3 1)	3-8 1)	12-20 1)	73-78 1)	2-10 1)	
l	oil		gas	204	55-94 1)	100 1)	1.5-2 1)	1.5-8 1)	12-20 1)	73-74 1)	2 1)	
g	gas		natural	301	0.3-8 1)	60-250 1)	4-10 1)	2-4 1)	13-20 1)	53-57 1)	1-3 1)	
g	gas		liquified petroleum gas	303	0.04 1)	100 1)	2.1 1)	0.9	13 1)	65 1)	1 1)	

1) CORINAIR90 data, area sources

2)	SO_x:	8,480	g/Mg	(1989) /1/
		2,320	g/Mg	(1991) /1/
		10	g/Mg charged	Cupola furnace /2/
3)	NO_x:	210	g/Mg	(1989) /1/
		200	g/Mg	(1991) /1/
		800	g/Mg charged	Cupola furnace /2/
		80	g/Mg charged	Curing furnace /2/
4)	VOC:	450	g/Mg charged	Blow chamber
		500	g/Mg charged	Curing oven
5)	CO:	8,120	g/Mg	(1989) /1/
		< 7,400	g/Mg	(1991) /1/
6)	CO_2:	67.4	kg/Mg product	General for 1989 /1/
		168	kg/Mg product	General for 1991 /1/

7) It is assumed, that emission factors cited within the table are related to combustion sources in mineral wool production. Footnotes may also include emission factors for other process emissions.

9 SPECIES PROFILES

No general applicable profile for dust emissions available.

10 UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed per ton wool is estimated to be D.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge about measurements related to abatement techniques is limited.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The production of mineral wool is a semi-continuous process but no further quantitative information is available.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Emission inventory in The Netherlands, 1992. Emission to air and water.

Personal information and experience during emission inventories 1975 - 1995

Emission factors to be used for the building industry, TNO report 89/091 (1989 - in dutch)

Environmental Protection Agency

Compilation of Air Pollutant Emission Factors AP 42

16 VERIFICATION PROCESSES

Verification of the emissions can be done by comparing emission estimates with measurements at the individual plants.

17 REFERENCES

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/4/ EPA (ed.): AP 42; CD-Rom; 1995

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SNAP CODE: **030319**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Bricks And Tiles

NOSE CODE: **104.11.10**

NFR CODE: **1 A 2 f**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within bricks and tiles production. However, in the following if useful for description, also non-combustion emissions are mentioned.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of fuel use related emissions released from the production of bricks and tiles to total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 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_2O	NH_3
Bricks and Tiles	030319	0.3	0.3	0	0	0.3	0.6	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

The emission of fluorides is also relevant but no information is currently available at the European level.

3 GENERAL

3.1 Description of activities

The manufacture of bricks and related products such as clay pipe, pottery, and some types of refractory brick involves the mining, grinding, screening, and blending of the raw materials, clay with additives such as caoline or limestone, and the forming, cutting or shaping, drying or curing, and firing of the final product. /4/

To start the forming process, clay is mixed with water, usually in a pug mill. The three principal processes for forming bricks are stiff mud, soft mud, and dry press. In the stiff mud process, sufficient water is added to give the clay plasticity, and bricks are formed by forcing the clay through a die. Wire is used in separating bricks. All structural tile and most brick are formed by this process. The soft mud process is usually used with clay too wet for the stiff mud process. The clay is mixed with water to a moisture content of 20 to 30 percent, and the bricks are formed in molds. /4/

Three stages of heating are almost invariably involved /5/:

- The initial drying period, in which appreciable volumes of hot air must be passed through the setting in order to remove moisture until the ware is completely dry.
- The oxidation preheating period, in which chemically combined water is removed and oxidation of any carbonaceous matter in the green product is completed.
- The finishing period, during which the required final temperature of 950 - 1100 °C is attained and soaking time allowed to obtain uniformity of heat treatment and develop the required degree of vitrification and maturity.

3.2 Definitions

3.3 Techniques

Two types of kilns can be distinguished, the intermittent and the continuous kiln:

- Intermittent kilns (discontinuous)
  Intermittent kilns are mainly used to fire special products not amenable to continuous practice and where flexibility is of more importance than high thermal efficiency or large output of any one product. Unavoidable heat loss from the firing of these kilns is considerable /5/.

