

SNAP CODE :

030203

SOURCE ACTIVITY TITLE :

Blast Furnaces Cowpers

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.

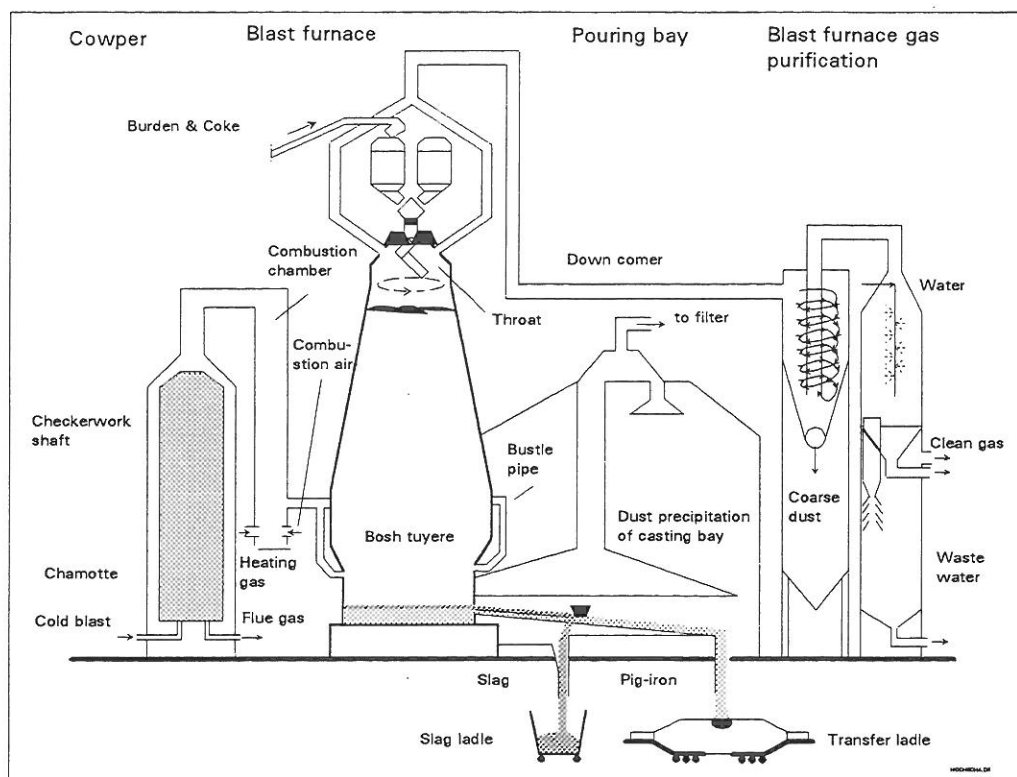


Figure 1: Flow diagram of the blast furnace process /cf. 9/

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	NMVOG	CH ₄	CO	CO ₂	N ₂ O	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/m³ of particulates. /2, 3/

3.4 Emissions

Blast furnace gas contains about 21 - 28 % CO, inert components (50 % N₂, 23 % CO₂), some sulphur compounds and high amounts of dust (from iron ore, sinter and coke) /cf. 7, 8/. CO₂ 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 (CO₂). Sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and CH₄) and nitrous oxide (N₂O) are of less relevance. Emissions of dust which may contain heavy metals, are also of relevance /cf. 3/. Emissions of ammonia (NH₃) 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 SO₂ 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:

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

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):

$$A_{\text{COR}} = F \cdot H_u \cdot A_{\text{Stat}} \quad (2)$$

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]	NM VOC ⁴⁾ [g/GJ]	CH ₄ ⁴⁾ [g/GJ]	CO ⁵⁾ [g/GJ]	CO ₂ ³⁾ [kg/GJ]	N ₂ O [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; CH₄ 10; CO 15; N₂O 12 [g/GJ]²⁾

coke oven coal: NAPFUE 107; NO_x 141; NMVOC 2; CH₄ 0.03; CO 120; CO₂ 15 10³-108 10³; N₂O 3 [g/GJ]²⁾

residual oil: NAPFUE 203; SO₂ 223-305; NO_x 112-521; NMVOC 3; CH₄ 3-112; CO 13-15; CO₂ 76 10³ -78 10³; N₂O 2.8-14 [g/GJ]²⁾

gas oil: : NAPFUE 204; NMVOC 2.5-6.2; CH₄ 2.5; CO 12; CO₂ 74 10³; N₂O 14 [g/GJ]²⁾

²⁾ CORINAIR90 data

³⁾ CO₂: 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/ US-EPA (ed.): Compilation of the Pollutant Emission Fraction; Version 1; Stationary Point and 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
- /7/ Parker, Albert (ed.): Industrial Air Pollution Handbook; Maidenhead (England); 1978
- /8/ Havenaar, P.; Santen, D. J.; Verrier, K.: Blast furnace gas fired co-generation plant; *in*: Combustion Technology 1994, VGB Technische Vereinigung der Großkraftwerksbetreiber 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 Institut für Umweltforschung; Karlsruhe; 1995 (to be published)

18. BIBLIOGRAPHY

19. RELEASE VERSION; DATE AND SOURCE:

Version : 2.0

Date : December 1995

Source : Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D- 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax.: 0049-721-758909

SNAP CODE :

030204

SOURCE ACTIVITY TITLE :

Plaster Furnaces

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.

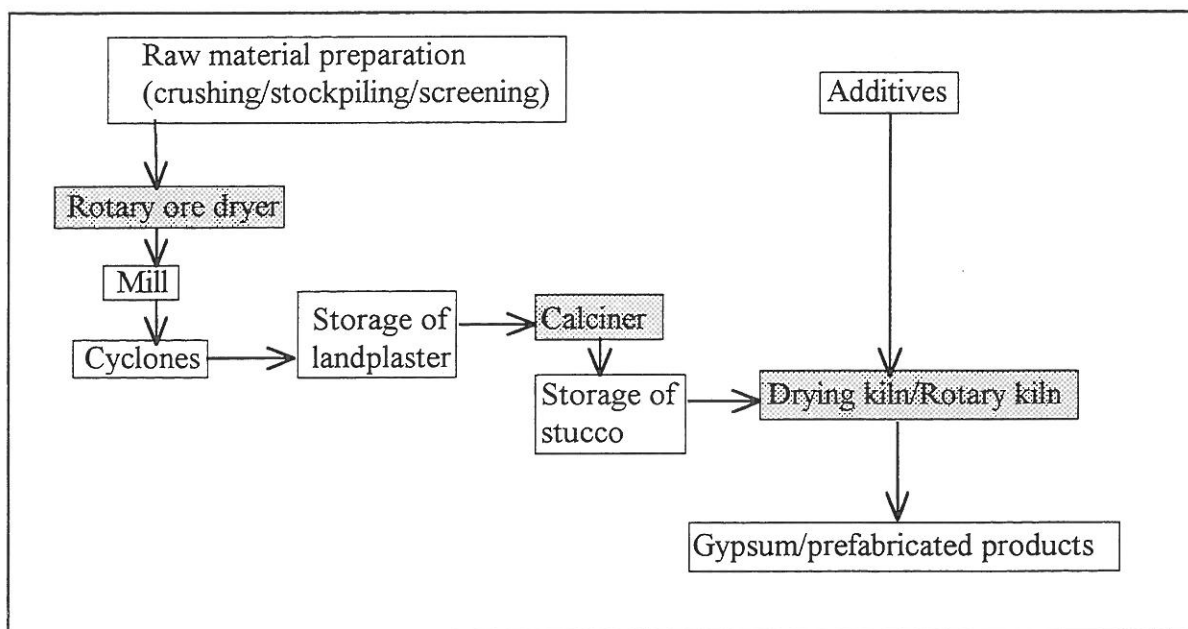


Figure 1: Basic steps of gypsum manufacturing process

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 ₂ O	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 $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) 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 $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$), the gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) 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 (CO₂). Emissions of volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO) and ammonia (NH₃) are of less relevance. Normally, emissions of nitrous oxide (N₂O) are not relevant¹. Emissions of heavy metals are of less relevance.

Emissions of sulphur dioxide (SO₂) 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 SO₂ 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

SO₂ 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).

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

¹ The amount of N₂O reported in CORINAIR90 (see Table 1) is considered to be too high.

“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:

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

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):

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

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 SO₂, NO_x, NMVOC or NH₃. 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 [g/GJ]	NO _x ¹⁾ [g/GJ]	NMVOC ⁶⁾ [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [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⁾
g	gas		natural	301	4 ³⁾	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/Mm³ 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/m³ 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

Version : 2.0

Date : December 1995

Source : Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D- 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax.: 0049-721-758909

SNAP CODE : 030301

SOURCE ACTIVITY TITLE : Sinter Plants

NACE CODE : 27

PARCOM CODE : 2.1.1

1. ACTIVITIES INCLUDED

The sinter process is an ore pretreatment step in the production of iron and non-ferro metals.

2. CONTRIBUTION TO TOTAL EMISSION

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

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO ₂	NO _x	NMVOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃
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 heavy metals from sinter plants are also relevant but have not been quantified at the European level. This chapter (version 2.0) currently only addresses heavy metal emissions.

3. GENERAL

3.1. Description of activities

The activities in the sinter plants include:

- treatment of the ores by crushing and sieving
- mixing of treated ores, cokes and flux compounds
- combustion and agglomeration of a mixture of crushed ores, cokes, small sintered agglomerates and flux compounds
- sieving of the sintered agglomerates
- cleaning of the combustion off-gases

The sintering process is a pretreatment step in the production of iron and non-ferro metals where fine particles of metal ores are agglomerated into nodules, briquettes, sinter or pellets. Agglomeration of the fine particles is necessary to increase the passageway for the gases during the furnace blasting process. The strength of the particles is also increased by agglomeration.

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 incomplete crushed ores 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 remainder 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.

3.3. Techniques used during the sintering process

The sintering process is used for several primary metal production processes, each having different designs.

3.4. Emissions during the sintering process

The mixing, crushing and sieving processes cause dust emissions. They are removed by a cyclone separator and a fabric filter. The captured dust can, after separation, be reused in the sintering process.

4. SIMPLER METHODOLOGY

Simpler methodologies relating the emissions to number of employees or economic (production) statistics are not available for this chapter.

5. DETAILED STATE-OF-THE-ART 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. The dust from the cyclones is reused in the sintering process and can rather easily be analyzed to measure the average metal composition. The amount of dust not-recovered can be estimated from off-gas measurements. From this information the heavy metal emissions can be estimated. The emission of organics can only be estimated from measurements of the off-gases.

6. ACTIVITY STATISTICS

Standard production statistics available from UN, International Iron and Steel Institute etc.

7. POINT SOURCE CRITERIA

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

8. EMISSION FACTORS, QUALITY CODES AND REFERENCES

The emission factors as presented are calculated on the basis of emission divided by the amount of product. This calculation is given in formule 1.

$$E(\text{factor}) = \frac{\bar{\phi}(\text{gas}) * \bar{C}(\text{contamination})}{M(\text{production})} \quad [1]$$

E(factor) : emission factor (g/Mg)
 N(gas) : average gasflow (m³ air/year production)
 C(contamination) : average concentration of compound in the off-gas (g/m³)
 M(production) : production during a year (ton product/year)

The emission calculation is based on average values because the ores, fuel and remainder stream change frequently in composition.

Emission factors found in literature are given in table 1.

Table 1. Emission factors for emissions to air for sintering plants (g.Mg⁻¹ product)

Substance	Ref [1]	Ref [2]	Ref [3] ¹	Ref [3] ²	Ref [4]	Ref [5]	Ref [6]	Ref [7]	Range of emission factor
Abatement (dust)	electro-filters	unknown	unknown		cyclones	electro-filters	electro-filters	cyclones	
Arsenic	0.05	-	0.025	0.009	0.05	-	-	0.08	0.009-0.08
Cadmium	0.13	-	3*10 ⁻⁴	0.09	0.13	-	0.02-0.12	-	4*10 ⁻⁴ -0.12
Chromium	-	-	0.13	0.09	0.05	0.56	-	-	0.05-0.56
Copper	0.05	1	0.25	0.36	0.13	0.23	-	-	0.05-1
Mercury	0.04	-	6*10 ⁻⁵	0.01	0.04	-	-	-	6*10 ⁻⁵ -0.04
Nickel	-	-	0.19	0.14	-	1.0	-	-	0.14-1.0
Lead	9.92	9	0.13	4.5	10	2.1	-	15.3	0.13-15.3
Selenium	-	0.02	1*10 ⁻⁴	0.019	-	-	-	-	0.0001-0.02
Zinc	11.6	-	0.13	0.9	0.37	2.1	-	-	0.13-11.6
Dioxines	6*10 ⁻⁶	-	-	-	-	-	-	-	n.r.a.

n.r.a.= No range available

¹ = Diffuse sources, cold; ² = Abated process emissions

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

The quality classification of the emission factors is estimated to be B-C.

11. WEAKEST ASPECTS FOR IMPROVEMENT IN CURRENT METHODOLOGY

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

12. SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13. TEMPORAL DISAGGREGATION CRITERIA

Sintering can be considered as a continuous process.

14. ADDITIONAL COMMENTS

15. SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency
Compilation of Air Pollutant Emission Factors (AP 42)
PARCOM-ATMOS Emission Factors Manual

16. VERIFICATION PROCEDURES

Verification of the emissions can be done 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.

17. REFERENCES

- 1 Spindocument "Productie van primair ijzer en staal"; Annema, J.A., Albers, R.A.W.; Boulan, R.P.; RIVM (reportnr. 736301131); november 1992 (in Dutch)
- 2 PARCOM-ATMOS Emission Factors Manual Actualized version 1993.

18. BIBLIOGRAPHY

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

19. RELEASE VERSION, DATE, AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M.Berdowski, P.F.J.van der Most, J.M.Slaager
TNO-MEP,
P.O.Box 6011,
2600 JA Delft,
The Netherlands

SNAP CODE : 030302

SOURCE ACTIVITY TITLE : Reheating Furnaces Steel and Iron

NACE CODE : 27

PARCOM CODE : 2.1

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 B421 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 ₂ O	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

For emissions other than heavy metals, multiplying the emission factors with the appropriate energy consumption yields the emission. For heavy metals, simpler methodologies relating the emissions to statistics are not available.

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.

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

Because reheating furnaces in iron and steel plants are part of a general production process, no separate emission factors have been found for heavy metals.

