

SNAP CODE: **030311**
040612

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

NOSE CODE: **104.11.02**
105.11.21

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

ISIC: **2394**

1 ACTIVITIES INCLUDED

This chapter covers emissions from both the combustion and mechanical processes used to produce cement.

2 CONTRIBUTION TO TOTAL EMISSION

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

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

| Source-activity | SNAP-code | Contribution to total emissions [%] | | | | | | | | | | |
|----------------------|-----------|-------------------------------------|-----------------|--------|-----------------|-----|-----------------|------------------|-----------------|------|------------------|---------------------|
| | | SO ₂ | NO _x | NM VOC | CH ₄ | CO | CO ₂ | N ₂ O | NH ₃ | TSP | PM ₁₀ | PM _{2.5} * |
| Cement | 030311 | | | | | | | | | | | |
| Typical contribution | | 0.8 | 2.3 | 0 | 0 | 0.2 | 2.1 | 0.3 | - | 11.8 | 5.96 | 3.60 |
| Highest value | | | | | | | | | | 48.2 | 23.1 | 14.5 |
| Lowest value | | | | | | | | | | 1.70 | 1.08 | 0.68 |

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

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

- = no emissions are reported

The emitted dust may contain heavy metals, particularly so when wastes are burnt as fuel, see Baart et al. (1995). The average relative contribution from the cement production industry to the total emission of heavy metals has been presented for European countries in Table 2.2.

Table 2.2: Average relative contribution of the production of cement to the total emission of heavy metals in European countries (Baart et al., 1995)

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

Cement production may be an important source of mercury as well as the metals presented in Table 2.2. It was estimated that on a global scale cement contributes with about 1.0 % to the total emissions of the element emitted from anthropogenic sources (Pacyna and Pacyna, 1996). However, Table 2.3 gives the contribution of cement to total emissions of heavy metals and POPs from the OSPARCOM-HELCOM-UNECE emission inventory, and the estimate for mercury is a 15 % contribution.

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

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

3 GENERAL

3.1 Description

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

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

Types of fuels used vary across the industry. Cement kilns are highly energy-intensive and fuel costs have a critical effect on profitability. Historically, some combination of coal, oil, and natural gas was used, but over the last 15 years, most plants have switched to coal.

However, in recent years a number of plants have switched to systems that burn a combination of coal and waste fuel.

3.2 Definitions

Portland cement a type of hydraulic cement usually made by burning a mixture of limestone and clay in a kiln

Kiln a furnace for burning fuel and cement clinker

3.3 Techniques

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

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

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

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

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

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

3.4 Emissions

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

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

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

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

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

is mainly incorporated into the cement clinker by chemical combination. (IPCC, 1995; EPA, 1995).

The 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. 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 (IPCC, 1995; EPA, 1995). IPCC BREF document (EUROPEAN COMMISSION, 2001) report an estimated emission of CO₂ at 900 to 1000 kg/tonne clinker, related to a specific heat demand of approximately 3500 to 5000 MJ/tonne clinker, but also depending on fuel type.

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

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

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

Fluorine compounds in the feed constituents are partly volatilised into gaseous acidic fluorides at the high temperatures in the kiln. However, such acidic compounds are immediately neutralised (in the form of solid calcium fluoride) by the alkaline constituents in both the clinker and the feed. Thus, 88 - 98 % of the fluoride content of the feed materials is trapped in the clinker and the remainder deposits on dust particles and is mainly removed by the dust control devices. Chlorine compounds behave in a similar manner to those of fluorine.