  Two main types of intermittent kiln are used in the heavy clay industry; the rectangular down-drought and the round down drought. Both muffle and open-flame conditions are used with each type. In muffle firing the gases from the fires are not allowed to make contact with the goods being fired, heat transfer being obtained almost entirely by radiation from the muffle walls. With open-flame firing, which is used to a much larger extent, all gases and flames from the fires pass through setting spaces among the ware before the combustion products are finally exhausted through the flue system. /5/

  Each kiln is usually connected to a separate stack. The draught in the kiln is controlled by means of a damper at the base of the stack. /5/

- Continuous kilns
  Continuous kilns are especially applicable to the firing of standard products where large throughput is desired. Recuperation of heat from cooling goods and from the kiln gases makes this kind of kiln more thermally efficient. The economic advantages of mass production and high thermal efficiency are obtained from the use of continuous kilns. /5/

  Two distinct firing principles are used in continuous practice. In car tunnel kilns the pre-heating, firing and cooling zones are fired and the goods travel through these zones on cars or bogie carriages operated by an external pusher mechanism. These tunnels may be either straight or annular, a moving hearth being used in the annular kiln instead of cars. /5/

In the second type of continuous kiln the goods are set in the kiln and remain stationary while preheating, firing and cooling zones move round the kiln. With this type, one continuous tunnel may be used or the kiln system may consist of a number of transverse arch chambers connected through suitable chamber openings. /5/

Most commonly natural gas is burned to heat the ovens, but other fuels are possible. Energy consumption is typically around 2 - 2.5 GJ per ton.

3.4 Emissions

Pollutants released are dust, sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), fluoride ($F_{g)}$, Chlorine (Cl_g) and ammonia (NH_3). According to CORINAIR90 the main relevant pollutants are SO_2, NO_x, CO, and CO_2 (see also table 1).

Pollution from the brick making industry is predominantly confined to stack emissions of kiln exhaust gases. The pollutants in the exhaust gas originate mainly from impurities within the clay, although firing with coal or heavy fuel oil will make a significant contribution to the overall emissions to atmosphere. Such impurities will produce fluoride emissions from the fluorine containing components of the clay minerals; sulphur oxides from iron pyrites or other sulphur bearing minerals (e.g. sulphates); and odorous gases from organic materials occurring naturally within the clay or added to the clay during processing The sulphur content of clay varies widely, with the majority of the clays. Combustion products are emitted from the fuel consumed in the dryer and the kiln. /cf. 5/

However, natural gas is mainly employed for firing and the use of heavy oil and coal has declined. Overall, about 2 % of the sulphur oxides emitted are in the form of sulphur trioxide. Research work in the UK on sulphur dioxide emissions from tunnel kilns gave total sulphur dioxide levels up to 480 mg/m³. /cf. 4, 5/

In the combustion process, oxides of nitrogen will be produced from the oxidation of chemically bound nitrogen in the fuel, the clay and from atmospheric nitrogen. In general, the higher the temperature the greater the production of nitrogen oxides. /5/

3.5 Controls

The following main categories of techniques are available for dealing with these pollutants and may be applicable for this process: dry absorption, condensation, wet scrubbing, flue gas desulphurisation, incineration and wet/dry absorption.

- Dry Absorption :
  Most flue gas cleaning systems currently in operation within the brick industry are dry absorption based processes. Two systems are employed, packed bed filters and cloth filters.

  - Packed Bed Filters :

In the packed bed filter system, fluoride sorption is achieved using a filter bed of granular limestone (calcium carbonate) through which the flue gas passes. Fluorine, and other pollutants are absorbed on the filter media which also allows for dust deposition, thereby avoiding the need for a separate dust filter. The efficiency of these units is generally high, with typical levels in the treated gas quoted as being: e.g. for fluorine < 5 mg/m³ as hydrogen, fluoride, sulphur trioxide 90 % removal, sulphur dioxide 10-15 % removal and particulate matter < 50 mg/m³.

- Cloth Filters :
  Lime or hydrated lime is injected into the gas stream to absorb the gaseous fluorine and sulphur compounds. The resulting fluorspar and gypsum are then removed from the gas stream using cloth filters. The removal efficiencies for such a system are reported to be as follows: Fluorine (99 %), sulphur trioxide (75 %), sulphur dioxide (5 to 10 %) and dust (< 50 mg/m³). The main advantage of the standard cloth filter system its ability to operate in high sulphur environments, possibly up to 2,000 mg/m³ sulphur dioxide since blockage is less likely.

- Condensation :
  The principle behind these systems is to cool the gas down to such a degree that the pollutants are precipitated by condensation. The condensates so produced contain hydrofluoric and sulphuric acids which are highly aggressive. The condensates are then neutralised with castic soda or milk of lime. In practice milk of lime is usually selected because it is cheaper than caustic soda. Reported estimates of the typical removal efficiencies that can be achieved by this technique are for fluorine (90 %), sulphur trioxide (50 %) and sulphur dioxide (15 %).