For emissions other than heavy metals, table 3 contains fuel use related 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 3: Emission factors for reheating furnaces in steel and iron production

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 ₂ O [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⁾ 143-1,503 ³⁾	100- 240 ³⁾	3-5 ¹⁾³⁾ 3 ³⁾	3-5 ¹⁾³⁾ 1.5 ³⁾	15 ¹⁾ , 12- 15 ³⁾	76-78 ¹⁾ 73-78 ³⁾	3-14 ¹⁾ 2-14 ³⁾		
l oil gas	204	94-1,410 ³⁾	80-100 ³⁾	2.5 ¹⁾ 1.5 ³⁾	2.5 ¹⁾ 1.5 ³⁾	12 ¹⁾³⁾	74 ¹⁾ 69-74 ³⁾	3 ¹⁾ 2-14 ³⁾		
l oil shale-oil	211	503 ¹⁾	158 ¹⁾			13 ¹⁾				
g gas natural	301	0.87-58 ¹⁾ 0.3-58 ³⁾	58-187 ¹⁾ 58-125 ³⁾	2.5-4 ¹⁾ 1-4 ³⁾	2.5-4 ¹⁾ 1-5 ³⁾	5.5-13 ¹⁾ 8-25 ³⁾	55-56 ¹⁾ 52-57 ³⁾	1.5-3 ¹⁾ 0.8-3 ³⁾		
g gas liquified petroleum gas	303	0.04 ³⁾	100 ³⁾	2.1 ³⁾	0.9 ³⁾	13 ³⁾	65 ³⁾	1-3 ³⁾		
g gas coke oven	304	23-715 ¹⁾ 60 ³⁾	84-207 ¹⁾ 85 ³⁾	2.5 ¹⁾³⁾	2.5 ¹⁾³⁾	12-17 ¹⁾ 15 ³⁾	42-46 ¹⁾ 45 ³⁾	3 ¹⁾ , 1 ³⁾		
g gas blast furnace	305	57-831 ¹⁾ 18-830 ³⁾	145- 831 ¹⁾ 25-830 ³⁾	0.25-2.5 ³⁾		12-69 ¹⁾ 10-14 ³⁾	192 ¹⁾³⁾ 290 ³⁾	3 ¹⁾ , 1-2.4 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 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.

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] US-EPA (ed.): AP 42 CD-Rom; 1994
- [3] Parker, Albert (ed.): Industrial Air Pollution Handbook; Maidenhead, Berkshire (England); 1978
- [4] EPA (ed.): AIRS Facility Subsystem, EPA-Doc: 450/4-90-003, Research Triangle Park, March 1990

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE, AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J.van der Most.
TNO
P.O.Box 6011,
2600 JA Delft,
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030303
SOURCE ACTIVITY TITLE :	Gray Iron Foundries
NACE CODE :	275
PARCOM CODE :	2.1.8

1. ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within gray iron foundries. The gray 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 B421 up to B428.

2. CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from gray 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 ₂ O	NH ₃
Gray 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. Gray 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 separated 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 ($\gg 1500$ °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-lead, 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 (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O) and ammonia (NH₃). The emissions are released through the stack. According to CORINAIR90 the main relevant pollutants are CO and CO₂ (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 gray 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 gray iron foundries⁷⁾

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 ₂ O [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 gray 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 m³ Mg⁻¹ off-gases) and 40% of cold blast air off-gases (300 m³ Mg⁻¹ off-gases), using an average dust concentration of 300 mg m⁻³. The emission factors are calculated from formula 1:

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

[Dust]_{average} : Average dust concentration in off-gases

Flow_{off-gases} : Average flow of off-gases

[Metal composition]_{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 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 monday to friday from \pm 7.00 hour to \pm 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
- [2] AVNEG; 1990 personal communication
- [3] Basic document Cadmium; Slooff, W., Ros, J.P.M.; RIVM report number 758476002; July 1987 (in Dutch)
- [4] Basic report Zinc; Haskoning; 1990 (in dutch)
- [5] Energy use for basic metal industry; Braun; 1990
- [6] Foundries 1987-1988 (SBI 34.0); Industrial production statistics; Central Office of Statistics; 1990
- [7] Air Note L214 concerning foundries (I); DHV-MT; 1990
- [8] Air Note L215 concerning foundries (II); DHV-MT; 1990
- [9] Emission Registration 13, Report Emission Registration Netherlands; Ministry VROM; May 1990
- [10] Atmospheric data from the Emission Registration concerning ferro and non-ferro companies; RIVM; 1991
- [11] Handbook of emission factors, Part 2: Industrial sources; Government Publishing Office, The Hague; 1983
- [12] Handbook of Model Descriptions of atmospheric emissions from the Iron Casting Foundries; TA-Luft; 1983
- [13] Die Europäische Giesserei-Industrie; Annual Statistic Report from the Association Committee of European Foundries; 1992
- [14] Industrial emission in the Netherlands, 5th inventory round - 1990; Publicatiereeks Emissieregistratie; Ministry VROM; 1993
- [15] Datenerhebung über die Emissionen Umweltgefährdenden Schwermetalle; Jöckel, W., Hartje, J.; Forschungsbericht 91-104 02 588 TÜV Rheinland e.V. Köln; 1991
- [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

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE, AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J. van der Most, W. Mulder
TNO,
P.O.Box 6011,
2600 JA Delft,
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030304

SOURCE ACTIVITY TITLE : Primary Lead Production

NACE CODE : 2743

PARCOM CODE : 2.2.2.

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 ₂ O	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 pollutant 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 SO₂ stream can vary from 1.4 to 7.2 g/m³, 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 % SO₂, or two streams are taken, a strong stream (5 to 7 % SO₂) from the feed end of the machine and a weak stream (less than 0.5 % SO₂) 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 SO₂ 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 SO₂ 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/m³, and dual stage plants can attain levels of 1.6 g/m³. Typical efficiencies of dual stage plants in removing sulphur oxides can exceed 99 %. Other technically feasible SO₂ 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

Compound	Sweden [2]		Poland [3]			Germany [4]	Pacyna [5,6]
	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/m³) 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 production⁶⁾

Type of fuel				NAPFUE code	Emission factors						
					SO ₂ ³⁾ [g/GJ]	NO _x ⁴⁾ [g/GJ]	NM VOC ⁵⁾ [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [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 SO₂ 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 SO₂); other process emissions are not covered.

10. UNCERTAINTY ESTIMATES

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

11. WEAKEST ASPECTS 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
- 2 Preliminary note on guidelines on measures and methods for heavy metals emissions control for the primary non-ferrous metal industry in the framework of the ECE task force "Heavy metal emissions" Presented by Sweden on meeting Berlin 21-24 january 1992
- 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 Umweltgefährdenden 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
- 6 Survey on heavy metal sources and their emission factors for the ECE countries; Pacyna, J.M.; Proc. 2nd Mtg Task Force Heavy Metals Emissions, ECE Convention on Long-range Transboundary Air Pollution Working Group on Technology, Prague, 15-17 October 1991; page 27-55; 1990
- 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

Version : 2.0

Date : November 1995

Source: J.J.M.Berdowski, P.F.J.van der Most, C. Veldt, J.P.J. Bloos
TNO;
P.O.Box 6011;
2600 JA Delft,
The Netherlands

Supported by: O. Rentz, D. Oertel
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-75890

SNAP CODE :	030305
SOURCE ACTIVITY TITLE :	Primary Zinc Production
PARCOM-ATMOS CODE :	2.2.3
NACE CODE :	2743

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 ₂ O	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

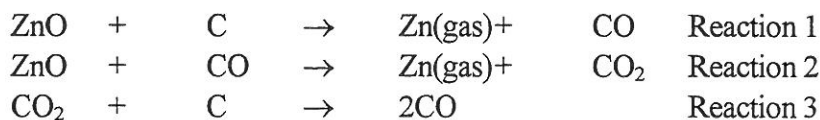
The roasted ores are leached in electrolytic cell acid. The zinc oxide dissolves in the acid solution, but the zinc ferro does not. After a separation step the raw zinc sulphate solution goes to the purification process and the insoluble matter to the jarosite precipitation process.

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 $[(\text{NH}_4)_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}]$. After separation the zinc containing solution goes to the first leaching process and the insoluble matter to a second leaching process. The insoluble matter is contacted in the second leaching process with a strong acid solution. The zinc ferro and almost all the other metals dissolve in the strong acid solution. After separation the zinc and iron containing solution is returned to the jarosite precipitation process where the iron and the insoluble matter are removed.

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

The thermal smelting zinc production process

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



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

The vaporized zinc is condensed by external condensers.

3.2 Definitions

Zinc concentrate	Enriched zinc ores which contain 85 wt% zinc sulphide and 8-10 wt% iron sulphide. The overall zinc concentration is about 50 wt%.
Roasting process	The zinc concentrate is oxidized, converting the zinc sulphide to zinc oxide, and partly to zinc ferro. The off-gas contains sulphur dioxide and traces of chlorine, fluorine and mercury. These compounds are removed by an air cleaning process (sulphur dioxide is converted into sulphuric acid). The solid product of the roasting process is called roast good.
First leaching process	The leaching process is the dissolving of the zinc oxide in an acid solution. The insoluble matter is separated and transported to the jarosite precipitation process.
Jarosite precipitation process	During the jarosite precipitation process the dissolved iron is precipitated. The iron is converted to ammoniumjarosite which does not dissolve in strong acid solution. The solution is transported back to the first leaching process and the insoluble matter (ammoniumjarosite, zinc ferro and other metals) is transported to a second leaching process.
Second leaching process	The insoluble matter of the jarosite precipitation process is contacted with a strong acid solution. The zinc ferro and several metals dissolve in the acid solution, but the jarosite does not. The solution with dissolved zinc and metals is transported back to the jarosite precipitation process and the insoluble matter is removed from the process (jarosite).
Purification process	During the purification process the traces of metal pollution in the zinc sulphate solution are removed by adding zinc dust. These metals would disturb the electrolytic separation of the zinc and decrease the quality of the electrolytic precipitate. The metals are removed by filtration from the purified zinc sulphate solution.
Electrolytic zinc production	Zinc is electrolytically separated from the purified zinc sulphate solutions. The zinc precipitates on the electrodes and can be removed as zinc sheets.
Thermal smelting process	Roasted zinc concentrates are melted at about 1100 °C in the presence of a carbon source. Zinc oxide is reduced to zinc and vaporized.
Zinc condensation	Vaporized zinc is condensed in several traps.
Casting process	The zinc sheets are melted and the zinc melt is casted in blocks which are suitable for transport.

3.3 Emissions

The emissions of 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:

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

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:

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

where

$[\text{Flow}]_{\text{gas}}$:	Gas flow of a certain subprocess which emits heavy metals to air ($\text{m}^3 \cdot \text{year}^{-1}$);
d:	Duration of the period of emission of heavy metals to air (per subprocess) (year);
$[\text{Metal composition}]_{\text{gas}}$:	Average concentration of heavy metals in emitted gas (g m^{-3} gas);
$[\text{Zinc}]_{\text{production}}$:	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 ($\text{g} \cdot \text{Mg}^{-1}$ product) as reported by several countries/authors

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

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

2) limited abatement.

Table 8.2.: 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

Fuel				Emission factors							
s	coke	hc	coke oven	NAPFUE-code	SO ₂ ³⁾ [g/GJ]	NO _x ⁴⁾ [g/GJ]	NMVOC ⁵⁾ [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [g/GJ]
s	coke	hc	coke oven	107	463 ²⁾	35 ²⁾				105 ²⁾	
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) 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 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 emission factors AP-42

PARCOM-ATMOS Emission Factors Manual

16. VERIFICATION PROCEDURES

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

17. REFERENCES

- 1 EPA (ed.): AIR Facility Subsystem, EPA-Doc. 450/4-90-003, Research Triangle Park, 1990
- 2 US-EPA (ed.): AP 42 CD-Rom; 1995
- 3 US-EPA (ed.): AP 42 CD-Rom; 1994
- 4 Datenerhebung über die Emissionen Umweltgefährdenden Schwermetalle; Jockel, W., Hartje, J.; Forschungsbericht 91-104 02 588, TÜV Rheinland e.V. Köln; 1991
- 5 Heavy metals emission to air in Poland for years 1980-1992, Hlawiczka, S., Zeglin, M., Koterska, A., Inst. Ecol. Ind. Areas, Report 0-2.081, Katowice, 1995 (in Polish)
- 6 Spindocument "Productie van primair zink"; Matthijssen, A.J.C.M., Meijer, P.J.; RIVM (reportnr. 736301113); november 1992 (in Dutch)
- 7 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

- 8 Survey on heavy metal sources and their emission factors for the ECE countries; Pacyna, J.M.; Proc. 2nd Mtg Task Force Heavy Metals Emissions, ECE Convention on Long-range Transboundary Air Pollution Working Group on Technology, Prague, 15-17 October 1991; page 27-55; 1990
- 9 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

No additional bibliography.

19. RELEASE VERSION, DATE, AND SOURCE

Version : 2.0

Date : November 1995

Source: J.J.M.Berdowski, P.F.J.van der Most, C. Veldt, J.P.J. Bloos
TNO;
P.O.Box 6011;
2600 JA Delft,
The Netherlands

Supported by: O. Rentz, D. Oertel
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-75890

SNAP CODE : **030306**
040300

SOURCE ACTIVITY TITLE : **Primary Copper Production**

PARCOM-ATMOS CODE : **2.1**

NACE CODE : **27.44**

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 sulfur, 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 sulfur dioxide and heavy metals on fine particles occur during all the above mentioned processes.

Both, emissions from fuel combustion and industrial processes are discussed here.

2. CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions of sulfur 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 sulfur 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 1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO ₂	NO _x	NM VOC	CH ₄	CO	CO ₂	N ₂ O	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.

3. GENERAL

3.1. Description

The traditional pyrometallurgical copper smelting process is illustrated in figure 1 (after 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 sulfur 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 sulfide, ferrous sulfide, 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 sulfide 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 pulverized 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 sulfide 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 sulfur dioxide. In contrary, electric arc furnaces do not produce fuel combustion gases, so flow rates are lower and so are the sulfur dioxide concentrations.

The final step in the production of blister copper is converting. The rest of iron and sulfur 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, sulfur, tellurium, and

zinc. There are various converting technologies applied in the copper production. The temperature in the converting furnace reaches 1100 C.

Figure 1: Typical primary copper smelter process (adapted from EPA, 1993)

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.

3.3. Controls

Emission controls on copper smelters are employed for controlling sulfur dioxide and particulate matter emissions resulting from roasters, smelting furnaces, and converters. Control of sulfur dioxide emissions is achieved by absorption to sulfuric acid in the sulfuric

acid plants, which are commonly a part of copper smelting plants. Reverberatory furnace effluent contains minimal SO₂ and is usually released directly to the atmosphere with no SO₂ reduction. Effluents from the other types of smelter furnaces contain higher concentrations of SO₂ and are treated in sulfuric acid plants before being vented. Single-contact sulfuric acid plants achieve 92.5 to 98 % conversion of SO₂ from plant effluent gas. Double-contact acid plants collect from 98 to more than 99 % of the SO₂. Absorption of the SO₂ in dimethylaniline solution has also been used in US-American smelters to produce liquid SO₂. (EPA, 1995).

Electrostatic precipitators (ESPs) are the common particulate matter control devices employed at copper smelting 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).