Some kilns do burn hazardous waste as supplemental fuel. Other types of non-hazardous liquid and solid wastes used as supplemental fuels include tyres, waste oil, and wood chips. Dioxins (PCDDs) and furans (PCDFs) were first detected in stack emissions from portland cement kilns in the early 1980s (e.g. EPA, 1994). They were detected at low concentrations and were thought to be caused by the co-firing of liquid hazardous waste with conventional fossil fuels. Recently more information has become available on the possible formation

mechanisms of dioxins in the portland cement kilns. The following mechanisms have been suggested:

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

3.5 Controls

Emission reduction is usually obtained by reducing the dust emissions. Electrostatic precipitators (ESPs) and fabric filters (FFs) are most widely used on both kilns and clinker coolers. For electrostatic precipitation dust concentrations of 30 - 40 mg/m³ can be achieved. For fabric filters a value of 20 to 50 mg/m³ is common. A few gravel bed filters have also been used to control clinker cooler emissions. Fugitive emission sources are normally captured by a ventilation system and fabric filters used to collect the dust.

A portion of heavy metals in the flue gas will also be removed with particles. However, the most volatile heavy metals are present on very fine particles, often penetrating both ESPs and FFs. It is proposed that further reduction of dust concentrations in the flue gas to 10 mg/m³ should be achieved in order to obtain reasonable reduction of heavy metals.

Emissions of sulphur dioxide are best reduced by use of low sulphur raw materials. Removal of sulphur dioxide from the exhaust gases is possible using injection of calcium hydroxide into the air stream - after the preheater for minor reductions, or by a separate fluid bed absorber for significant reductions. However, the alkaline nature of the cement provides for direct absorption of 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 (IPCC, 1995; EPA, 1995).

Flue gas desulphurisation equipment also reduces the concentration of gaseous mercury present in the flue gas. This reduction can be as high as 50 %. Further reduction of up to 85 % can be achieved through the application of very expensive measures such as injection of activated carbon or application of activated carbon beds.

Oxides of nitrogen can be reduced by applying the following techniques (EPA, 1995):

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

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

4 SIMPLER METHODOLOGY

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

Tier 1: a method using readily available statistical data on the intensity of processes (“activity rates”) and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

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

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

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

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

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

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

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

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

5 DETAILED METHODOLOGY

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

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

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

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

6 RELEVANT ACTIVITY STATISTICS

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

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

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

7 POINT SOURCE CRITERIA

Cement production plants are regarded as point sources if plant specific data are available. When emissions care is needed to distinguish ground level emissions (from mechanical processes) from combustion related emissions released via a chimneystack.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors For Use With Simpler Methodology

A summary of default emission factors for use with a simpler methodology for estimating emissions are provided in Table 8.1a and Table 8.1b. The emission factors are mainly extracted from the Integrated Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001). Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030311; fuel used in the process does not have to be taken into account in 0301.

Table 8.1a: Emission Factors for Cement production

| Pollutant | Emission factor | Units |
|--|-----------------|-----------------------------------|
| Particulate matter ⁽¹⁾ | | |
| TSP | 600 | g/tonne cement |
| PM ₁₀ | 510 | g/tonne cement |
| PM _{2.5} | 180 | g/tonne cement |
| Nitrogen oxides | | |
| Average ⁽³⁾ | 2100 | g/tonne of clinker ⁽²⁾ |
| BAT ^(3,4) | 700 | g/tonne of clinker |
| Sulphur oxides ⁽⁴⁾ | | |
| raw materials with little or no volatile sulphur | 20 | g/tonne of clinker |
| raw materials with high volatile sulphur | | |
| average | 2400 | g/tonne of clinker |
| BAT ⁽⁵⁾ | 600 | g/tonne of clinker |
| Volatile organic compounds ⁽³⁾ | 110 | g/tonne clinker |

⁽¹⁾ When information on type of facilities and abatement used is available, the corresponding emission factors for particulates (CEPMEIP) in Table 8.2g can also be used in the simple methodology. The here referred emission factor for particulate matter is for the most used technology in the EU; Conventional Cement production plant with an ESP on the main stack and smaller fabric filters for moderate control of fugitive sources

⁽²⁾ Production capacities for clinker (intermediate product) and cement slightly differ and a correction factor needs to be used to transform the emission factor to cement. This factor is in order of magnitude of 0.8 [IPPC, BREF].