- Wet scrubbing :
  Wet scrubbing systems aim to produce contact between the scrubbing liquid and the pollutant, in order to promote absorption and/or precipitation processes. Levels of efficiency of removal have been claimed for fluorine 99 %, sulphur dioxide 15 % and particulates 87 %.

- Incineration :
  Incineration of odours may also be undertaken externally to the kiln for successful removal of these odorous compounds.

- Wet/dry absorption :
  A sulphur dioxide absorber (either lime, sodium carbonate or bicarbonate solution or slurry) is injected into the exhaust gas stream upstream of any dust collection equipment. This process removes about 70 % of sulphur in the gas stream.

4 SIMPLER METHODOLOGY

The simpler methodology involves applying an appropriate emission factor to either production or energy consumption statistics.

5 DETAILED METHODOLOGY

If an extensive measuring programme is available the emissions can be calculated on for an individual plant.

6 ACTIVITY STATISTICS

Standard production and energy statistics available from national or international statistical publications.

7 POINT SOURCE CRITERIA

The production of bricks and tiles can be considered as an area source. However, production is usually connected to high chimneys that can be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

For the situation in the Netherlands, the following can be proposed:

Emission factors are given for three types of clay:

class A: clay products that after firing are “red” coloured.
class B: clay products that after firing are “yellow” coloured.
class C: clay products that after firing are “white” coloured.

Emission factors in kg per ton product:

	class A ‘red’	**class B ‘yellow**	**class C ‘white**
SO_2	0.175	0.040	0.600
SO_3	0.030	0.050	0.055
dust *	0.050	0.050	0.050
F_g	0.170	0.060	0.250
Cl_g	0.040	0.035	0.110

Emission factors in kg per m^3 of natural gas used:

	class A **‘red’**	**class B** **‘yellow**	**class C** **‘white**
NO_x	0.0032	0.0032	0.0032
CO	0.0080	0.0100	0.0160
CO_2	2.3000	3.7000	3.0000
C_xH_y	0.0011	0.0011	0.0011

* dust consists of clay particles, the composition may vary widely.

The following Table 2 contains fuel related emission factors for the production of bricks and tiles based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 2 - 100 GJ/Mg product has been reported.

Table 2: Emission factors for the production of bricks and tiles[7]

					Emission factors							
Type of fuel				NAPFUE code	SO_2[2] [g/GJ]	NO_x[3] [g/GJ]	NMVOC[4] [g/GJ]	CH_4[4] [g/GJ]	CO[5] [g/GJ]	CO_2[6] [kg/GJ]	N_2O [g/GJ]	NH_3 [g/GJ]
s	coal	hc	coking	101	159[1]	569[1]		1[1]		86[1]		
s	coal	hc	steam	102	407-787[1]	150-334[1]	15-21[1]	0.3-15[1]	10-120[1]	79-95[1]	4-14[1]	
s	coal	hc	sub-bituminous	103	170[1]	30[1]	15[1]	15[1]	50[1]	99[1]	8[1]	
s	coal	bc	brown coal/lignite	105	500-2,900[1]	140-300[1]	1.5-20[1]	1.5-100[1]	14-110[1]	86-113[1]	3-14[1]	
s	coal	bc	briquettes	106	175[1]	140[1]	15[1]	15[1]	100[1]	97-98[1]	3.5[1]	
s	coke	hc	coke oven	107	400-540[1]	140-300[1]	0.5-15[1]	0.5-15[1]	15-100[1]	100-105[1]	4-14[1]	
s	coke		petroleum	110	680[1]	200[1]	1.5[1]	1.5[1]	97[1]	102[1]	3[1]	
s	biomass		wood	111	130[1]	130-200[1]	48-50[1]	30-32[1]	160[1]	83-102[1]	4-14[1]	
l	oil		residual	203	57-1,470[1]	57-330[1]	3-57[1]	0.1-8[1]	10-234[1]	76-78[1]	2-15[1]	
l	oil		gas	204	55-1,410[1]	54-330[1]	1.5-2.5[1]	1-8[1]	10-54[1]	72-74[1]	2-14[1]	
l	kerosene			206	68.6[1]		2[1]	1[1]	12[1]	71[1]	14[1]	
l	gasoline		motor	208	44.7[1]		2[1]	1[1]	12[1]	71[1]	14[1]	
g	gas		natural	301	0.4-8[1]	50-330[1]	4-26[1]	0.4-4[1]	10-343[1]	34-66[1]	1-4[1]	
g	gas		liquified petroleum gas	303	0.04-2[1]	20-100[1]	1-4[1]	1[1]	13[1]	60-65[1]	1-3[1]	
g	gas		coke oven	304	9.6[1]	50[1]	2.5[1]	2.5[1]	10[1]	44-49[1]	1.5[1]	