3.4. Emissions

Pollutants released are sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂) and nitrous oxide (N₂O). According to CORINAIR90 the main relevant pollutants are SO₂ and CO (see also table 1).

Primary copper smelters are a source of sulfur oxides (SO_x). Emissions are generated from the roasters, smelting furnaces, and converters. Fugitive emissions are generated during material handling operations. Remaining smelter operations use material containing very little sulphur, resulting in insignificant SO₂ emissions (EPA, 1995). Here only emissions from combustion processes with contact are relevant.

Table 2 shows typical average SO₂ concentrations from the various smelter units.

Table 2: Typical sulfur 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 ₂ SO ₄ plant	0.2 - 0.26
Double contact H ₂ SO ₄ plant	0.05

It can be assumed, that the SO₂ concentrations given in Table 2 take into account emissions from fuel sulfur and ore sulfur.

4. SIMPLER METHODOLOGY

The simpler methodology for sulfur 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 sulfur dioxide depend on the copper production technology, the type and efficiency of control equipment, and sulfur content of copper ores.

Emission factors for trace elements depend on similar parameters to the sulfur 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.

5. DETAILED METHODOLOGY

The detailed methodology to estimate emissions of sulfur 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, smelting, 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. 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 sulfur 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 sulfur 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 sulfur dioxide, which can be increased to 2.5 % by oxygen enrichment of the air. Flash smelting produces sulfur 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 sulfur dioxide concentrations ranging from almost 0 to 10 % and averaging about 4 to 5 %. Sulfuric acid is the most common sulfur product recovered from metallurgical gases. A production schematic for single and double contact sulfuric acid plant is shown in figure 2. The production data and maximum sulfur dioxide emissions for sulfuric acid processes are presented in table 3 (Environment Canada, 1982).

Table 4 contains fuel related emission factors for primary copper 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 value for the specific energy consumption of 100 GJ/Mg product has been reported.

Figure 2: Single and double contact sulphuric acid plant schematic (adapted from Environment Canada, 1982)

Table 3: Production data and maximum sulfur dioxide emissions for sulfuric acid processes (adpoted from Environment Canada, 1982)

Sulfuric acid recovery process	SO ₂ removal	SO ₂ concentration in input gas (vol. %)	Maximum sulfur 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 ₂ SO ₄
Double contact process	99.5 %	10 %	1.7 g SO ₂ /m ³ 3.3 kg SO ₂ /t H ₂ SO ₄
	99.5 %	6 %	1.0 g SO ₂ /m ³ 3.3 SO ₂ /t H ₂ SO ₄
	99.0 %	10 %	3.5 g SO ₂ /t H ₂ SO ₄ 6.6 kg SO ₂ /t H ₂ SO ₄
	99.0 %	6 %	1.9 g SO ₂ /m ³ 5.5 kg SO ₂ /t H ₂ SO ₄

Table 4: Emission factors for primary copper production⁶⁾

Type of fuel				NAPFUE code	Emission factors		NMVOC ⁵⁾ [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [g/GJ]
s	coal	bc	briquettes		SO ₂ ³⁾ [g/GJ]	NO _x ⁴⁾ [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⁾	

¹⁾ CORINAIR90 data, area sources

²⁾ CORINAIR90 data, point sources

³⁾ SO_x: (EPA, 1990)

140,000	g/Mg conc. ore processed	multiple hearth roaster
90,000	g/Mg conc. ore processed	reverberatory smelting furnace after roaster
311,500	g/Mg conc. ore processed	converter, all configurations
0	g/Mg conc. ore processed	fire (furnace) refining
500	g/Mg conc. ore processed	ore concentrate dryer
160,000	g/Mg conc. ore processed	reverberatory smelting furnace with ore charge, without roasting
180,000	g/Mg conc. ore processed	fluidised bed roaster
120,000	g/Mg conc. ore processed	electric smelting furnace
0	g/Mg conc. ore processed	electrolytic refining
410,000	g/Mg conc. ore processed	flash smelting
500	g/Mg conc. ore processed	roasting, fugitive emissions
2,000	g/Mg conc. ore processed	reverberatory furnace, fugitive emissions
65,000	g/Mg conc. ore processed	converter, fugitive emissions
50	g/Mg conc. ore processed	anode refining furnace, fugitive emissions
3,000	g/Mg conc. ore processed	slag cleaning furnace, fugitive emissions
50	g/Mg conc. ore processed	converter slag returns, fugitive emissions
3,750	g/Mg conc. ore processed	slag cleaning furnace
160,000	g/Mg conc. ore processed	reverberatory furnace with converter
180,000	g/Mg conc. ore processed	fluidised bed roaster with reverberatory furnace and converter
500	g/Mg conc. ore processed	concentrate dryer with electric furnace, cleaning furnace and converter
500	g/Mg conc. ore processed	concentrate dryer with flash furnace and converter
140,000	g/Mg conc. ore processed	multiple hearth roaster with reverberatory furnace and converter
300,000	g/Mg conc. ore processed	fluidised bed roaster with electric furnace and converter
90,000	g/Mg conc. ore processed	reverberatory furnace after multiple hearth roaster
80,000	g/Mg conc. ore processed	reverberatory furnace after fluidised bed roaster
120,000	g/Mg conc. ore processed	electric furnace after concentrate dryer
410,000	g/Mg conc. ore processed	flash furnace after concentrate dryer
45,000	g/Mg conc. ore processed	electric furnace after fluidised bed roaster
17,209 · S	g/m ³ fuel	primary metal production, process heaters, NAPFUE 204, S = sulphur content of fuel
19,006 · S	g/m ³ fuel	primary metal production, process heaters, NAPFUE 203, S = sulphur content of fuel

Emission factors of SO₂ given here may contain emissions from combustion of fuel as well as emissions from ore sintering.

⁴⁾ NO_x: (EPA, 1990)

1,800	g/Mg conc. ore processed	multiple hearth roaster
2,900	g/Mg conc. ore processed	reverberatory smelting furnace after dryer
0	g/Mg conc. ore processed	converter, all configurations
5,150	g/Mg conc. ore processed	reverberatory smelting furnace with ore charge, without roasting
0	g/Mg conc. ore processed	refined metal finishing operations, electrolytic refining
2,397	g/m ³ fuel	primary metal production, process heaters, NAPFUE 204
6,591	g/m ³ fuel	primary metal production, process heaters, NAPFUE 203

⁵⁾ VOC: (EPA, 1990)

4.5	g/Mg conc. ore processed	multiple hearth roaster
7.5	g/Mg conc. ore processed	reverberatory smelting furnace after dryer
2	g/Mg conc. ore processed	ore concentrate dryer
1.5	g/Mg conc. ore processed	reverberatory smelting furnace with ore charge, without roasting
24	g/m ³ fuel	primary metal production, process heaters, NAPFUE 204
34	g/m ³ fuel	primary metal production, process heaters, NAPFUE 203

⁶⁾ It is assumed, that emission factors cited within the table are related to combustion sources in primary copper production (except of SO₂). Footnotes may contain emission factors for total emissions (fuel and process related).

A list of emission factors for several trace elements emitted from copper smelters is presented in Table 5. 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 5.

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 5 can only be used in a simpler emission estimation methodology.

Table 5: 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

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 sulfates 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 sulfur 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 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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

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

13. TEMPORAL DISSAGGREGATION CRITERIA

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

14. ADDITIONAL COMMENTS

15. SUPPLEMENTARY DOCUMENTS

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.

Environment Canada, Environmental Protection Service. Air Pollution Emissions and Control Technology: Primary Copper Industry. Economic and Technical Review Report EPS 3-AP-82-4, Air Pollution Control Directorate, July 1982.

16. VERIFICATION PROCEDURES

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

17. REFERENCES

Environment Canada (1982) Air pollution emissions and control technology: primary copper industry. Environment Canada, Environmental Protection Service, Economic and Technical Review Report EPS 3-AP-82-4, Ottawa, Canada.

EPA (1993) Locating and estimating air emissions from sources of mercury and mercury compounds. The U.S. Environmental Protection Agency, EPA-454/R-93-023, Research Triangle Park, NC.

EPA (1995) AP 42 CD-Rom. The U.S. Environmental Protection Agency, Research Triangle Park, NC.

Jaques A.P. (1987) Summary of emissions of antimony, arsenic, cadmium, copper, lead, manganese, mercury and nickel in Canada. Environment Canada, Conservation and Protection, Environmental Analysis Branch, Ottawa, Canada.

Jockel W. and Hartje J. (1991) Datenerhebung über die Emissionen Umweltgefährdender Schwermetalle, Forschungsbericht 91-104 02 588, TUV Rheinland, Cologne, Germany.

Nriagu J.O. and Pacyna J.M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333, 134-139.

Pacyna J.M. (1987a) Methods for air pollution abatement. In: E.E. Pickett, ed. *Atmospheric Pollution*, Hemisphere Publ. Corp., Washington DC.

Pacyna J.M. (1987b) Atmospheric emissions of arsenic, cadmium, lead and mercury from high temperature processes in power generation and industry. In: T.C. Hutchinson and K.M. Meema, eds., *Lead, Mercury, Cadmium and Arsenic in the Environment*, Wiley, Chichester, the United Kingdom.

Pacyna J.M. (1989) Technological parameters affecting atmospheric emissions of trace elements from major anthropogenic sources. In: J.M. Pacyna and B. Ottar, eds., *Control and Fate of Atmospheric trace Metals*, Kluwer Academic Publ., Dordrecht, the Netherlands.

Pacyna J.M. (1994) Emissions of heavy metals in Europe. In: *Background Document for the EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants*, Beekbergen, the Netherlands, 3-6 May, 1994.

Pacyna J.M., Zwozdziak A., Zwozdziak J. and Matyniak Z. (1981) Physico-chemical transformations of pollutants in the individual environmental media. Technical University of Wroclaw, Report SPR-14/81, Wroclaw, Poland (in Polish).

PARCOM (1991) Report of the 9th Meeting of the Working Group on Atmospheric Input of Pollutants to Convention Waters, London, 5-8 November, 1991.

PARCOM (1992) Emission Factor Manual PARCOM-ATMOS. Emission factors for air pollutants 1992. P.F.J. van der Most and C. Veldt, eds., TNO Environmental and Energy Research, TNO Rept. 92-235, Apeldoorn, the Netherlands.

UN ECE (1994) State-of-the-art report on heavy metals emissions. UN Economic Commission for Europe, Convention on Long-range Transboundary Air Pollution, Task Force on Heavy Metals Emissions, Prague, the Czech Republic.

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : December 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: + 47 63898155
Fax: + 47 63898050

Supported by : Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030307
040300

SOURCE ACTIVITY TITLE : Secondary Lead Production

PARCOM-ATMOS CODE : 3.0

NACE CODE : 27.43

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 refinery, producing about 40 % of the total lead production (e.g. 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 such lead alloys 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 (e.g. Environment Canada, 1983; Parker, 1978).

2. CONTRIBUTIONS TO TOTAL EMISSIONS

There are several trace elements which 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 the secondary lead production contributes well below 1 % of the total atmospheric emissions of lead, antimony, selenium, and zinc. Similar contribution of atmospheric emissions during the secondary lead production was estimated for the European emissions in the early 1980's (Pacyna, 1983). However, a secondary lead smelter or refinery can be an important emission source on a local scale.

The contribution of emissions released from secondary lead 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	NMVOG	CH ₄	CO	CO ₂	N ₂ O	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

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 process into refined lead, lead alloys or lead oxide. The high proportion of scrap-acid batteries which is re-processed provides feed for the alloy lead market (e.g. Barbour et al., 1978).

Removal of some organic components in the input materials is often necessary prior to the secondary smelting of lead storage batteries in the blast furnaces. At present this can be achieved through the application of impact crushing or drum breaking followed by heavy media separation or elutriation to isolate the metal and organic fractions. These operations are utilized in bulk battery processing techniques, e.g. Stolberger, Tonolli, Penarroya, etc. The heavy media to be separated in these techniques are often made up from a slurry of battery paste fractions. As the disposal of organic materials containing lead, which were produced during the separation is very much restricted, the development of other methods was stimulated, such as the Bergsoe and Oerlikon whole battery processes. In the former method the battery is processed in a blast furnace with an incinerator. In the Oerlikon process, batteries are treated in a co-current kiln where the organic material is burned (e.g. Barbour et al., 1978).

Atmospheric emissions of various pollutants are also generated during the treatment of lead-containing materials in (1) rotary furnaces or sweating tubes (for materials which contain a small percentage of lead), and (2) reverberatory furnaces (for materials of high lead content).

Fuming of slags generated in lead smelting is an important operation mostly due to the re-use of zinc, frequently associated with lead in various concentrates and products. Both, zinc and lead are distilled and re-collected after oxidation as a fume, which becomes the feed to a plant for zinc metal winning. Large amounts of gases and particles are generated during the slag fuming operation.

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. Controls

Most of the secondary lead smelters are equipped with dust removing installations, such as baghouses. The control efficiency of these installations is often very high reaching 99.9 %.

Exhaust gases often pass through waste heat boilers. Wet scrubbers are sometimes in place for the reduction of SO₂.

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 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 lead 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 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, very often high point sources, e.g. with up to 100 m high stacks if plant specific data are available.

8. EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 2 contains fuel related emission factors for secondary lead production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/m³ fuel), 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 values for the specific energy consumption have been reported from 38.5 and 100 GJ/Mg product.

Table 2: Emission factors for secondary lead production⁷⁾

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 ₂ O [g/GJ]
l	oil	residual	203							
l	oil	gas	204							
g	gas	natural	301	8 ¹⁾ , 0.85 ²⁾	60 ¹⁾²⁾ , 110 ⁶⁾	10 ¹⁾	2 ¹⁾	30 ¹⁾ , 7 ²⁾	55 ¹⁾²⁾	3 ¹⁾

¹⁾ CORINAIR90 data, area sources

²⁾ CORINAIR90 data, point sources

³⁾ SO _x : (EPA, 1990)	0	g/Mg charged	Pot furnace
	40,000	g/Mg charged	Reverberatory furnace
	26,500	g/Mg charged	Blast furnace (cupola)
	17.26	g/l burned	Pot furnace heater, NAPFUE 204
	9,611	g/Mm ³ burned	Pot furnace heater NAPFUE 301
	17,209 · S	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204, S = sulphur content of fuel
	19,006 · S	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203, S = sulphur content of fuel
⁴⁾ NO _x : (EPA, 1990)	0	g/Mg charged	Pot furnace
	150	g/Mg charged	Reverberatory furnace
	50	g/Mg charged	Blast furnace (cupola)
	2.4	g/l burned	Pot furnace heater, NAPFUE 204
	2,242,573	g/Mm ³ burned	Pot furnace heater NAPFUE 301
	2396.78	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204
	6591.15	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203
⁵⁾ VOC: (EPA, 1990)	0.024	g/l burned	Pot furnace heater, NAPFUE 204
	44,851	g/Mm ³ burned	Pot furnace heater, NAPFUE 301
	23.97	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204
	33.55	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203
	44,851	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 301
	44,851	g/m ³ fuel	Secondary metal production, process heaters, process gas

⁶⁾ It is assumed, that emission factors cited within the table are related to combustion sources in secondary lead production; other process emissions are not covered.