⁽³⁾ Mean value of NO_x emission measurements at more than 50 preheater rotary cement kilns from “*British Cement Association, Prevention and abatement of NO_x emissions, International Cement Review, p. 51-59, October 1997*” as reported in *EUROPEAN COMMISSION, 2001*

⁽⁴⁾ Using average of ranges in mg/m³ and exhaust gas volumes around 2000 m³/tonne of clinker from *EUROPEAN COMMISSION, 2001*

⁽⁵⁾ The BAT for reducing NO_x emissions are a combination of general primary measures, primary measures to control NO_x emissions, staged combustion and selective non-catalytic reduction (SNCR) as reported in *EUROPEAN COMMISSION, 2001*

⁽⁶⁾ The best available techniques for reducing SO₂ emissions are a combination of general primary measures and absorbent addition for initial emission levels not higher than about 1200 mg SO₂/m³ and a wet or dry scrubber for initial emission levels higher than about 1200 mg SO₂/m³.

Table 8.1b: Metal and specific VOCs Emission Factors for Cement production

| Pollutant | Emission factor | Units |
|---------------------------|------------------------|---------------------|
| Arsenic | 0.2 | g/tonne cement |
| Cadmium | 0.01 | g/tonne cement |
| Chromium | 1 | g/tonne cement |
| Copper | 0.4 | g/tonne cement |
| Mercury | 0.1 | g/tonne cement |
| Nickel | 0.1 | g/tonne cement |
| Lead | 0.2 | g/tonne cement |
| Selenium | 0.002 | g/tonne cement |
| Zinc | 2 | g/tonne cement |
| Dioxins and furans | 0.2 | µg TEQ/tonne cement |
| Hexachlorobenzene | 11 | µg TEQ/tonne cement |
| Polyaromatic hydrocarbons | 3 | mg/tonne cement |
| Polychlorinated biphenyls | 1 | µg/tonne cement |

8.2 Reference Emission Factors for Use With Detailed Methodology

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

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030311; fuel used in the process does not have to be taken into account in 0301