[1] CORINAIR90 data, area sources

[2] SO_x:

354	g/Mg	General (1992) /1/
2,000	g/Mg product	Curing and firing, oil fired tunnel kilns /2/
3,665	g/Mg product	Curing and firing, coal fired tunnel kilns /2/
2,950	g/Mg product	Curing and firing, gas fired periodic kilns /2/
6,065	g/Mg product	Curing and firing, oil fired periodic kilns /2/

[3]	NO_x:	500	g/Mg product	General /3/
		120	g/Mg product	General (1992), NAPFUE 301 (94 %) /1/
		90	g/Mg product	Curing and firing, gas fired tunnel kilns /2/
		550	g/Mg product	Curing and firing, oil fired tunnel kilns /2/
		725	g/Mg product	Curing and firing, coal fired tunnel kilns /2/
		250	g/Mg product	Curing and firing, gas fired periodic kilns /2/
		810	g/Mg product	Curing and firing, oil fired periodic kilns /2/
		1,175	g/Mg product	Curing and firing, coal fired periodic kilns /2/
[4]	VOC:	10	g/Mg product	Curing and firing, coal fired periodic kilns /2/
		50	g/Mg product	Curing and firing, oil fired periodic kilns /2/
		5	g/Mg product	Curing and firing, gas fired periodic kilns /2/
		5	g/Mg product	Curing and firing, coal fired tunnel kilns /2/
		35	g/Mg product	Curing and firing, coal fired tunnel kilns /2/
		15	g/Mg product	Curing and firing, coal fired tunnel kilns /2/
	NMVOC:	< 500	g/Mg product	General for porous bricks, for FRG, DN and UK, released by waste raw material /3/
[5]	CO:	1,600	g/Mg product	EPA-value, ceramic industry /3/
		30	g/Mg product	Curing and firing, gas fired tunnel kilns /2/
		60	g/Mg product	Curing and firing, oil fired tunnel kilns /2/
		715	g/Mg product	Curing and firing, coal fired tunnel kilns /2/
		75	g/Mg product	Curing and firing, gas fired periodic kilns /2/
		95	g/Mg product	Curing and firing, oil fired periodic kilns /2/
		1,195	g/Mg product	Curing and firing, coal fired periodic kilns /2/
		240	g/GJ	General, (1992), NAPFUE 301 (94 %) /1/
[6]	CO_2:	61	kg/GJ	General, (1992), NAPFUE 301 (94 %) /1/

[7] It is assumed, that emission factors cited within the table are related to combustion sources in bricks and tiles production. Footnotes may also include emission factors for other process emissions.

9 SPECIES PROFILES

A profile of the clay used would be useful. This information is not available.

10 UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed per ton product is estimated to be C.

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 FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The production of bricks and tiles can be considered as a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Emission inventory in The Netherlands, 1992. Emission to air and water.

Emission factors to be used for the building industry, TNO report 89/091.

Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP-42

16 VERIFICATION PROCESSES

Verification of the emissions can be done by comparing the results of the calculations with measurements at the individual plant.

17 REFERENCES

/1/ Huizinga, K.; Verburgh, J. J.; Mathijsen, A. J. C. M.: Großkeramische Industrie; RIVM-report 736301112; RIZA-report 92.003/12; 1995
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SNAP CODE: **030320**

SOURCE ACTIVITY TITLE: **PROCESSES WITH CONTACT**
Fine Ceramics Materials

NOSE CODE: **104.11.11**

NFR CODE: **1 A 2 f**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within the production of fine ceramics. However, in the following if useful for description, also non-combustion emissions are mentioned.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of fuel use related emissions released from the production of fine ceramics to total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 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_2O	NH_3
Fine Ceramics Materials	030320	0.2	0.1	-	-	0.3	0.3	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description of activities

The manufacture of ceramic clay involves the conditioning of the basic ores by several methods. These include the separation and concentration of the minerals by screening, floating, wet and dry grinding, and blending of the desired ore varieties. The basic raw materials in ceramic clay manufacture are kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and montmorillonite [$(Mg, Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$] clays. Caoline or limestone are used as additives. The clays are refined by separation and bleaching, blended, kiln-dried, and formed into such items as whiteware, heavy clay products (brick, etc.), various stoneware, and other products such as diatomaceous earth, which is used as a filter aid. /4/

The oven temperature reaches about 1100 ^{o}C. Most commonly natural gas is burned to heat the ovens, but other fuels are possible. Electric heated ovens are used in small scale ovens. Usually a tunnel shaped oven is used, but other types are used as well.

3.2 Definitions

3.3 Techniques

It can be assumed, that similar techniques are in use as described in chapter B3319.