⁷⁾ Bremmer, 1995.

A list of emission factors for several trace elements emitted from secondary lead 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 lead production or different production technologies used at present. Therefore, the factors in table 2 can only be used in a simpler emission estimation methodology.

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

Element	Estimates by Pacyna (1986)	Estimates in Canada (Jacques, 1987)	PARCOM program (PARCOM, 1992)	Environment in Canada (1983)	Estimates in the U.K. (Leech, 1993)	Estimates in Austria (Schneider, 1994)	Suggested
Arsenic						8	?
Cadmium	2.5		2.5		2.5	3.0	2.5
Copper		1.0					1.0
Lead	770	200	130	100-300	200	150	100-300
Zinc	300		300		300	150	300
Control	ESP, ca. 99% efficiency	Based on questionnaires. Most plants use ESPs with 99% efficiency	Unspecified	Unspecified	ased on mission factors y Pacyna and ARCOM	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 lead production. It can be assumed that the majority of trace elements volatilized from scrap and other lead-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 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). Even bigger 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. Obviously, 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 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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

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

13. TEMPORAL DISSAGGREGATION CRITERIA

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

14. ADDITIONAL COMMENTS

15. SUPPLEMENTARY DOCUMENTS

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.

Environment Canada, Environmental Protection Service. National Inventory of Sources and Emissions of Lead. Economic and Technical Review Report EPS 3-EP-83-6, Air Pollution Control Directorate, November 1983.

16. VERIFICATION PROCEDURES

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

17. REFERENCES

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.

Bremmer, H. J. (1995) Secundaire Non-Ferroindustrie; RIVM-report 773006174; RIZA-report 92.003/74.

Environment Canada (1983) National Inventory of Sources and Emissions of Lead. Environment Canada, Environmental Protection Service, Economic and Technical Review Report EPS 3-EP-83-6, Ottawa, Canada.

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

ILZSG (1985) World Directory: Secondary Lead Plants. International Lead and Zinc Study Group Report, London.

Jaques A.P. (1987) Summary of emissions of antimony, arsenic, cadmium, copper, lead, manganese, mercury and nickel in Canada. Environment Canada, Conservation and Protection, Environmental Analysis Branch, Ottawa, Canada.

Leech P.K. (1993) UK atmospheric emissions of metals and halides 1970-1991. Warren Spring Laboratory Rept. LR 923, Stevenage, UK.

Nriagu J.O. and Pacyna J.M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333, 134-139.

Pacyna J.M. (1983) Trace element emission from anthropogenic sources in Europe. Norwegian Institute for Air Research, NILU Rept. TR 10/82, Lillestrøm, Norway.

Pacyna J.M. (1989) Technological parameters affecting atmospheric emissions of trace elements from major anthropogenic sources. In: J.M. Pacyna and B. Ottar, eds., Control and Fate of Atmospheric trace Metals, Kluwer Academic Publ., Dordrecht, the Netherlands.

Pacyna J.M. (1994) Emissions of heavy metals in Europe. In: Background Document for the EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants, Beekbergen, the Netherlands, 3-6 May, 1994.

PARCOM (1992) Emission Factor Manual PARCOM-ATMOS. Emission factors for air pollutants 1992. P.F.J. van der Most and C. Veldt, eds., TNO Environmental and Energy Research, TNO Rept. 92-235, Apeldoorn, the Netherlands.

Parker A. (ed) (1978) Industrial Air Pollution Handbook, McGraw-Hill Book Comp. Ltd., London

Schneider M. (1994) Heavy metal emissions in Austria. Umweltbundesamt report to the UN ECE Task Force on Heavy Metals Emissions. Wien, March, 1994.

UN ECE (1994) State-of-the-art report on heavy metals emissions. UN Economic Commission for Europe, Convention on Long-range Transboundary Air Pollution, Task Force on Heavy Metals Emissions, Prague, the Czech Republic.

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : December 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: +47 63898155
Fax: +47 63898050

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030308 040300
SOURCE ACTIVITY TITLE :	Secondary Zinc Production
PARCOM-ATMOS CODE :	3.0
NACE CODE :	27.43

1. ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions during the production of zinc in secondary zinc smelters. There are more about 200 secondary zinc smelters in the world, producing about 20 % of the total lead production (e.g. Pacyna, 1989). 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 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 elements which can be emitted during the secondary zinc production. However, these emissions 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. Similar contribution of atmospheric emissions during the secondary zinc production was estimated for the European emissions in the beginning of the 1980's (Pacyna, 1983). 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 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 ₂ O	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

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, is processed in a two-stage separation-refining process (e.g. Barbour et al., 1978). The melting stage, known as sweating, is usually carried out in small, sloping-hearth reverberatory type furnaces provided with some means of agitating or stirring the charge, or sometimes in rotary kilns. At the end of a cycle, the molten zinc is separated from unmeltable constituents, which sink to the bottom of the furnace, and is cast for subsequent purification, if required, by distillation or refluxing. Some secondary zinc is processed to zinc dust.

A more sophisticated type of sweating operation involves holding scrap in a basket and raising to closely controlled temperature in a molten salt bath. 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).

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.

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.

3.2. Definitions

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

3.3. 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 the concentrations below 10 mg/m³.

Afterburners are reported for non-ferro-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 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 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 zinc 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 zinc 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 zinc smelters should be regarded as point sources if plant specific data are available.

8. EMISSION FACTORS, QUALITY CODES AND REFERENCES

Very limited information exists in the literature on emission factors for pollutants emitted during the secondary zinc production. Table 2 contains fuel related emission factors for secondary zinc production based on CORINAIR90 data in [g/GJ]. Techniques 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 value for the specific energy consumption of 38.5 GJ/Mg product has been reported.

Table 2: Emission factors for secondary zinc production⁵⁾

Type of fuel				NAPFUE code	Emission factors				
s	coke	hc	coke oven		SO ₂ ²⁾ [g/GJ]	No _x ³⁾ [g/GJ]	NMVOC ⁴⁾ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]
s	coke	hc	coke oven	107		27 ¹⁾		535 ¹⁾	105 ¹⁾
g	gas		natural	301	0.85 ¹⁾	60 ¹⁾		7 ¹⁾	55 ¹⁾

- 1) CORINAIR90 data, point sources
- 2) SO₂: (EPA, 1990)
 - 0 g/Mg product Pot furnace
 - 0 g/Mg zinc used Galvanising kettle
 - 9,150 g/Mg product Calcining kiln
 - 10,000 g/Mg zinc oxide prod. Retort distillation / oxidation
 - 20,000 g/Mg zinc oxide prod. Muffle distillation / oxidation
 - 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)
 - 950 g/Mg product Pot furnace
 - 200 g/Mg zinc used Galvanising kettle
 - 100 g/Mg product Rotary sweat furnace
 - 3,950 g/Mg zinc oxide produced Retort distillation / oxidation
 - 55,000 g/Mg zinc oxide produced Muffle distillation / oxidation
 - 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)
 - 0 g/Mg product Retort furnace
 - 30 g/Mg product Calcining kiln
 - 2 g/Mg processed Concentrate dryer
 - 1,200 g/Mg product Kettle sweat furnace, general metallic scrap / reverberatory sweat furnace, general metallic scrap / kettle sweat furnace, residual metallic scrap / reverberatory sweat furnace, residual metallic scrap / reverberatory sweat furnace, residual metallic scrap
 - 1,200 g/Mg product Reverberatory sweating / rotary sweating / muffle sweating / kettle (pot) sweating / electric resistance sweating
 - 1,200 g/Mg product Kettle (pot) melting furnace
 - 1,250 g/Mg product Crucible melting furnace, scrap smelting
 - 2,600 g/Mg product Reverberatory melting furnace, scrap smelting
 - 90 g/Mg product Electric induction melting furnace, scrap melting
 - 24 g/m³ fuel Primary metal production, process heaters, NAPFUE 204
 - 34 g/m³ fuel Primary metal production, process heaters, NAPFUE 203
 - 44,851 g/m³ fuel Primary metal production, process heaters, NAPFUE 301
 - 44,851 g/m³ fuel Primary metal production, process heaters process gas

⁵⁾ It is assumed, that emission factors cited within the table are related to combustion sources in secondary zinc production. Footnotes may contain emission factors for total emissions (fuel and process related).

Pacyna (1986) provides an uncontrolled emission factor of 9 kg Zn/tonne zinc produced. No information is available on emission factors for other trace elements.

9. SPECIES PROFILES

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

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.

11. WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Development of emission factors for trace elements and improvement of zinc emission factors is necessary in order to obtain emission estimates for the secondary zinc production. The improvement should focus on preparing individual emission factors for major industrial technologies currently employed in the zinc 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 zinc in various secondary zinc furnaces.

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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

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

13. TEMPORAL DISSAGGREGATION CRITERIA

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

14. ADDITIONAL COMMENTS

15. SUPPLEMENTARY DOCUMENTS

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

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

17. REFERENCES

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.

ILZSG (1985) World Directory: Secondary Lead Plants. International Lead and Zinc Study Group Report, London.

Nriagu J.O. and Pacyna J.M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333, 134-139.

Pacyna J.M. (1983) Trace element emission from anthropogenic sources in Europe. Norwegian Institute for Air Research, NILU Rept. TR 10/82, Lillestrøm, Norway.

Pacyna J.M. (1989) Technological parameters affecting atmospheric emissions of trace elements from major anthropogenic sources. In: J.M. Pacyna and B. Ottar, eds., *Control and Fate of Atmospheric trace Metals*, Kluwer Academic Publ., Dordrecht, the Netherlands.

Pacyna J.M. (1994) Emissions of heavy metals in Europe. In: *Background Document for the EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants*, Beekbergen, the Netherlands, 3-6 May, 1994.

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

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : December 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: +47 63898155
Fax: +47 63898050

Supported by : Rentz, Otto; Oertel, Dagmar
 Institute for Industrial Production
 University of Karlsruhe (TH)
 Hertzstraße 16, Bau 06.33
 D - 76187 Karlsruhe
 Federal Republic of Germany
 Tel.: 0049-721-608-4460 or -4569
 Fax: 0049-721-758909

SNAP CODE :	030309
	040300
SOURCE ACTIVITY TITLE :	Secondary Copper Production
PARCOM-ATMOS CODE :	3.0
NACE CODE :	27.44

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 ₂ O	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, shredder metals, and
- copper-iron scrap like electric motors or parts thereof, plated scrap, circuit elements and switchboard units, telephone scrap, transformers, and shredder 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 thermally 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 available 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/m³), 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 production⁷⁾

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 ₂ O [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 ³⁾ , 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/m ³ fuel	Secondary metal production, process heaters NAPFUE 204, S = sulphur content of fuel
	19,006 · S	g/m ³ 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/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204
	6,591	g/m ³ 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/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204
	34	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203
	44,851	g/Mm ³ fuel	Secondary metal production, process heaters, NAPFUE 301

⁵⁾ CO₂: Locally contaminated scrap input, brass production (Bremmer, 1995)

⁶⁾ CO₂: 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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

Not applicable.

13. TEMPORAL DISSAGGREGATION 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

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.

Bremmer H. J.(1995) Secundaire Non-Ferroindustrie; RIVM-report 773006174; RIZA-report 92.003/74.

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

Jaques A.P. (1987) Summary of emissions of antimony, arsenic, cadmium, copper, lead, manganese, mercury and nickel in Canada. Environment Canada, Conservation and Protection, Environmental Analysis Branch, Ottawa, Canada.

Leech P.K. (1993) UK atmospheric emissions of metals and halides 1970-1991. Warren Spring Laboratory Rept. LR 923, Stevenage, UK.

Nriagu J.O. and Pacyna J.M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333, 134-139.

Pacyna J.M. (1983) Trace element emission from anthropogenic sources in Europe. Norwegian Institute for Air Research, NILU Rept. TR 10/82, Lillestrøm, Norway.

Pacyna J.M. (1989) Technological parameters affecting atmospheric emissions of trace elements from major anthropogenic sources. In: J.M. Pacyna and B. Ottar, eds., Control and Fate of Atmospheric trace Metals, Kluwer Academic Publ., Dordrecht, the Netherlands.

Pacyna J.M. (1994) Emissions of heavy metals in Europe. In: Background Document for the EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants, Beekbergen, the Netherlands, 3-6 May, 1994.

PARCOM (1992) Emission Factor Manual PARCOM-ATMOS. Emission factors for air pollutants 1992. P.F.J. van der Most and C. Veldt, eds., TNO Environmental and Energy Research, TNO Rept. 92-235, Apeldoorn, the Netherlands.

Parker A. (ed) (1978) Industrial Air Pollution Handbook, McGraw-Hill Book Comp. Ltd., London

Schneider M. (1994) Heavy metal emissions in Austria. Umweltbundesamt report to the UN ECE Task Force on Heavy Metals Emissions. Wien, March, 1994.

UN ECE (1994) State-of-the-art report on heavy metals emissions. UN Economic Commission for Europe, Convention on Long-range Transboundary Air Pollution, Task Force on Heavy Metals Emissions, Prague, the Czech Republic.

18. BIBLIOGRAPHY

To be completed

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : December 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: +47 63898155
Fax: +47 63898050

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030310
040300

SOURCE ACTIVITY TITLE : Secondary Aluminium Production

PARCOM-ATMOS CODE : 3.0

NACE CODE : 27.42

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. Secondary aluminium industry is characterized 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 1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO ₂	NO _x	NMVOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃
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

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 CO₂ and H₂O. 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/ m³.

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 2 contains fuel related emission factors for secondary aluminium production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/m³), 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 1.7 up to 3.5 GJ/Mg product has been reported.