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

| Type of fuel | | NAPFUE code | Emission factors | | | | | | N ₂ O [g/GJ] |
|---------------------|-------------------------|-------------|---|--|---|---|--|--|---|
| | | | SO ₂ [g/GJ] | NO _x [g/GJ] | NM VOC [g/GJ] | CH ₄ [g/GJ] | CO [g/GJ] | CO ₂ [kg/GJ] | |
| s coal | hc coking | 101 | 569 ¹⁾ , 85-165 ²⁾ | 701 ¹⁾ , 450-709 ²⁾ | | 1 ¹⁾²⁾ | | 86 ¹⁾²⁾ | |
| s coal | hc steam | 102 | 44-880 ¹⁾ , 35-600 ²⁾ | 150-170 ¹⁾ , 0.4-575 ²⁾ | 15 ¹⁾ , 15-33 ²⁾ | 14.7-15 ¹⁾ , 0.3-15 ²⁾ | 10-110 ¹⁾ , 18-100 ²⁾ | 93-94 ¹⁾ , 78-101 ²⁾ | 12 ¹⁾ , 3-12 ²⁾ |
| s coal | hc sub-bituminous | 103 | 134-154 ¹⁾ , 1,260 ²⁾ | 57 ¹⁾ , 820-1,300 ²⁾ | | | 22 ¹⁾ | 99 ¹⁾ , 320-420 ²⁾ | 8 ²⁾ |
| s coal | hc brown coal/lignite | 105 | 25 ²⁾ | 575 ²⁾ | 15 ²⁾ | 15 ²⁾ | | 100-113 ²⁾ | 3.5 ²⁾ |
| s coal | hc briquettes | 106 | 11 ²⁾ | 575 ²⁾ | 15 ²⁾ | 15 ²⁾ | 100-260 ²⁾ | 97-98 ²⁾ | 3.5 ²⁾ |
| s coke | hc coke oven | 107 | 25 ²⁾ | 575 ²⁾ | 15 ¹⁾ , 0.5 ²⁾ | 15 ¹⁾ , 0.5 ²⁾ | 110 ¹⁾ , 100 ²⁾ | 108 ¹⁾ , 100-105 ²⁾ | 14 ¹⁾ , 4 ²⁾ |
| s coke | petroleum | 110 | 355-511 ¹⁾ , 85-1,200 ²⁾ | 300-568 ¹⁾ , 0.4-575 ²⁾ | 1.5 ¹⁾ , 1.5-15 ²⁾ | 1.5 ¹⁾ , 1-15 ²⁾ | 10-70 ¹⁾ , 15-100 ²⁾ | 99-102 ¹⁾ , 97-102 ²⁾ | 14 ¹⁾ , 3-14 ²⁾ |
| s waste | municipal | 115 | 161 ¹⁾ | 200 ¹⁾ | 15-40 ¹⁾ | 15-40 ¹⁾ | 70 ¹⁾ | 100-121 ¹⁾ | 5-12 ¹⁾ |
| s waste | industrial | 116 | 135 ²⁾ | 0.4-568 ²⁾ | | 0.2 ²⁾ | 1429 ²⁾ | 83 ²⁾ | 4 ²⁾ |
| l oil | residual | 203 | 131- 1,030 ¹⁾ , 16-1,079 ²⁾ | 150-220 ¹⁾ , 0.4-575 ²⁾ | 3 ¹⁾ , 3-10 ²⁾ | 1-3 ¹⁾ , 1-5 ²⁾ | 15-20 ¹⁾ , 8-79 ²⁾ | 76-79 ¹⁾²⁾ | 2-15 ¹⁾²⁾ |
| l oil | gas | 204 | 4-1,410 ²⁾ | 0.4-575 ²⁾ | 1.5 ¹⁾ , 1.5-2.5 ²⁾ | 1-5 ¹⁾ , 1-8 ²⁾ | 12 ¹⁾ , 12-79 ²⁾ | 74 ¹⁾ , 74 ²⁾ | 73- 12 ¹⁾ , 2-14 ²⁾ |
| l gasoline | motor | 208 | | | 2.5 ¹⁾ | 2.5 ¹⁾ | 12 ¹⁾ | 72 ¹⁾ | 12 ¹⁾ |
| l oil | shale-oil | 211 | | | | | | 78 ¹⁾ | |
| g gas | natural | 301 | 0.1-135 ²⁾ | 175 ¹⁾ , 60-560 ²⁾ | 2.5 ¹⁾ , 2.5-18.4 ²⁾ | 2.5 ¹⁾ , 0.4-5 ²⁾ | 20 ¹⁾ , 10-120 ²⁾ | 53-56 ¹⁾ , 55-69 ²⁾ | 3 ¹⁾ , 1-3.7 ²⁾ |
| g gas | liquified petroleum gas | 303 | 0.04 ²⁾ | 100 ²⁾ | 2.5 ¹⁾ , 2.1 ²⁾ | 2.5 ¹⁾ , 0.9 ²⁾ | 20 ¹⁾ , 13 ²⁾ | 65 ¹⁾²⁾ | 3 ¹⁾ , 1 ²⁾ |
| g gas | coke oven | 304 | 0.6 ²⁾ | 575 ²⁾ | 2.5 ²⁾ | 2.5 ²⁾ | 10 ²⁾ | 44 ²⁾ | 1.5 ²⁾ |
| Data quality rating | | | B | B | D | D | C | C | D |

PROCESSES WITH CONTACT

Activities 030311 & 040612

ic030311

1) CORINAIR90 data, area sources

2) CORINAIR90 data, point sources

Technique related emission factors are listed in Tables 8.2b through 8.2g for sulphur dioxide, nitrogen oxides, non-methane VOCs, CO, methane, and particulate matter. Only for particulates (Table 8.2g) some information exists on the type and efficiency of abatement techniques. All other factors in these tables seem to be valid for emissions from uncontrolled processes.