3.4 Emissions

Pollutants released are dust, sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), fluoride ($F_{g)}$, Chlorine (Cl_g) and ammonia (NH_3). According to CORINAIR90 the main relevant pollutants are SO_2, NO_x, CO, and CO_2 (see also table 1).

In the Netherlands, emissions from fine ceramic materials production represent scarcely 5 % of the emissions from bricks and tiles production /2/. The high temperatures of the firing kilns are also conductive to the fixation of atmospheric nitrogen and the subsequent release of NO_x.

It can be assumed, that formation mechanisms and formation processes of pollutants are similar to those described in chapter B3319. /cf 4/

3.5 Controls

Emission reduction techniques are almost non-existent.

4 SIMPLER METHODOLOGY

The simpler methodology involves applying an appropriate emission factor to either production or energy consumption statistics.

5 DETAILED METHODOLOGY

If an extensive measuring programme is available, emissions can be calculated on for an individual plant.

6 ACTIVITY STATISTICS

Standard production and energy statistics available from national or international statistical publications.

7 POINT SOURCE CRITERIA

The production of fine ceramics is usually executed in rather small plants can be considered as area sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

For the situation in the Netherlands, the following can be proposed:
Emission factors are given in kg per ton product:

SO_2:	0.2 - 2.7
F_g :	0.2 - 2.8
Cl_g:	0.1
CO_2:	300 - 1600
NO_x:	0.6 - 2.0
dust *:	0.35 - 0.80

* dust consists of clay particles, the composition may vary widely.

The following Table 2 contains fuel related emission factors for the production of fine ceramics based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 8.8 - 100 GJ/Mg product has been reported.

Table 2: Emission factors for the production of fine ceramics 7)

					Emission factors							
	Type of fuel			NAPFUE code	SO_2 3) [g/GJ]	NO_x 4) [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO 5) [g/GJ]	CO_2 6) [kg/GJ]	N_2O [g/GJ]	NH_3 [g/GJ]
s	coal	hc	steam	102	650 1)	160 1)	15 1)	15 1)	100 1)	93 1)	4 1)	
s	coal	hc	sub-bituminous	103	610 1), 609 2)	40 1), 39 2)	1.5	1.5 1)		99 1)2)	8 1)	
s	coal	bc	brown coal/lignite	105	600 1)	140 1)	15 1)	15 1)	100 1)	113 1)	3.5 1)	
s	coal	bc	briquettes	106	220 1)	140 1)	15 1)	15 1)	100 1)	98 1)	3.5 1)	
s	coke	hc	coke oven	107	145 1), 144 2)	45 1)2)	2.5 1)	2.5 1)		105 1)2)		
s	coke	bc	coke oven	108	650 1)	220 1)	5 1)	15 1)	90 1)	86 1)	3 1)	
s	biomass		wood	111		200 1)	50 1)	30 1)		83-92 1)	4-14 1)	
l	oil		residual	203	143-1,494 1)	100-180 1)	3-4 1)	0.1-5 1)	10-15 1)	73-78 1)	2-14 1)	
l	oil		gas	204	85-1,410 1)	70-100 1)	1.5-2.5 1)	1-2.5 1)	10-12 1)	73-74 1)	2-14 1)	
l	kerosene			206	69 1)	80 1)	2 1)	1 1)	12 1)	71 1)	14 1)	
l	gasoline		motor	208	45 1)	80 1)	2 1)	1 1)	12 1)	71 1)	14 1)	
g	gas		natural	301	0.3-8 1)	44-330 1)	2.5-10 1)	0.4-4 1)	10-111 1)	53-69 1)	1-3.7 1)	
g	gas		liquified petroleum gas	303	0.04-2 1)	20-100 1)	1-2 1)	1-4 1)	13 1)	60-65 1)	1-3 1)	
g	gas		coke oven	304	0.04-12 1)	50-100 1)	2.5-4 1)	2.5-4 1)	10-13 1)	49-59 1)	1-1.5 1)	

1) CORINAIR90 data, area sources

2) CORINAIR90 data, point sources

3)	SO_x:	9,611	g/Mm³ fuel	Mineral products, process heaters, NAPFUE 301 /1/
		290	g/Mg product	General, SO_2 260 g/Mg, SO_x 30 g/Mg /2/
		210	g/Mg product	Future Value /2/

[4] NO_x: 850 g/Mg product /2/

[5] CO: 1,600 g/Mg product EPA value for ceramic industry
130 g/Mg product /2/

[6] CO_2: 255 kg/Mg product General /2/

[7] It is assumed, that emission factors cited within the table are related to combustion sources in the production of fine ceramics. Footnotes may also include emission factors for other process emissions.

9 SPECIES PROFILES

A profile of the clay used might be useful. This information however is not usually available.