Table 2: Emission factors for secondary aluminium production⁶⁾

Type of fuel			NAPFUE code	Emission factors						
				SO ₂ ²⁾ [g/GJ]	No _x ³⁾ [g/GJ]	NM VOC ⁴⁾ [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [g/GJ]
l	oil	residual	203	143 ¹⁾	100 ¹⁾	3 ¹⁾	5 ¹⁾	12 ¹⁾	73 ¹⁾	10 ¹⁾
l	oil	gas	204	1,410 ¹⁾	100 ¹⁾			12 ¹⁾	75 ¹⁾	
g	gas	natural	301						87-100 ⁵⁾	54-58 ⁵⁾

¹⁾ CORINAIR90 data, area sources

²⁾ SO _x : (EPA, 1990)	1,750	g/Mg product	Sweating furnace
	1,250	g/Mg product	Smelting furnace, crucible
	450	g/Mg product	Smelting furnace, reverberatory
	150	g/Mg product	Burning, drying
	537	g/Mg product	Heavily contaminated scrap input
	10	g/Mg charged	Pouring, casting
	17,209 · S	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204, S=sulphur content of fuel
	19,006 · S	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203, S=sulphur content of fuel
³⁾ NO _x : (EPA, 1990)	300	g/Mg product	Sweating furnace
	850	g/Mg product	Smelting furnace, crucible
	380	g/Mg product	Smelting furnace, reverberatory
	250	g/Mg product	Burning, drying
	750	g/Mg product	Annealing furnace
	750	g/Mg product	Slab furnace
	5	g/Mg product	Pouring, casting
	350	g/Mg product	Can manufacture
	350	g/Mg product	Rolling, drawing, extruding
	2,397	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204
	6,591	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203
⁴⁾ VOC: (EPA, 1990)	1,200	g/Mg product	Sweating furnace
	1,250	g/Mg product	Smelting furnace, crucible
	100	g/Mg product	Smelting furnace, reverberatory
	16,000	g/Mg product	Burning, drying
	650	g/Mg product	Foil rolling
	1,200	g/Mg product	Foil converting
	2	g/Mg product	Annealing furnace
	2	g/Mg product	Slab furnace
	70	g/Mg product	Pouring, casting
	150,000	g/Mg product	Can manufacture
	45	g/Mg product	Rolling, drawing, extruding
	24	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 204
	34	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 203
	44,851	g/m ³ fuel	Secondary metal production, process heaters, NAPFUE 301
	44,851	g/m ³ fuel	Secondary metal production, process heaters, process gas

⁵⁾ Very weakly contaminated scrap input (Bremmer, 1995)

⁶⁾ It is assumed, that emission factors cited within the table are related to combustion sources in secondary aluminium production. Footnotes may contain emission factors for total emissions (fuel and process related).

Fine particle emission factors cited in U.S. EPA (1973) and Economopoulos (1993) are presented in Table 3.

Table 3: Emission factors for fine particles from the secondary aluminium production (U.S.EPA, 1973).

Type of operation	Emission factor, g/tonne Al produced		
	Uncontrolled	Baghouse	Electrostatic precipitator
1) Sweating furnace (Pre-treatment)	7250	1650	-
2) Smelting			
- Crucible furnace	950	-	-
- Reverberatory furnace	2150	650	650
3) Chlorination ^{*1}	500	25	-

^{*1} in kg/tonne chlorine used

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).

A dioxin emission factor of 0.13 g/ aluminium produced was also cited in PARCOM (1992).

9. SPECIES PROFILES

Not applicable.

10. 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 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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

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

13. TEMPORAL DISSAGGREGATION CRITERIA

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

14. 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.

17. REFERENCES

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.

Bremmer H. J. (1995) Secundaire Non-Ferroindustrie; RIVM-report 773006174; RIZA-report 92.003/74.

Economopoulos A.P. (1993) Assessment of sources of air, water, and land pollution. A guide to rapid source inventory techniques and their use in formulating environmental control strategies. Part one: Rapid inventory techniques in environmental pollution. World Health Organization, Geneva.

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

PARCOM (1992) Emission Factor Manual PARCOM-ATMOS. Emission factors for air pollutants 1992. P.F.J. van der Most and C. Veldt, eds., TNO Environmental and Energy Research, TNO Rept. 92-235, Apeldoorn, the Netherlands.

Parker A. (ed) (1978) Industrial Air Pollution Handbook, McGraw-Hill Book Comp. Ltd., London

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.

UN (1994) Statistical Yearbook - 1992. United Nations, Department for Economic and Social Information and Policy Analysis, Statistical Division, New York, NY.

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : December 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: +47 63898155
Fax: +47 63898050

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030311
SOURCE ACTIVITY TITLE :	Cement
NACE CODE :	26500
PARCOM CODE :	2.8.1.

1. ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within cement production. A detailed description of non-combustion processes in cement industry can be found in chapter B4612. However, in the following if useful for description, also non-combustion emissions are mentioned.

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 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 ₂ O	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. For heavy metal emissions, specific figures for this source activity are available from Baart *et al.* (1995). /1/ 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.

Table 2: Average relative contribution of the production of cement to the total emission of heavy metals in European countries

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

3. GENERAL

3.1. Description

The majority of the cement production is concentrated on two types of cement: portland cement and blast furnace cement.

In general, portland cement is produced from raw cement clinker which is being fired in a rotary kiln with gypsum anhydrite. This process is followed by dry milling and shipment. Blast furnace cement is produced by milling fired cement clinker, pre-dried blast furnace slag and gypsum anhydrite. The milled material is ready for shipment.

Types of fuels used vary across the industry. 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. /cf. 6/

3.2. Definitions

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.

3.3. Techniques

3.4. Emissions

Dust emissions result from activities such as handling raw materials, on site transportation, firing of clinker, milling and shipment.

Nitrogen oxides (NO_x), sulphur dioxide (SO₂), carbon monoxide (CO), and carbon dioxide (CO₂) are the primary emissions in the manufacture of portland cement. Small quantities of volatile organic compounds (NMVOC, methane (CH₄)), nitrous oxide (N₂O), and ammonia (NH₃) also may be emitted (see also table 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. /cf. 6/

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. /cf. 6, 7/

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 klinker by chemical combination. /cf. 6, 7/

The CO₂ 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 CO₂. Substantial quantities of CO₂ are also generated through calcining of limestone or other calcareous material (see chapter B4612). This calcining process thermally decomposes CaCO₃ to CaO and CO₂. The amount of CO₂ released in the calcining process is about 500 kilograms (kg) per Mg of portland cement produced. Total CO₂ emissions from the pyroprocess depend on energy consumption and generally fall in the range of 0.85 to 1.35 Mg of CO₂ 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. /cf. 6, 7/

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. /cf. 6/

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. /8/

3.5. Controls

Emission reduction is usually obtained by reducing the dust emissions. Electrostatic precipitation and fabric filters are most widely used. For electrostatic precipitation dust concentration of 30 - 40 mg/m³ can be achieved. For fabric filters a value of 20 to 50 mg/m³ is common.

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 airstream - 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 SO₂ into the product, thereby mitigating the quantity of SO₂ emissions in the exhaust stream. Depending on the process and the source of the sulphur, SO₂ 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 SO₂. /cf 6, 7/

Oxides of nitrogen can be reduced by applying the following techniques /cf. 7/:

- 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. /8/

4. SIMPLER METHODOLOGY

Multiplying the relevant emission factor listed in section 8 with the appropriate energy consumption or production figure yields the emission.

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 the dust for the total process.

6. ACTIVITY STATISTICS

Standard production and energy consumption statistics.

7. POINT SOURCE CRITERIA

The cement production plants are usually connected to high chimneys and should 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:

PORTLAND CEMENT PRODUCTION, DRY PROCESS:

fuel preparation

energy : 0.3 GJ/ton cement

dust : 0.02 kg/ton cement

clinker firing

energy : 3.6 GJ/ton cement

dust* : 0.1 kg/ton cement

SO₂ : 0.6 kg/ton cement

NO_x : 2.0 kg/ton cement

CO : 0.4 kg/ton cement

CO₂ process : 430 kg/ton cement

CO₂ fuel : 325 kg/ton cement

cement milling dust : 0.1 kg/ton cement

cement shipping dust : 0.03 kg/ton cement

BLAST FURNACE CEMENT

raw materials transport

dust : 0.05 - 0.06 kg/ton cement

cement drying, milling, shipping

dust : 0.04 - 0.08 kg/ton cement

energy : 0.5 - 0.7 GJ/ton cement

* Dust is the main source of heavy metals. The emission factors are determined by the composition of the basic material and the type of fuels used for firing. An illustration of the range of emission factors to be expected is given in table 3. This table is derived from the PARCOM-ATMOS Emission Factors Manual.

Table 3: Examples of emission factors for heavy metals from cement production in g/Mg cement

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

- Not available

The following Table 4 contains fuel related 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 4: Emission factors for the production of cement⁸⁾

Type of fuel				NAFFUE code	Emission factors							
					SO ₂ ²⁾ [g/GJ]	NO _x ³⁾ [g/GJ]	NM VOC ⁴⁾ [g/GJ]	CH ₄ ⁷⁾ [g/GJ]	CO ⁶⁾ [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [g/GJ]	NH ₃ [g/GJ]
s	coal	hc	coking	101	569 ¹⁾ , 85-16 ⁵⁾	701 ¹⁾ , 450-709 ⁵⁾		1 ¹⁾⁵⁾		86 ¹⁾⁵⁾		
s	coal	hc	steam	102	44-880 ¹⁾ , 35-600 ⁵⁾	150-170 ¹⁾ , 0.4-575 ⁵⁾	15 ¹⁾ , 15-33 ⁵⁾	14.7-15 ¹⁾ , 0.3-15 ⁵⁾	10-110 ¹⁾ , 18-100 ⁵⁾	93-94 ¹⁾ , 78-101 ⁵⁾	12 ¹⁾ , 3- 12 ⁵⁾	
s	coal	hc	sub-bituminous	103	134-154 ¹⁾ , 1,260 ⁵⁾	57 ¹⁾ , 820-1,300 ⁵⁾			22 ¹⁾	99 ¹⁾ , 320-420 ⁵⁾	8 ⁵⁾	
s	coal	hc	brown coal/lignite	105	25 ⁵⁾	575 ⁶⁾	15 ⁵⁾	15 ⁵⁾		100-113 ⁵⁾	3.5 ⁵⁾	
s	coal	hc	briquettes	106	11 ⁵⁾	575 ⁶⁾	15 ⁵⁾	15 ⁵⁾	100-260 ⁵⁾	97-98 ⁵⁾	3.5 ⁵⁾	
s	coke	hc	coke oven	107	25 ⁵⁾	575 ⁵⁾	15 ¹⁾ , 0.5 ⁵⁾	15 ¹⁾ , 0.5 ⁵⁾	110 ¹⁾ , 100 ⁵⁾	108 ¹⁾ , 100-105 ⁵⁾	14 ¹⁾ , 4 ⁵⁾	
s	coke		petroleum	110	355-511 ¹⁾ , 85-1,200 ⁵⁾	300-568 ¹⁾ , 0.4-575 ⁵⁾	1.5 ¹⁾ , 1.5-15 ⁵⁾	1.5 ¹⁾ , 1-15 ⁵⁾	10-70 ¹⁾ , 15-100 ⁵⁾	99-102 ¹⁾ , 97-102 ⁵⁾	14 ¹⁾ , 3- 14 ⁵⁾	
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 ⁵⁾	0.4-568 ⁵⁾		0.2 ⁵⁾	1429 ⁵⁾	83 ⁵⁾	4 ⁵⁾	
l	oil		residual	203	131-1,030 ¹⁾ , 16-1,079 ⁵⁾	150-220 ¹⁾ , 0.4-575 ⁵⁾	3 ¹⁾ , 3-10 ⁵⁾	1-3 ¹⁾ , 1-5 ⁵⁾	15-20 ¹⁾ , 8-79 ⁵⁾	76-79 ¹⁾⁵⁾	2-15 ¹⁾⁵⁾	
l	oil		gas	204	4-1,410 ⁵⁾	0.4-575 ⁵⁾	1.5 ¹⁾ , 1.5-2.5 ⁵⁾	1-5 ¹⁾ , 1-8 ⁵⁾	12 ¹⁾ , 12-79 ⁵⁾	74 ¹⁾ , 73- 74 ⁵⁾	12 ¹⁾ , 2- 14 ⁵⁾	
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 ⁵⁾	175 ¹⁾ , 60-560 ⁵⁾	2.5 ¹⁾ , 2.5-18.4 ⁵⁾	2.5 ¹⁾ , 0.4-5 ⁵⁾	20 ¹⁾ , 10-120 ⁵⁾	53-56 ¹⁾ , 55-69 ⁵⁾	3 ¹⁾ , 1- 3.7 ⁵⁾	
g	gas		liquified petroleum gas	303	0.04 ⁵⁾	100 ⁵⁾	2.5 ¹⁾ , 2.1 ⁵⁾	2.5 ¹⁾ , 0.9 ⁵⁾	20 ¹⁾ , 13 ⁵⁾	65 ¹⁾⁵⁾	3 ¹⁾ , 1 ⁵⁾	
g	gas		coke oven	304	0.6 ⁵⁾	575 ⁵⁾	2.5 ⁵⁾	2.5 ⁵⁾	10 ⁵⁾	44 ⁵⁾	1.5 ⁵⁾	

1)	CORINAIR90 data, point sources		
2)	SO _x :	5,100 g/Mg product	Dry process kilns /1/
		5,100 g/Mg product	Wet process kilns /1/
		258 g/Mg cement	Cement production /2/
		191 g/Mg cement	Cement production /2/
		0.023 g/GJ	Clinker production /3/
		50 g/GJ	Clinker production /3/
3)	NO _x :	1,400 g/Mg product	Dry process kilns /1/
		1,400 g/Mg product	Wet process kilns /1/
		2,100 g/Mg product	Dry process kilns /4/
		1,800 g/Mg product	Semi-wet process kilns /4/
		1,100 g/Mg product	Wet process kilns /4/
		1.2 g/GJ	Clinker production /3/
		130-220 g/GJ	Cement production /3/
		600 g/Mg clinker	Clinker production (80 % NO _x reduction 20 % energy saving)
		1,376 g/Mg cement	Cement production (1988) /2/
		1,296.5 g/Mg cement	Cement production (1993) /2/
		1,111 g/GJ	Cement/lime industry, kiln: natural gas /5/
		527 g/GJ	Cement/lime industry, kiln: oil /5/
		527 g/GJ	Cement/lime industry, kiln: coal /5/
4)	VOC:	10 g/Mg product	Dry process kilns /1/
		50,600 g/Mg cement	Cement production (1988) /2/
		49,406 g/Mg cement	Cement production (1993) /2/
5)	CORINAIR90 data, area sources (preliminary data)		
6)	CO:	83 g/GJ	Cement/lime industry, kilns: natural gas /5/
		79 g/GJ	Cement/lime industry, kilns: oil /5/
		79 g/GJ	Cement/lime industry, kilns: coal /5/
7)	CH ₄ :	1.1 g/GJ	Cement/lime industry, kilns: natural gas /5/
		1.0 g/GJ	Cement/lime industry, kilns: oil /5/
		1.0 g/GJ	Cement/lime industry, kilns: coal /5/
8)	It is assumed, that emission factors cited within the table are related to combustion sources in cement industry. Footnotes may also include emission factors for other process emissions.		

9. SPECIES PROFILES

An analysis of dust emissions from clincker firing in the Netherlands gave results presented in table 5. The composition is given in mg per ton cement:

Table 5: Composition of dust from clincker firing

Substance	concentration in dust
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

10. UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed per ton cement is estimated to be D.

11. WEAKEST ASPECTS IN CURRENT METHODOLOGY

Knowledge on 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 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

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

13. TEMPORAL DISAGGREGATION CRITERIA

Cement production can be considered as a continuous process.