Table 8.2b: Emission factors for SO₂ from cement production

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

Table 8.2c: Emission factors for NO_x from cement production

| Process type | Abatement type | Abatement efficiency | Fuel type | Unit | Emission factor | Data Quality Code | Country or region |
|---|----------------|----------------------|-------------|------------------|-----------------|-------------------|-------------------|
| Dry process kiln | N/A | N/A | N/A | kg/tonne product | 1.4-2.1 | E | USA |
| Wet process kiln | N/A | N/A | N/A | kg/tonne product | 1.1-1.4 | E | USA |
| Semi-wet process kiln | N/A | N/A | N/A | kg/tonne product | 1.8 | E | USA |
| Clinker production | N/A | N/A | N/A | g/GJ | 1.2 | E | USA |
| Clinker production (80% NO _x reduction, 20% energy saving) | N/A | N/A | N/A | kg/tonne clinker | 0.6 | E | USA |
| Cement production | N/A | N/A | N/A | g/GJ | 130-220 | E | USA |
| Cement production | N/A | N/A | N/A | kg/tonne cement | 1.3-1.4 | E | USA |
| Cement/lime industry, kiln | N/A | N/A | Natural gas | kg/GJ | 1.1 | E | USA |
| Cement/lime industry, kiln | N/A | N/A | Oil | kg/GJ | 0.5 | E | USA |
| Cement/lime industry, kiln | N/A | N/A | Coal | kg/GJ | 0.5 | E | USA |

N/A - Data not available

Table 8.2d: Emission factors for NMVOC from cement production

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

N/A - Data not available

Table 8.2e: Emission factors for CO from cement production

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

N/A - Data not available

Table 8.2f: Emission factors for CH₄ from cement production

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

N/A - Data not available

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Table 8.2g: Emission factors for particles from cement production

| Process type | Abatement type | Abatement efficiency | Fuel type | Unit | Emission factor | | | Data Quality Code* | Country or region |
|--|---|----------------------|-----------|----------------|-----------------|------------------|-------------------|--------------------|-------------------|
| | | | | | TSP | PM ₁₀ | PM _{2.5} | | |
| Cement production (conventional plant) | ESP on main stack and smaller fabric filters for moderate control of fugitive sources | N/A | N/A | g/tonne cement | 600 | 510 | 180 | E (1,5) | EU (CEPMEIP) |
| Cement production | Limited control fugitive sources; ESP in main stack | ESP < 97% | N/A | g/tonne cement | 2000 | 800 | 300 | E (1,5) | EU (CEPMEIP) |
| Cement production (modern facility) | Additional fabric filters on the oven stack; effective control of fugitive sources | N/A | N/A | g/tonne cement | 200 | 180 | 80 | E (1,5) | EU (CEPMEIP) |

N/A - Data not available

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by

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multiplying the range with the uncertainty factor. Example (first row in Table 8.2g): The uncertainty in the emission factor for PM_{2.5} from a conventional cement production plant with an ESP on the main stack and smaller fabric filters for moderate control of fugitive sources is 1.5. The emission factor with uncertainty range will therefore be 510 gram per tonne cement with an uncertainty range of 340 (510/1.5) to 765 (510x1.5).

The emission factors for particles are dominated by the PM emissions arising from the kilns. Emissions for manufacturing of raw material and the processing and handling of the product are significantly lower. Emission factors for milling where emissions are controlled are in the range of 4 – 14 g TSP / ton material processed (AP42, table 11.6-3).

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

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

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

- Data not available

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

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

Concentrations of dioxins and furans in the flue gas after passing the control equipment in the cement production are presented in Table 8.1b after a compilation of data by the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Emission Control Committee in Germany (Umweltbundesamt, 1996) and information obtained from Schreiber et al. (1995), EPA (1994), and (Quass, 1997).