10 UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed per ton product is estimated to be D.

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 FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

The production of fine ceramics can be either a continuous or a discontinuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Emission inventory in The Netherlands, 1992. Emission to air and water.

Emission factors to be used for the building industry, TNO report 89/091(1989) (in Dutch).

Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP 42

16 VERIFICATION PROCESSES

Verification of the emissions can be done by comparing the results of the calculations with measurements at the individual plant.

17 REFERENCES

/1/ EPA (ed.): AIRS Facility subsystem; EPA-Doc 450/4-90-003; Research Triangle Park; 1990
/2/ Huizinga, K.; Verburgh, J. J.; Mathijsen, A. J. C. M.; Loos, B.: Fijnkeramische Industrie; RIVM-report 736301124; RIZA-report 92.003/24; 1992
/3/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook; Second Edition; Comission of the European Communities; Paris; 1992
/4/ EPA (ed.): AP 42, CD-Rom, 1995

18 BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP 42 may be used.

19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **030321**

SOURCE ACTIVITY: **PROCESSES WITH CONTACT**
Paper-mill Industry (Drying Processes)

NOSE CODE: **104.07.01**

NFR CODE: **1 A 2 d**

1 ACTIVITIES INCLUDED

The activities described are related to the production of paper in paper mills. In this chapter only the drying process within a paper mill is taken into account. Other process emissions are covered by chapters B462, B463 and B464 respectively. However, in the following if useful for description, also non-combustion emissions are mentioned.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of fuel use related emissions released from drying processes in paper mills to total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 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_2O	NH_3
Paper-mill Industry	030321	0.1	0	0	-	0	0.1	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description of activities

After a beating process paper pulp is introduced into the paper mill in concentrations of about 1 %. Mineral pigments or fillers are added to improve the brightness, opacity, and surface smoothness. Substances added are for instance china clay, calcium sulphate, calcium carbonate, or titanium dioxide. The final drying process of the sheets consists in passing the sheets over a series of steamheated cylinders.

Paper mills produce pulp from wood, either by chemical or by mechanical processes. Other paper mills use purchased pulp, non-wood fibres, or recovered paper fibres to manufacture paper. The production of pulp and paper requires considerable amounts of steam and power. Most mills produce their own steam in one or more industrial boilers which burn fossil fuels and/or wood residues. Mills that pulp wood with a chemical process (kraft, sulphite, soda,

semi-chemical) normally combust their spent pulping liquor in a combustion unit, e.g., kraft recovery furnace, to recover pulping chemicals for subsequent reuse. These units are also capable of providing process steam and power for mill operations. /1/ Emissions from the steam generation in boilers have to be allocated to SNAP category 030100.
For the drying of 1 t of chemical pulp, 1,5 t of steam is necessary. /2/

3.2 Definitions

3.3 Techniques

Drying processes can be divided in the contact drying process, convective drying process and infrared drying process. The most common process used is the contact drying process, where the paper sheet is dried over a drying basket, which is fed by hot air (pressure of 1.5 - 3.5 at). The drying process of paper is influenced by the temperature of the drying basket, the thickness and density of the paper produced, the dehydrateability of the paper, etc. /2/

3.4 Emissions

Fuel use related pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O) and ammonia (NH_3). According to CORINAIR90 the main relevant pollutants are SO_2, and CO_2 (see also table 1).

Emissions from boilers used to generate steam and power account for the majority of emissions from pulp and paper mills, with kraft pulp mill emission sources (recovery furnace, lime kiln, reduced sulphur gas oxidation) accounting for most of the remainder. It should be mentioned that a very recent analysis of SO_2 measurement data for combination boilers (boilers that co-fire coal or oil with wood residues) strongly suggests that a considerable amount of SO_2 capture occurs due to the alkaline nature of the wood ash. /1/ Coal and oil combustion in boilers now accounts for 75 % of the total SO_2 emissions from paper mills. /cf.1/

Emissions from fuel burning in boilers represent the majority of the total NO_x, while kraft pulping sources accounted for almost all of the remainder. /1/ Total NO_x-emissions are affected by fuel use practices. Most mills have one or more multi-fuel boilers and fuel choices are often governed by availability and price. /1/ Increased coal and wood use can result in increased NO_x-emissions, since add-on NO_x-controls are not obligatory in most areas. /cf 1/

3.5 Controls

SO_2 control systems (scrubbers, lime injection) are installed in the mills. NO_x-controls are not obligatory in most areas. /cf 1/

4 SIMPLER METHODOLOGY

The emissions of the paper industry as a whole might be calculated by establishing a relationship with economic statistics.