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
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

- /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: AIRS Facility subsystem, EPA-Doc 450/4-90-003, Research Triangle Park, March 1990
- /3/ Hackl, A.; Mauschitz, G.: Emissionen aus Anlagen der österreichischen Zementindustrie; Vienna 1995
- /4/ Smit, J. R. K.: Produktie van Cement; RIVM-report 73601136;RIZA-report 92.003/41; Maart 1993
- /5/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook,; second Edition, Commission of the European Communities; Paris; 1992

- /6/ IPCC (ed.): Greenhouse Gas Inventory Reference Manual, Volume 3, 1995
- /7/ EPA (ed.): AP42 CD-Rom; 1995
- /8/ Her Majesty's Inspectorate of Pollution (HMSO) (ed.): Cement Manufacture and Associated Processes; Environmental Protection Act 1990; Process Guidance Note IPR 3/1; London; 1992

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 : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J. van der Most, R. Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by : Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030312

SOURCE ACTIVITY TITLE : Lime

PARCOM-ATMOS CODE :

NACE CODE : 26.52

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

Atmpsppheric 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 ₂ O	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 sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O). According to CORINAIR90 the main relevant pollutants are SO₂, NO_x, CO and CO₂ (see also table 1).

Sulfur dioxide emissions are influenced by several factors, including the sulfur content of the fuel, the sulfur content and mineralogical form (metal sulfide like pyrite, or sulfates 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 SO₂ emission factors are likely to vary significantly from the average emission factors presented here. The dominant source of sulfur emissions is the kiln's fuel, particularly coal and petroleum derived coke, where the levels of sulfur may be as high as 5 % by weight. The amount of sulfur present will vary widely according to the nature of the deposits used. During the calcining operation, sulfide and sulfates are decomposed to yield sulfur dioxide. On combustion of the fuel, the sulfur compounds present in the fuel are oxidised to sulfur dioxide, and pass through the burning zone of the kiln with the exhaust gases (EPA, 1995; HSMO, 1992).

When sulfur containing fuels are burnt, for practical purposes sulfur in the kiln exhaust may be assumed to be emitted as sulfur dioxide, although there is usually some sulfur trioxide formed. In the case of lime manufacture in shaft kilns, much of the sulfur re-combines with the burnt lime and the emissions of sulfur 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 sulfur is expelled as sulfur 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 sulfur oxide can be reduced by using low sulfur fuels and by limiting the sulfur contents of the fuel and raw materials. Sulfur dioxide emissions may be further reduced if the polluting equipment is fitted to desulfurise 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 sulfur is retained in the burnt lime. In most circumstances, especially in shaft kilns, only a small fraction of the sulfur 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			

Operation	Total suspended particles	SO ₂	NO _x	CO
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
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 works⁸⁾

Type of fuel				NAPFUE code	Emission factors						
					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 ₂ O [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⁾	95-98 ¹⁾	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⁾	300 ¹⁾	1.5 ¹⁾	1.5 ¹⁾	70-75 ¹⁾	97-99 ¹⁾	10-14 ¹⁾
s	biomass		wood	111	120-2,852 ²⁾	200-300 ²⁾	1.5-112 ²⁾	1.5-15 ²⁾	10-133 ²⁾	95-105 ²⁾	3-14 ²⁾
s	waste		industrial	116	5.2 ¹⁾	103-200 ¹⁾	48-50 ¹⁾	30-32 ¹⁾	1430- 6772 ¹⁾	92 ¹⁾	4-14 ¹⁾
l	oil		residual	203	47-1,470 ¹⁾	100-310 ¹⁾	3-4 ¹⁾	3-8 ¹⁾	12-6000 ¹⁾	73-78 ¹⁾	2-14 ¹⁾
l	oil		gas	204	94-1,712 ²⁾	170-215 ²⁾	3-46 ²⁾	1-3 ²⁾	7-94 ²⁾	75-78 ²⁾	2.5-14 ²⁾
g	gas		natural	301	85-305 ¹⁾	70-310 ¹⁾	1.5-2.5 ¹⁾	1-8 ¹⁾	10-20 ¹⁾ , 76 ²⁾	72-74 ¹⁾	2-14 ¹⁾
g	gas		coke oven	304	0.1-8 ¹⁾	50-111 ¹⁾	2.5-10 ¹⁾	0.4-4 ¹⁾	20-6000 ¹⁾	55-56 ¹⁾	1-3.7 ¹⁾
g	gas		blast furnace	305	0.9 ²⁾	14-100 ²⁾	2.5 ²⁾		13-17 ²⁾	53 ²⁾	1.5 ²⁾
g	gas		coke oven and blast furnace gas	306	15 ²⁾	83 ²⁾			84 ²⁾		
					63 ²⁾	286 ²⁾		2.5 ³⁾	286 ²⁾		
					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⁾ CH₄: 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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

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

13. TEMPORAL DISSAGGREGATION 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.

Economopoulos A.P. (1993) Assessment of sources of air, water, and land pollution. A guide to rapid source inventory techniques and their use in formulating environmental control strategies. Part one: rapid inventory techniques in environmental pollution. World Health Organization, Rept. WHO/PEP/GETNET/93.1-A, Geneva.

EPA (1990) AIRS Facility subsystem, EPA-Doc 450/4-90-003, Research Triangle Park.

EPA (1995) AP42 CD-Rom; Research Triangle Park.

HMSO 1992 Lime Manufacture and Associated Processes; Her Majesty's Inspectorate of Pollution, Environmental Protection Act 1990; Process Guidance Note IPR 3/1; London.

IPCC (1995) Greenhouse Gas Inventory Reference Manual, Volume 3.

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

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.

UN (1994) Statistical Yearbook - 1992. United Nations, Department for Economic and Social Information and Policy Analysis, Statistical Division, New York, NY.

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : December 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: +47 63898155
Fax: +47 63898050

Supported by : Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030313

SOURCE ACTIVITY TITLE: Asphalt Concrete Plants

PARCOM-ATMOS CODE :

NACE CODE : 26.6

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 ₂ O	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 DISSAGGREGATION CRITERIA FOR AREA SOURCES

13. TEMPORAL DISSAGGREGATION 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

19. RELEASE VERSION, DATE AND SOURCE

Version : 1.0

Date : 2 May, 1995

Source : Jozef M. Pacyna
Norwegian Institute for Air Research (NILU)
P.O.Box 100
2007 Kjeller
Norway
Phone: + 47 63898155
Fax: + 47 63898050

SNAP CODE :	030314
SOURCE ACTIVITY TITLE :	Flat Glass
NACE CODE :	26110
PARCOM CODE :	2.8.2

1. ACTIVITIES INCLUDED

The activities described are related to the combustion processes within the production of flat glass. A detailed description of non-combustion processes in glass industry can be found in chapter B4614. However, in the following if useful for description, also non-combustion emissions are mentioned.

2. CONTRIBUTION TO TOTAL EMISSION

The contribution of emissions released from flat glass 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 ₂ O	NH ₃
Flat Glass	030314	0.1	0.3	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

The emission of fluorides and of dust and heavy metals are also important.

3. GENERAL

3.1. Description of activities

Glass is mostly soda-lime glass, which is manufactured from sand, limestone, soda ash and broken glass. The mixture is heated in a melting furnace at temperatures up to 1500 °C. The molten glass is most frequently shaped following the float-glass principle, in which liquid tin is used.

3.2. Definitions

3.3. Techniques

Glass melting furnaces can be categorised, by their fuel source and method of heat application, into four types: recuperative, regenerative, unit, and electric melter. The recuperative, regenerative, and unit melter furnaces can be fuelled by either gas or oil. The current trend is from gas-fired to oil-fired. Recuperative furnaces use a steel heat exchanger, recovering heat from the exhaust gases by exchange with the combustion air. Regenerative furnaces use a lattice of brickwork to recover waste heat from exhaust gases. 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/

The furnace most commonly used is a continuous regenerative furnace. A furnace may have either side or end ports that connect brick checkers to the inside of the melter. The purpose of brick checkers is to conserve fuel by collecting furnace exhaust gas heat, which, when the air flow is reversed, is used to preheat the furnace combustion air. As material enters the melting furnace through the feeder, it floats on the top of the molten glass already in the furnace. As it melts, it passes to the front of the melter and eventually flows through a throat leading to the refiner. In the refiner, the molten glass is heat conditioned for delivery to the forming process. /6/ (see also chapter B4614)

In principle glass melting furnace designs are in operation as described in the chapter B 3315 „Container glass production“.

A typical energy consumption is 7 GJ per ton glass produced.

3.4. Emissions

Emissions such as: F, Cl and dust are produced by the melting process. Dust emission can also result from handling raw materials as well as from the melting process. Heavy metals will be present in the dust.

Other 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 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/ These emissions have to be allocated to SNAP 040614.

Sulphur oxides result from the decomposition of the sulphates in the batch and sulphur in the fuel /5/. 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/

Nitrogen oxide emissions arise both from the combustion process itself and from the volatilisation of nitrates in the batch. The amount of nitrogen oxides produced by the combustion process is mainly dependant upon the flame temperature, gas residence time and extent of oxygen enrichment. 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. In some frit formulations, nitrates are added to ensure that the melt is fully oxidised, thereby controlling the colours formed by those metal ions which are capable of existing in more than one oxidation state. No more than the minimum nitrate addition consistent with achieving this objective should be used. /8/ NO_x are from 90 to 97 % emitted as NO.

3.5. Controls

Using fuels low in or free of sulphur will result in a substantial reduction of SO₂-emissions. The selection of fuels depends on their availability and on the furnace design. /7/

The sorption of SO₂ (e.g. by supply of appropriate sorbents) requires more sophisticated process techniques. The removal efficiency for sorption of SO₂ can attain 10 to 50 %, varying by technique applied (e.g. dry/nearly dry). /cf 7/

A certain reduction in the formation of NO_x and of the heat consumption simultaneously, can be achieved by varying the excess air. The excess air in the combustion chamber should be kept as low as technically possible. The usage of supplemental electrical heat, as practised at some individual glass melters, may result in some additional reduction of NO_x formation. Primary measures are still in the testing state. Secondary measures for No_x control are in the state of development /cf 7/.

Flue gas recirculation makes a slight further reduction possible (requires technical changes), achieving a NO_x-reduction of 10 to 50 vol.-%. By staging of combustion air about half of the original NO_x-concentration can be realised by furnace optimisation: reducing air ratio and sealing burner blocks. /cf 9/

Emissions from combustion can also considerably be reduced by input of recycled glass due to reduced energy demand of the process (e.g. 1 t of recycled glass may reduce the energy demand up to 20 %).

Dust emissions from handling raw materials can be reduced using fabric filters or using different handling techniques.

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. RELEVANT ACTIVITY STATISTICS

Standard production and energy statistics available from national or international statistical publication.

7. POINT SOURCE CRITERIA

The production of flat glass is usually connected to medium size 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 for flat glass are given in kg per ton glass.

handling/shipping:

dust: 0.15 kg per ton

melting oven:

SO₂ 3.0 kg per ton

CO₂ 140 kg per ton

F_g 0.055 kg per ton

Cl_g 0.06 kg per ton

dust 0.37 kg per ton

fuel:

SO₂ 3.0 (fuel oil) kg per ton

CO₂ 530 kg per ton

NO_x 5.5 kg per ton

CO 0.09 kg per ton

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 2.

Table 2: Emission Factors for glass production in g/ton glass generalized for the situation in Germany.

Substance	Emission factor	Range
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 3: Emission factors for flat glass production⁶⁾

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 ₂ O [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 outlet 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 outlet 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 outlet 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.

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 per ton glass:

Substance	Concentration
Aluminum	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

The quality classification of the emission factors expressed per ton product is estimated to be C-D.

11. WEAKEST ASPECTS CURRENT METHODOLOGY

Knowledge about measurements related to abatement techniques is limited for heavy metals and dust emissions.

12. SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13. TEMPORAL DISAGGREGATION CRITERIA

The production of flat glass can be considered as a continuous process.

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.

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 by comparing the calculated emissions with measurements at an individual plant.

17. REFERENCES

- /1/ EPA (ed.): AIRS Facility subsystem, EPA-Doc 450/4-90-003, Research Triangle Park, March 1990
- /2/ Loos, B.: Produktie van Glas, Glas vezel en Glaswol; RIVM-report 736301115; RIZA-report 92.003/15; 1992
- /3/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook,; second Edition, comission of the European Communities, Paris; 1992
- /4/ Bundesumweltministerium (ed.). Erster Bericht der Regierung der Bundesrepublik Deutschland nach dem Rahmenübereinkommen der Vereinten Nationen über Klimaänderungen; 1994
- /5/ EPA (ed.): AP42 CD-Rom; 1995
- /6/ EPA (ed.): AP42 CD-Rom; 1994
- /7/ VDI (ed.): Emissionsminderung Glasshütten / Emission Control Gass Manufacture; VDI 2578; Düsseldorf; 1988
- /8/ Her Majesty's Inspectorate of Pollution (ed.): Glass Manufacture and Production Glass Frit and Enamel Frit; Environmental Protection Act 1990; Process Guidance Note IPR 3/5; London; 1992
- /9/ Barklage-Hilgefoot, H.J; Sieger, W.: Primary measures for the NOx-Reduction on Glass Melting Furnaces, in: Glasstechnik Bericht 62 (1989) 5

/10/ Jockel, W, and J.Hartje (1991) Datenerhebung über die Emissionen Umweltgefährdenden Schwermetalle. Forschungsbericht 91-1-4 02 588; TÜV Rheinland e.V. Köln.

18. BIBLIOGRAPHY

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

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M.Berdowski, P.F.J.van der Most, R.Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030315
SOURCE ACTIVITY TITLE :	Container Glass
NACE CODE :	26130
PARCOM CODE :	2.8.4

1. ACTIVITIES INCLUDED

The activities described are related to combustion process within the production of container glass. A detailed description of batch gas processes in glass industry can be found in chapter B4613. However, in the following if useful for description, also batch gas process steps are mentioned.

2. CONTRIBUTION TO TOTAL EMISSION

The contribution of emissions released from container glass 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 ₂ O	NH ₃
Container Glass	030315	0.1	0.2	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

The emissions of fluorides and some heavy metals may also be relevant.

3. GENERAL

3.1. Description

Commercially produced glass can be classified as soda-lime, lead, fused silica, borosilicate, or 96 % silica. Soda-lime glass consists of sand, limestone, soda ash, and cullet (broken glass). The manufacture of such glass is carried out in four phases: preparation of raw material, melting in a furnace, forming and finishing. /cf 4/ (see also chapter B4614)

3.2. Definitions

3.3. Techniques

In the glass melting furnace, the raw materials are heated to temperatures ranging from 1,500 to 1,700 °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. /4/

For the production of container glass ca. 70 % of the furnaces are operating with oil and ca. 30 % with natural gas.