Emission data from kilns in operation coming from IPPC BREF document (EUROPEAN COMMISSION, 2001) is given in Table 8.2i. The emission ranges within which kilns operate depend largely on the nature of the raw materials, the fuels, the age and design of the plant, and also on the requirements laid down by the permitting authority. Mass figures are based on 2000 m³/tonne clinker and 1 million tonnes clinker/year. Emission ranges are one-year

averages and are indicative values based on various measurement techniques. O₂-content is normally 10%.

Typical kiln exhaust gas volumes expressed as m³/tonne of clinker (dry gas, 101.3 kPa, 273 K) are between 1700 and 2500 for all types of kilns. Suspension preheater and precalciner kiln systems normally have exhaust gas volumes around 2000 m³/tonne of clinker (dry gas, 101.3 kPa, 273 K).

There are also releases of particulates from all milling operations i.e. raw materials, solid fuel and product. There is potential for the release of particulates from any outside storage of raw materials and solid fuels as well as from any materials transport systems, including cement product loading. The magnitude of these releases can be significant if these aspects are not well engineered or maintained and being released at low level can lead to local nuisance problems.

Table 8.2i: Emission ranges from European cement kilns from IPPC BREF document (EUROPEAN COMMISSION, 2001)

| Pollutant | mg/Nm ³ | kg/tonneclinker | tonnes/year |
|---------------------------------------|-----------------------------|-----------------|------------------|
| NO _x (as NO ₂) | <200–3000 | <0.4-6 | 400-6000 |
| SO ₂ | <10–3500 | <0.02-7 | <20-7000 |
| Dust | 5–200 | 0.01-0.4 | 10-400 |
| CO | 500–2000 | 1-4 | 1000-4000 |
| CO ₂ | 400-520 g/Nm ³ | 800-1040 | 0.8-1.04 million |
| TOC | 5-500 | 0.01–1 | 10-1000 |
| HF | <0.4-5 | <0.8-10 g/t | <0.8-10 |
| HCl | <1-25 | <2-50 g/t | <2-50 |
| PCDD/F | <0.1-0.5 ng/Nm ³ | <200-1000 ng/t | <0.2-1 g/year |
| Metals: | | | |
| Σ(Hg,Cd,Tl) | 0.01-0.3 (mainly Hg) | 20-600 mg/t | 20-600 kg/year |
| Σ(As,Co,Ni,Se,Te) | 0.001-0.1 | 2-200 mg/t | 2-200 kg/year |
| Σ(Sb,Pb,Cr,Cu,Mn,V,Sn,Zn) | 0.005-0.3 | 10-600 mg/t | 10-600 kg/year |

9 SPECIES PROFILES

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

Table 9.1: Composition of dust from clinker firing

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

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

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

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

In general, no reliable information exists at present on physical and chemical species of trace elements emitted during the cement production. It can be assumed that the majority of trace elements volatilised from the raw material and fuel enter the atmosphere on fine particles. Very general information collected by Pacyna (1987) appears to indicate that elemental forms, oxides and sulphates are the major chemical forms of atmospheric trace elements from the cement production.

10 UNCERTAINTY ESTIMATES

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

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

Uncertainties associated with the emissions of PM_{2.5} are indicated in Table 8.2g.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

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

The fuel specific emission factors provided in Table 8.1 are related to point sources and area sources without specification. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested to develop emission factors, which include technical or fuel dependent explanations concerning emission factor ranges. Emission factors also need to be generated, which specifically relate to different levels of abatement on different types of plant.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

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

13 TEMPORAL DISAGGREGATION CRITERIA

Cement production can be considered as a continuous process.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

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

Personal information and experience during emission inventories 1975 - 1995

Emission factors to be used for the building industry, TNO report 89/091
Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP 42
PARCOM-ATMOS Emission Factors Manual

16 VERIFICATION PROCESSES

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

17 REFERENCES

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18 BIBLIOGRAPHY

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

19 RELEASE VERSION, DATE AND SOURCE

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