5 DETAILED METHODOLOGY

A detailed methodology is possible if sufficient measurements are available for the situation in the individual plant.

6 RELEVANT ACTIVITY STATISTICS

Production and energy consumption statistics, for instance as produced by the United Nations or IEA are available.

7 POINT SOURCE CRITERIA

Paper production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Emission factors based on estimations of a mean energy use and information from the emission inventory in The Netherlands have been calculated in a SPIN document. These factors are given in table 2.

Table 2: Emission factors for the drying process in paper mills

Substance	**Emission factor in g/Mg paper produced.**
carbon monoxide	0.05
carbon dioxide	450
nitrogendioxide	0.25
hydrocarbons	0,005

If a calculation is based on known fuel consumption for a given plant the factor is C. If it is only used in a default approach the uncertainty is D.

The following Table 3 contains fuel related emission factors for paper mills based on CORINAIR90 data in [g/GJ]. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg pulp) has to be taken into account, which is process and country specific. At this stage no data for the definition of appropriate conversion factors are available.

Table 3: Emission factors for paper mills[3]

					Emission factors							
	Type of fuel			NAPFUE code	SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]	NH_3 [g/GJ]
s	coal	hc	steam	102	992[1]	150[1]	15[1], 5[2]	15[1], 1[2]	70[1], 20[2]	98[1], 91[2]	14[1], 75[2]	2[2]
s	coal	hc	sub-bituminous	103	992[1]	150[1]	15[1]	15[1]		99[1]	14[1]	
s	coal	hc/bc	patent fuels	104	701[1]	150[1]	15[1]	15[1]	70[1]	94[1]	14[1]	
s	biomass		wood	111	5.2[1] 343[2]	115-200[1] 972[2]	50[1]	30[1]	10[1]	92[1][2]	4-14[1]	
s	waste		wood	116	5.2[1] 0.8-20[2]	115[1] 100-117[2]	50[1] 3-10[2]	30[1] 1[2]	30[2]	83[1]	4[1] 4-25[2]	2[2]
s	sludge		sewage	118			10[2]	1[2]	30[2]		4[2]	2[2]
l	oil		residual	203	28-149[1] 168-190[2]	123-180[1]	3-7.4[1] 3[2]	1-3[1], 1[2]	5-15[1] 10[2]	76-79[1] 76[2]	2.5-14[1] 5[2]	2[2]
l	oil		gas	204	139-305[1]	80[1]	1.5-2[1]	1-1.5[1]	12[1]	73[1]	14[1]	
l	kerosene			206	69[1]	80[1]	2[1]	1[1]	12[1]	71[1]	14[1]	
l	gasoline		motor	208	45[1]	80[1]	2[1]	1[1]	12[1]	71[1]	14[1]	
g	gas		natural	301	0.5-8[1]	60-100[1]	4[1]	4[1]	13[1]	55-57[1]	2.5-3[1]	
g	gas		liquified petroleum gas	303	2[1]	20-100[2]	1[3], 2[2]	1-4[1], 1[2]	13[1], 10[2]	60-65[1],56[2]	3[1], 2[2]	

[1] CORINAIR90 data, area sources [2] CORINAIR90 data, point sources

[3] It is assumed, that emission factors cited within the table are related to combustion sources in paper mills; other process emissions are not covered.

9 SPECIES PROFILES

The species profile is dependent on the fuel used for heat generation. The emission factors given above are based on a fuel profile of natural gas and oil.

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspects discussed here are related to emission factors from CORINAIR90.

The fuel specific emission factors provided in table 3 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 FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of plant capacity, employment or population statistics if plant specific data are not used/available.

13 TEMPORAL DISAGGREGATION CRITERIA

Paper production is usually a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Environmental protection agency Compilation of air pollutant emission factors AP-42 and standard literature about aluminium production.

Samenwerkingsproject procesbeschrijvingen industrie Nederland (SPIN) Papier en Kartonindustrie. RIVM report 736301135 (1991)(in dutch)

16 VERIFICATION PROCEDURES

Verification may be done by comparing the calculated emissions with measurements at an individual plant.

17 REFERENCES

/1/ Pinkerton, J. E.: Emission of SO_2 and NO_x from Pulp and Paper Mills; in: Air & Waste; 10(1993)43; p. 1404-1407
/2/ Ullmanns Enzyklopädie der Technischen Chemie, Bd. 17, S. 531 ff.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **030322**

SOURCE ACTIVITY: **PROCESSES WITH CONTACT**
Alumina Production

NOSE CODE: **104.12.13**

NFR CODE: **1 A 2 b**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within alumina production. Alumina production is an ore treatment step in the production of primary aluminium (SNAP code 040301, chapter B431).