Glass melting furnaces can be categorised by their fuel source and method of heat application, into four types: recuperative, regenerative, unit, and electric melter. The recuperative, regenerative, and unit melter furnaces can be fueled by either gas or oil. The current trend is the switch from gas-fired to oil-fired. Recuperative furnaces use a steel heat exchanger, recovering heat from the exhaust gases by exchange with the combustion air. Regenerative furnaces use a lattice of brickwork to recover waste heat from exhaust gases. 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. /4/

Both continuous and intermittent processes are used in glass melting. Mass production glasses are almost exclusively melted in large continuous tanks while smaller quantities such as those for hand-manufacture are made in intermittently operated pot furnaces. Glass batches are fed into melting furnaces especially designed and constructed for the type of glass to be produced and are melted at temperatures of between 1,450 and 1,600 °C. /5/

Individual types of furnaces often used are the following:

- Tank furnaces

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. Depending on the arrangement of the burners and the position of the flames, one differentiates between cross-fired and horseshoe-flame (end-fired) tanks. Small and medium-sized tanks are built as horseshoe-flame 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 5/

Another configuration of the tank furnace is the recuperatively-heated glass melting tank. In these furnaces the flames always flow in the same direction; the combustion air is preheated in ceramic or metal recuperators while the waste gas temperature is lowered simultaneously. In special cases waste heat boilers instead of recuperators, or in combination with recuperators, are installed. /cf 5/

The specific heat consumption of glass melting furnaces can vary between 4 and 30 MJ/kg and is a function of the type of glass and the furnace size. Fuel oil and natural gas are most often used as fuels although in some regions city gas is available. Liquefied gas is used in isolated cases. Coal dust combustion is not used. /5/

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. /5/

Sometimes, electrically-heated melting furnaces are used exclusively in which case flame heating serves only to start up the furnace, to support the heating of the melting tank or to heat the fore hearth (glass withdrawal basin). /5/

- Pot furnaces

In intermittently operated furnaces, glass is melted in special melting vessels called pots. 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. /cf 5/

The use of pot furnaces is confined to manually worked specialty glasses, with melting temperatures under 1,460 °C. City gas, natural gas, liquified 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 MJ/kg. /5/

- Electrically-heated furnaces

Glass melts are electrically conductive (ionic conduction). For normal furnace sizes and operating conditions, the heat energy necessary for melting and refining of the glass can be transmitted directly through electrodes in the glass. So far the application of electrical energy is confined to small and medium-sized melting furnaces for specialty glasses because of high operating cost. /cf 5/

A typical energy consumption is 5 - 7 GJ per ton glass produced.

3.4. Emissions

Emissions such as: gaseous F, Cl, Pb and dust are produced by the melting process.

Dust emission can result from handling raw materials as well as from the melting process.

Other pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O). According to CORINAIR90 the main relevant pollutants are SO₂, NO_x, and CO₂ (see also table 1).

The melting furnace contributes over 99 % of the total emissions from a glass plant, both particulates and gaseous pollutants. The fuel waste gas from glass melting furnaces consists mainly of carbon dioxide, nitrogen, water vapour, sulphur oxides and nitrogen oxides. The main pollutant emitted by the batch plant is particulates in the form of dust. /cf 4, 5/

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. If a nitrate refining is required for reasons of product quality, the NO_x emission can be significantly higher. The SO₃-content is 5 to 10 % of the SO₂-content. The amount of SO₃ depends on the excess air and the combustion temperature. /cf. 5/

The proportion of the air-polluting components in the fuel waste gas depends on the type of the firing fuel, its heating value, the combustion air temperature, the burner design, the flame configuration, and the excess air supply. The sulphur oxides in the waste gases of glass melting furnaces originate from the fuel used, as well as from the molten batches. The SO₂ content of the waste gas generated from the sulphur content of the firing fuel amounts to 2 g/m³; the SO₃ content, according to the available measurements, is 5 to 10 % of the SO₂ content. The amount of SO₃ depends on the excess air and the combustion temperature. The high temperatures required to melt the glass cause nitrogen oxides to form during the combustion of the fuel. Predominantly NO (ca. 95 %) is formed. Available test results show levels from 0.3 to 3.5 g/m³ (calculated as NO). The high levels are valid for high air preheating (e.g. regenerative installations), the lower levels for lower preheating (e.g. recuperative installations). /5/

Due to chemical reactions, batch gases consisting mainly of carbon dioxide are formed during the melting of the batches. Sulphur dioxide is found if the batches contain sulphates. The sulphur in the sulphates is partially bound in the glass as SO₃. The sulphur dioxide content of the waste gas originating from the batches depends largely on the sulphate content of the batches and the absorption ability of the glass and the dust for sulphur. /5/

Whenever salpeter must be used as a refining agent, approximately 2/3 of the nitrogen contained in it is emitted as NO_x together with the waste gases. The proportion of batch gases from exclusively flame-heated furnaces represents 3 to 5 % of the total gas volume. The point in time when the batch gases appear depends on design and operation of the furnace. In the case of pot furnaces that are intermittently operated, batch gases are released only during the start-up of the melting process. The batch gas proportion is nearly constant during the entire time in continuously-operated furnaces such as glass melting tanks. /5/

The majority of the translucent glasses are produced by the admixture of fluorides. The high melting temperature of the batches and the refining of the glass causes a partial evaporation of alkalis and at times of lead compounds, borates, fluorides, etc. /5/

The batch gas portion of the emissions has to be allocated to SNAP 040614.

Emission reduction techniques for exhaust gases are at this time not common. Certain emission reductions can be obtained by using oxygen instead of air for heating purposes. In the future it is possible that low-nox burners will be developed.

3.5. Controls

Processing techniques for the reduction of gaseous emissions are essentially restricted to the proper selection of firing fuels and raw materials, as well as to furnace design and operation. Using fuels low in or free of sulphur will result in a substantial reduction of SO₂-emissions. The selection of fuels depends on their availability and on the furnace design. The sorption of SO₂ (e.g. by supply of appropriate sorbents) requires more sophisticated process techniques. The removal efficiency for sorption of SO₂ can attain 10 to 50 %, varying by technique applied (e.g. dry/nearly dry). /cf 5/

The nitrogen oxides are emitted from 90 to 97 % as NO. A certain reduction in the formation of NO_x and of the heat consumption simultaneously, can be achieved by varying the excess air. The excess air in the combustion chamber should be kept as low as technically possible. The

usage of supplemental electrical heat, as practised at some individual glass melters, may result in some additional reduction of NO_x-formation (in research). Primary measures (firing techniques) for NO_x-reduction on glass melting tanks are still in the testing state. Secondary measures for NO_x-emissions are in the state of development /cf 5/.

Flue gas recirculation makes a slight further reduction of NO_x-emissions possible (requires technical changes), achieving a NO_x-reduction of 10 to 50 vol.-%. By staging of combustion air about half of the original NO_x-concentration can be realised by furnace optimisation: reducing air ratio and sealing burner blocks. /cf 6/

Emissions from combustion can also be reduced by input of recycled glass due to reduced energy demand of the process. For container glass up to 95 % of recycled glass can be used.

The waste gases of melting tanks for borate and lead glass are controlled with electrostatic and fabric filters. Electrostatic filters are also used in soda-lime glass melting tanks in the container glass industry. Emissions from electric melting tanks are also controlled by wet dust collectors. /5/

Emissions from handling raw materials can be reduced using fabric filters or using different handling techniques.

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 container glass is usually connected to medium size 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 for container glass are as follows:

handling/shipping:

dust: 0.03 - 0.15 kg per ton glass

melting oven:

SO ₂	1.2 kg per ton glass
CO ₂	150 kg per ton glass
F _g	0.014 kg per ton glass
Cl _g	0.05 kg per ton glass
dust	0.30 kg per ton glass

fuel:

SO ₂	3.0 (fuel oil) kg per ton glass
CO ₂	265 kg per ton glass
NO _x	3.8 kg per ton 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 /7/ produced some generalized emission factors for the situation in Germany. These factors, also used in the PARCOM-ATMOS Manual are given in table 2 in g/ton glass:

Table 2: Emission factors for glass production in g/ton glass generalized for the situation in Germany

Substance	Emission Factor	Range
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 3 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 3: Emission factors for container glass production⁷⁾

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 ₂ O [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⁾ CO₂: 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.

9. SPECIES PROFILES

No general applicable information is available.

10. UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed per ton glass is estimated to be D.

11. WEAKEST ASPECTS IN CURRENT METHODOLOGY

Knowledge about measurements related to abatement techniques is limited.

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.

13. TEMPORAL DISAGGREGATION CRITERIA

The production of container glass can be considered as a continuous process.

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.
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 by comparing the calculated emissions with measurements at an individual plant.

17. REFERENCES

- /1/ EPA (ed): AIRS Facility subsystem, EPA-Doc 450/4-90-003, Research Triangle Park, March 1990
- /2/ Loos, B.: Produktie van Glas, Glas vezel en Glaswol; RIVM-report 736301115; RIZA-report 92.003/15; 1992
- /3/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook; second Edition, commission of the European Communities, Paris; 1992
- /4/ EPA (ed.): AP42 CD-Rom; 1994
- /5/ VDI (ed.): Emissionsminderung Glasshütten / Emission Control Glass Manufacture; VDI 2578; Düsseldorf; 1988
- /6/ Barklage-Hilgefort, H.J; Sieger, W.: Primary measures for the NO_x-Reduction on Glass Melting Furnaces, in: Glasstechnik Bericht 62 (1989) 5
- /7/ Jockel, W, and J.Hartje (1991) Datenerhebung über die Emissionen Umweltgefährdenden Schwermetalle. Forschungsbericht 91-104 02 588; TÜV Rheinland e.V. Köln.

18. BIBLIOGRAPHY

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

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J. van der Most, R. Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030316
SOURCE ACTIVITY TITLE :	Glass Wool
NACE CODE :	26140
PARCOM CODE :	2.8.4

1. ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within glass wool production. The molten glass is spun into fibers, and treated with resins to form a wool-like product. A detailed description of batch gas processes in glass industry can be found in chapter B4614. 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 glass 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 ₂ O	NH ₃
Glass Wool	030316	0	0	-	-	-	-	-	-

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 national emission estimates are not available.

3. GENERAL

3.1. Description of activities

This type of glass is a boro-silicate glass, which is manufactured from sand, limestone, dolomite, boric-oxide and other oxides. The mixture is heated in a melting furnace at temperatures up to 1500 °C.

3.2. Definitions

Glasswool There exist two types of glass fibre products, textile and wool, which are manufactured by similar processes. Here only glasswool is taken into account.

3.3. Techniques

Glass melting furnaces can be categorised, by their fuel source and method of heat application, into four types: recuperative, regenerative, unit, and electric melter. The recuperative, regenerative, and unit melter furnaces can be fueled by either gas or oil. The current trend is from gas-fired to oil-fired. Recuperative furnaces use a steel heat exchanger, recovering heat from the exhaust gases by exchange with the combustion air. Regenerative furnaces use a lattice of brickwork to recover waste heat from exhaust gases. 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. Electric furnaces are currently used only for wool glass fiber production because of the electrical properties of the glass formulation. Unit melters are used only for the "indirect" marble melting process, getting raw materials from a continuous screw at the back of the furnace adjacent to the exhaust air discharge. /cf. 5/

The furnace most commonly used for glass melting is a continuous regenerative furnace. A furnace may have either side or end ports that connect brick checkers to the inside of the melter. The purpose of brick checkers is to conserve fuel by collecting furnace exhaust gas heat which, when the air flow is reversed, is used to preheat the furnace combustion air. As material enters the melting furnace through the feeder, it floats on the top of the molten glass already in the furnace. As it melts, it passes to the front of the melter and eventually flows through a throat leading to the refiner. In the refiner, the molten glass is heat conditioned for delivery to the forming process. /cf. 5/

Wool fiberglass insulation production lines usually consist of the following processes: preparation of molten glass, formation of fibers into a wool fiberglass mat, curing the binder-coated fiberglass mat, cooling the mat, and backing, cutting, and packaging the insulation. /5/ (see also chapter B4614)

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 fiber 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 fiber forming operation. /cf. 5/

During the formation of fibers into a wool fiberglass mat (the process is known as "forming" in the industry), glass fibers are made from molten glass, and a chemical binder is simultaneously sprayed on the fibers 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. Coloring agents may also be added to the binder. Two methods of creating fibers 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 fibers 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. /5/ (see also chapter B4614)

Energy consumption is typically around 12 GJ per ton glass produced

3.4. Emissions

Dust emission can result from handling raw materials as well as from the melting process.

Other pollutants released are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O). According to CORINAIR90 the main relevant pollutants are NO_x and SO₂ although they appear to make almost no contribution to the European total emissions (see also table 1).

The emissions from glass melting and refining include volatile organic compounds from the melt, raw material particles entrained in the furnace flue gas, and, if furnaces are heated with fossil fuels, combustion products. The variation in emission rates among furnaces is attributable to varying operating temperatures, raw material compositions, fuels, and flue gas flow rates. Of the various types of furnaces used, electric furnaces generally have the lowest emission rates, because of the lack of combustion products and of the lower temperature of the melt surface caused by bottom heating. /5/

Emissions generated during the manufacture of wool fiberglass insulation include solid particles of glass and binder resin, droplets of binder, and components of the binder that have vaporised. Test data show that approximately 99 percent of the total emissions from the production line are emitted from the forming and curing sections. /5/

Emissions, which do not result from the combustion process, have to be allocated to SNAP 040614 (see chapter B4614).

3.5. Controls

Emission control for furnaces in the glass melting and refining section is primarily fabric filtration. Fabric filters are effective on particulate matter (PM) and sulphur oxides (SO_x) and, to a lesser extent, on carbon monoxide (CO), nitrogen oxides (NO_x), and fluorides. The efficiency of these compounds is attributable to both condensation on filterable PM and chemical reaction with PM trapped on the filters. Reported fabric filter efficiencies on regenerative and recuperative wool furnaces are for PM, 95 percent; SO_x, 99 percent; and fluoride, 91 to 99 percent. Efficiencies on other furnaces are lower because of lower emission loading and pollutant characteristics. /cf 5/

The removal of organic compounds from the exhaust gases from the collecting and curing areas can be achieved using a wide range of measures. This includes mainly electrostatic precipitators and to a lesser extent incinerators, scrubbers and adsorbers. /4/

Emissions from handling raw materials can be reduced using fabric filters or using different handling techniques.

4. SIMPLER METHODOLOGY

The simpler methodology involves applying an appropriate emission factor to either production or energy statistics.

5. DETAILED METHODOLOGY

If an extensive measuring programme is available, emissions can be calculated on for an individual plant.

6. RELEVANT ACTIVITY STATISTICS

Standard production and energy statistics available from national or international statistical publications.

7. POINT SOURCE CRITERIA

The production of glass wool appears to be a minor source of emissions and hence can be regarded as an area source. However it could be regarded as point source if plant specific sources are available.

8. EMISSION FACTORS, QUALITY CODES AND REFERENCES

For the situation in the Netherlands, the following can be proposed:

Emission factors for several compounds in kg per ton glass wool are:

handling/shipping:

dust: 0.03 - 0.15 kg per ton glass

melting oven:

SO₂ 0.5 kg per ton glass

CO₂ 450 kg per ton glass

F_g 0.006 kg per ton glass

Cl_g 0.01 kg per ton glass

dust 0.04 (after dust collector) kg per ton glass

spinning/wool manufacturing:

formaldehyde 0.9 kg per ton glass

phenol(s) 0.3 kg per ton glass

ammonia 4.5 kg per ton glass

VOS 0.6 kg per ton glass

fuel:

SO₂ 5.0 (fuel oil) kg per ton glass

CO₂ 670 kg per ton glass

NO_x 2.8 kg per ton 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 in chapters B3314 and B3315 may be used.

The following Table 2 contains fuel related emission factors for the production of glasswool 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 2: Emission factors for the production of glasswool⁷⁾

Type of fuel			NAPFUE code	Emission factors						
				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 ₂ O [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⁾		8 ¹⁾	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.

9. SPECIES PROFILES

No general applicable profile for dust composition is available.

10. UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed as kg per ton glass is estimated to be D.

11. WEAKEST ASPECTS IN CURRENT METHODOLOGY

Knowledge about measurements related to abatement techniques is limited.

12. SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emissions could be disaggregated on the basis of plant capacity, employment or population statistics.

13. TEMPORAL DISAGGREGATION CRITERIA

The production of glass wool 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

PARCOM-ATMOS Emission Factors Manual.

16. VERIFICATION PROCESSES

Verification of the emissions can be done by comparing them with measurements at the individual plant.

17. REFERENCES

- /1/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook,; second Edition, comission of the European Communities; Paris; 1992.
- /2/ Loos, B.: Produktie van Glas, Glas vezel en Glaswol; RIVM-report 736301115; RIZA-report 92.003/15; 1992
- /3/ EPA (ed.): AIRS Facility subsystem; EPA-Doc 450/4-90-003; Research Triangle Park; 1990

- /4/ Her Majesty's Inspectorate of Pollution (HMSO) (ed.): Glass Fibres and Non-Asbestos Mineral Fibres; Environmental Protection Act 1990; Process Guidance Note IPR ¾; London; 1992
- /5/ EPA (ed.): AP42 CD-Rom; 1995

18. BIBLIOGRAPHY

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

19. RELEASE VERSION, DATE, AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J. van der Most, R. Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030317
SOURCE ACTIVITY TITLE :	Other Glass (including Special Glass)
NACE CODE :	26100
PARCOM CODE :	2.8.4

1. ACTIVITIES

This chapter covers emissions released from combustion processes within other glass production. The activities described are also related to the production of special glass. A detailed description of batch gas processes in glass industry can be found in chapter B4614. However, in the following if useful for description, also non-combustion emissions are mentioned.

2. CONTRIBUTION TO TOTAL EMISSION

Crystalware production is usually done in small plants.

The contribution of emissions due to fuel use, released from the production of other glass 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 ₂ O	NH ₃
Other Glass	030317	0	0.1	-	-	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 production process of special glass is not much different from the general glass melting process that is described in chapter B3315.

Emissions, other than these from fuel combustion, are covered by SNAP 040614 (see chapter B4614).

3.2. Definitions

3.2 Techniques

The production of special glass is similar to the the general glass melting process described in chapter B3315. In the glass melting furnace, the raw materials are heated to temperatures ranging from 1,500 to 1,700 °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. /4/ (see also chapter B4614)

Glass melting furnaces can be categorised, by their fuel source and method of heat application, into four types: recuperative, regenerative, unit, and electric melter. The recuperative, regenerative, and unit melter furnaces can be fueled by either gas or oil. The current trend is from gas-fired to oil-fired. Recuperative furnaces use a steel heat exchanger, recovering heat from the exhaust gases by exchange with the combustion air. Regenerative furnaces use a lattice of brickwork to recover waste heat from exhaust gases. 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. Electric furnaces are currently used only for wool glass fibre production because of the electrical properties of the glass formulation. Unit melters are used only for the "indirect" marble melting process, getting raw materials from a continuous screw at the back of the furnace adjacent to the exhaust air discharge. /4/

For some special glass, oil-firing is necessary.

3.4. Emissions

Pollutants released are dust, sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O). According to CORINAIR90 the main relevant pollutants are SO₂, NO_x, CO and CO₂ (see also table 1).

3.5. Controls

Here, it can be assumed, that the same abatement measures are applied as described in chapters B3314 - B3316. Emissions of nitrogen oxide, sulfur dioxide and dust are comparable with the emissions given in chapter B3315. Information about special emissions is scarce. Emissions of lead from lead crystal glass and cadmium for coloured glass are given below.

4. SIMPLER METHODOLOGY

The simpler methodology involves applying an appropriate emission factor to either production statistics or energy consumption figures.

5. DETAILED METHODOLOGY

If an extensive measuring programme is available, emissions can be calculated for an individual plant.

6. ACTIVITY STATISTICS

Standard production and energy consumption statistics from national or international statistical publications.

7. POINT SOURCE CRITERIA

The production of special glass is usually carried out at small plants that can be treated on an area basis. However, they can be regarded as point sources at a local level if plant specific data are available.

8. EMISSION FACTORS, QUALITY CODES AND REFERENCES

For the production of special glass the emission factors for general glass production as given in chapters B3314 and B3315 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 gram lead per 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. /6/
- For coloured glass an emission factor of 0.11-0.15 gram cadmium per Mg glass is mentioned.
- For the situation in Germany some specific information is given by Jockel and Hartje /5/. This information is given in table 2.

Table 2: Emission factors for heavy metals from special glass production in Germany in mg/kg product.

Substance	Emission Factor	Range
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 3 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 3: Emission factors for the production of other glass⁶⁾

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 ₂ O [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 ¹⁾	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

A general profile for the dust composition can not be given.

10. UNCERTAINTY ESTIMATES

The quality classification of the emission factors expressed per product is estimated to be D.

11. WEAKEST ASPECTS IN CURRENT METHODOLOGY

Knowledge about measurements related to abatement techniques is limited.

12. SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

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 special glass is usually a discontinuous process but no information is available on temporal profile.

14. ADDITIONAL COMMENTS

15. SUPPLEMENTARY DOCUMENTS

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 by comparing the calculated emissions with measurements at the individual plant.

17. REFERENCES

- /1/ Loos, B.: Produktie van Glas, Glas vezel en Glaswol; RIVM-report 736301115; RIZA-report 92.003/15; 1992
- /2/ EPA (ed.): AIRS Facility subsystem; EPA-Doc 450/4-90-003; Research Triangle Park; 1990
- /3/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook; second Edition, comission of the European Communities; Paris; 1992
- /4/ EPA (ed.): AP42 CD-Rom; 1994

- /5/ Jockel, W., and J.Hartje (1991) Datenerhebung über die Emissionen Umweltgefährdenden Schwermetalle. Forschungsbericht 91-104 02 588 TÜV Rheinland e.V. Köln.
- /6/ UK Energy Efficiency Office. Energy efficient environmental control in the glass industry. Good practice Guide no 127 (1994)

18. BIBLIOGRAPHY

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

19. RELEASE VERSION, DATE, AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M.Berdowski, P.F.J.van der Most, R. Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030318

SOURCE ACTIVITY TITLE : Mineral Wool

NACE CODE : 26230

PARCOM CODE : 2.8.4

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 fibers. The fibers 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 ₂ O	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 (MMMMF) 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 (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O). According to CORINAIR90 the main relevant pollutants are SO₂, NO_x, CO and CO₂ (see also table 1).

The cupola is a source of CO, CO₂ and NO_x emissions; SO₂ and H₂S 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 preparing 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 transferred 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:

SO₂ 1.5 kg per ton wool

CO₂ 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
 CO₂ 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 wool⁷⁾

Type of fuel				NAPFUE code	Emission factors							
					SO ₂ ²⁾ [g/GJ]	NO _x ³⁾ [g/GJ]	NMVO C ⁴⁾ [g/GJ]	CH ₄ ⁴⁾ [g/GJ]	CO ⁵⁾ [g/GJ]	CO ₂ ⁶⁾ [kg/GJ]	N ₂ O [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 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

- /1/ Kaskens, H. J. M.; Matthijsen, A. J. C. M.; Verburch, J. J.: Productie van steenwol; RIVM-report 736301114; RIZA-report 92.0003/14; 1992
- /2/ EPA (ed.): AIRS Facility Subsystem; EPA-Doc. 450/4-90-003; Research Triangle Park; 1990
- /3/ VDI (ed.): Emissionsminderungsanlagen zur Herstellung von Mineralfaserprodukten/Emission Control Facilities for the Production of Man-Made Mineral Fibres (MMMFM); VDI 3457; Düsseldorf; 1994
- /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

Version : 2.0

Date : November 1995

Source : P.F.J.van der Most, R.Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE :	030319
SOURCE ACTIVITY TITLE :	Bricks And Tiles
NACE CODE :	26400
PARCOM CODE :	2.8.4

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 ₂ O	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-draught and the round down draught. 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 (CH₄), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O), fluoride (F_g), Chlorine (Cl_g) and ammonia (NH₃). According to CORINAIR90 the main relevant pollutants are SO₂, NO_x, CO, and CO₂ (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 $< 5 \text{ mg/m}^3$ as hydrogen fluoride, sulphur trioxide 90 % removal, sulphur dioxide 10-15 % removal and particulate matter $< 50 \text{ mg/m}^3$.

- 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 ($< 50 \text{ mg/m}^3$). The main advantage of the standard cloth filter system is its ability to operate in high sulphur environments, possibly up to $2,000 \text{ mg/m}^3$ 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 caustic 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 m³ 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 _x H _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 tiles⁷⁾

Type of fuel				NAPFUE code	Emission factors							
					SO ₂ ²⁾ [g/GJ]	NO _x ³⁾ [g/GJ]	NMVO C ⁴⁾ [g/GJ]	CH ₄ ⁴⁾ [g/GJ]	CO ⁵⁾ [g/GJ]	CO ₂ ⁶⁾ [kg/GJ]	N ₂ O [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	303	0.04-2 ¹⁾	20-100 ¹⁾	1-4 ¹⁾	1 ¹⁾	13 ¹⁾	60-65 ¹⁾	1-3 ¹⁾	
g	gas		petroleum gas									
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/
NMVO:	< 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 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.; Mathijssen, A. J. C. M.: Großkeramische Industrie; RIVM-report 736301112; RIZA-report 92.003/12; 1995
- /2/ EPA (ed.): AIRS Facility subsystem; EPA-Doc 450/4-90-003; Research Triangle Park; 1990
- /3/ Bouscaren, M. R.: CORINAIR Inventory, Default Emission Factors Handbook; second Edition; Commission of the European Communities; Paris; 1992
- /4/ EPA (ed.): AP 42 CD-Rom; 1995
- /5/ Her Majesty's Inspectorate of Pollution (HMSO) (ed.): Ceramic Process; Environmental Protection Act 1990; Process Guidance IPR 3/6; London 1992

18. BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP 42 may be used.

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J. van der Most, R. Wessels Boer
TNO
P.O.Box 6011
2600 JA Delft
The Netherlands

Supported by : Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030320

SOURCE ACTIVITY TITLE : Fine Ceramics Materials

NACE CODE : 26250/26260

PARCOM CODE : 2.8.3

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 ₂ O	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 ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and montmorillonite $[(\text{Mg}, \text{Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}]$ 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 °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 (CH₄), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O), fluoride (F_g), Chlorine (Cl_g) and ammonia (NH₃). According to CORINAIR90 the main relevant pollutants are SO₂, NO_x, CO, and CO₂ (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 conducive 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 ceramics⁷⁾

Type of fuel				NAPFUE code	Emission factors							
					SO ₂ ³⁾ [g/GJ]	NO _x ⁴⁾ [g/GJ]	NM VOC [g/GJ]	CH ₄ [g/GJ]	CO ⁵⁾ [g/GJ]	CO ₂ ⁶⁾ [kg/GJ]	N ₂ O [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
290 g/Mg product
210 g/Mg product
Mineral products, process heaters, NAPFUE 301 /1/
General, SO₂ 260 g/Mg, SO_x 30 g/Mg /2/
Future Value /2/

⁴⁾ NO_x: 850 g/Mg product /2/

⁵⁾ CO: 1,600 g/Mg product
130 g/Mg product
EPA value for ceramic industry
/2/

⁶⁾ CO₂: 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 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.; Mathijssen, 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; Commission 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

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J. van der Most, R. Wessels Boer
TNO
P.O.Box 601
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

SNAP CODE : 030321

SOURCE ACTIVITY : Paper-mill Industry (Drying Processes)

NACE CODE : 21100

PARCOM CODE : 2.9.4

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 ₂ O	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 (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O) and ammonia (NH₃). According to CORINAIR90 the main relevant pollutants are SO₂ and CO₂ (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 SO₂ measurement data for combination boilers (boilers that co-fire coal or oil with wood residues) strongly suggests that a considerable amount of SO₂ 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 SO₂ 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

SO₂ 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
nitrogen dioxide	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 mills³⁾

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 ₂ O [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 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 SO₂ 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

Version : 2.0

Date : November 1995

Source : J.J.M. Berdowski, P.F.J.van der Most
TNO
P.O.Box 2611
2600 JA Delft
The Netherlands

Supported by : Rentz, Otto; Oertel, Dagmar
 Institute for Industrial Production
 University of Karlsruhe (TH)
 Hertzstraße 16, Bau 06.33
 D - 76187 Karlsruhe
 Federal Republic of Germany
 Tel.: 0049-721-608-4460 or -4569
 Fax: 0049-721-758909

SNAP CODE :	030322
SOURCE ACTIVITY :	Alumina Production
NACE CODE :	27420
PARCOM CODE :	2.2.4

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 ₂ O	NH ₃
Alumina 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 separated 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 compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O). Of these, according to CORINAIR90, the main relevant pollutants are SO₂ 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 production²⁾

Type of fuel				Emission factors						
				SO ₂ [g/GJ]	NO _x [g/GJ]	NM VOC [g/GJ]	CH ₄ [g/GJ]	CO [g/GJ]	CO ₂ [kg/GJ]	N ₂ O [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 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 Aluminiumschmelzflußelektrolyse (Entwurf); 1974

18. BIBLIOGRAPHY

19. RELEASE VERSION, DATE AND SOURCE

Version : 2.0

Date : November 1995

Source : J.J.M.Berdowski, P.F.J.van der Most
TNO
P.O.Box 2611
2600 JA Delft
The Netherlands

Supported by: Rentz, Otto; Oertel, Dagmar
Institute for Industrial Production
University of Karlsruhe (TH)
Hertzstraße 16, Bau 06.33
D - 76187 Karlsruhe
Federal Republic of Germany
Tel.: 0049-721-608-4460 or -4569
Fax: 0049-721-758909