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions related to fuel use, released from the alumina production to total emissions in countries of the CORINAIR90 inventory is minor, as indicated in table 1.

Table 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_2O	NH_3
Aluminia Production	030322	0	0	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description of activities

The base ore for primary aluminium production is bauxite. Alumina is produced by the Bayer process. In this process the ore is dried, ground in ball mills, and mixed with a leaching solution of sodium hydroxide at an elevated temperature and pressure, producing a sodium aluminate which is seperated from the impurities and cooled, during which the alumina precipitates. After washing to remove impurities the alumina is dried and calcined to produce a crystalline form of alumina.

3.2 Definitions

Bauxite	A hydrated oxide of aluminium consisting of 30-70 percent alumina and lesser amounts of iron, silicon and titanium.

3.3 Techniques

The calcination of the aluminium-hydroxide takes place in rotary kilns at about 1,300 °C or in fluidised bed furnaces at lower temperatures. The furnaces are fired with heavy oil and gas.

3.4 Emissions

The main emissions are dust emissions occurring during the grinding of the bauxite and the calcining of the aluminium hydroxide.

Pollutants related to fuel use are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compunds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2), and nitrous oxide (N_2O). Of these, according to CORINAIR90, the main relevant pollutants are SO_2 and NO_x (see also table 1).

3.5 Controls

Dust emissions can be abated by spray towers, floating bed scrubbers, quench towers, or electrostatic precipitators. The dust trapped in the calcining process is usually reused.

No information is available about control of gaseous emissions.

4 SIMPLER METHODOLOGY

The simpler methodology involves applying an appropriate emission factor to either production or energy consumption statistics.

5 DETAILED METHODOLOGY

A detailed methodology is possible if sufficient measurements are available about the situation in an individual plant.

6 RELEVANT ACTIVITY STATISTICS

Production and energy statistics for instance as produced by the United Nations or the IEA are available.

7 POINT SOURCE CRITERIA

Aluminium production plants containing an alumina production department can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

For the situation in the Netherlands, the following can be proposed:
Controlled and uncontrolled emission factors for dust are available for both sectors of the Bayer process. These emission factors are presented in Table 2.

Table 2: Emission factors for dust from alumina production in gram/kg aluminium produced

	Bauxite grinding	**Calcining**
Uncontrolled	3.0	100.0
Spray towers	0.5	30.0
Floating bed scrubber	0.85	28.0
Quench tower	0.5	17.0
Electrostatic precipitator	0.06	2.0

Source: EPA Compilation of air pollutant emission factors AP-42.

The composition of the dust is determined by the composition of the dust.

The following Table 3 contains fuel related emission factors for the alumina production based on CORINAIR90 data in [g/GJ]. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. At this stage no data for the definition of appropriate conversion factors are available.

Table 3: Emission factors for the alumina production[2)]

				Emission factors						
	Type of fuel		NAPFUE code	SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O
				[g/GJ]	[g/GJ]	[g/GJ]	[g/GJ]	[g/GJ]	[kg/GJ]	[g/GJ]
l	oil	residual	203	419[1)]	123[1)]	7.4[1)]	1[1)]	5[1)]	79[1)]	
g	gas	natural	301	8[1)]	60[1)]	10[1)]	2[1)]	30[1)]	55[1)]	

[1)] CORINAIR90 data, area sources

[2)] It is assumed, that emission factors cited within the table are related to combustion sources in alumina production; other process emissions are not covered.

9 SPECIES PROFILES

The species profile of the dust is directly related to the bauxite composition which may differ from location to location.

10 UNCERTAINTY ESTIMATES

The uncertainty classification of the emission factors expressed per kg aluminium is estimated to be C.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspects discussed here are related to fuel use related emission factors.

The fuel specific emission factors provided in table 3 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 FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Alumina production is usually a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency, Compilation of Air Pollutant Emission Factors. AP-42.

16 VERIFICATION PROCEDURES

Verification may be done by comparing the calculated emissions with measurements from individual plants.

17 REFERENCES

/1/ VDI (ed.): Auswurfbegrenzung - Aluminium-Monoxidgewinnung und Aluminium-schlmelzflußelektrolyse (Entwurf); 1974

18 BIBLIOGRAPHY

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SOURCE ACTIVITY TITLE: PROCESSES WITH CONTACT

ACTIVITY	**SNAP CODE**	**NOSE CODE**	**NFR CODE**
Magnesium Production (Dolomite Treatment)	**030323**	**104.12.14**	**1 A 2 b**
Nickel Production (Thermal Process)	**030324**	**104.12.15**	**1 A 2 b**
Enamel Production	**030325**	**104.09.01**	**1 A 2 f**
Other	**030326**	**104.12.16,17**	**1 A 2 f**

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

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