030311
Cement

Process description
The most important raw materials for the manufacture of cement are limestone and clay or a calcareous clay in which both components are already naturally mixed. The components are milled and dried with flue gases from the clinker kiln. Depending on the type of cement to be produced the following products may be added to the dried limestone subsequently: pyrite ash, fly ash from coal-fired power plants, sandy clay and filter ash from the electrostatic precipitator present. The mixture obtained is ground and subsequently fired in a rotary furnace to cement clinkers. For heating fuels and other combustible materials e.g. coal dust, petroleum coke, lignite, high-sulphurous oil and glycol bottom residues (distillation residues), used oil, used tyres, disposal site gases, heating oil S are used. Depending on the type of preheating of the material, it is differentiated between grate and cyclone preheating, whereby the starting materials are preheated to 800 °C. The raw materials pass through the rotary furnace towards the flame. In the hottest zone (sinter zone), the material being fired reaches temperatures of around 1450 °C. After fast cooling with ambient air, the clinkers are milled together with gypsum to give ready cement.

Cement Clinker
The production of cement includes (1) isolation and preparation of the raw materials, (2) drying, (3) burning of the raw material mixture to give cement clinker, (4) preparation of the other components of the cement, and (4) grinding of the cement components with calcium sulfate to regulate setting.

It is made from a mixture of raw materials which mainly contains calcium oxide, silicon dioxide, aluminum oxide, and iron (III) oxide in definite proportions.

The raw material mixture is burnt in a cement kiln to give cement clinker. It is heated to the sintering temperature of 1450 °C, which takes 40 min to 5 h, depending on the type
of kiln. It remains for ca. 10-20 min at this temperature and is cooled as quickly as possible after leaving the kiln.

In Europe, cement clinker is predominantly burnt in rotary kilns; shaft kilns are seldom used. Rotary kilns are refractory-lined tubes with a diameter up to about 6 m. They are inclined at an angle of 3-4 and rotate at 1.2-2 times/min. As a result of the inclination and rotation of the tube, the material to be burnt, fed into the top of the kiln, moves down the tube toward the coal dust, oil, or gas flame burning at the bottom of the tube. Near the flame, in the sintering or clinkering zone of the rotary kiln with a gas temperature of 1800-2000 °C, the temperature of the material being burnt reaches 1350-1500 °C, which is necessary for the formation of clinker.

Other Components of Cement

For production of special types of cement additional materials may be used:

Glassy Blast-Furnace Slag

Blast-furnace slag is formed from iron ore, coke ash, and limestone additives during the manufacture of pig iron in a blast furnace. It is removed from the furnace separately as running slag or together with molten pig iron as tapping slag.

Fly Ash
Fly ash is a fine-grained residue that is obtained from the combustion of coal dust. It accumulates in the electrical or mechanical dustcollection equipment that is connected to the steam generators of power plants.

It also contains crystalline particles of quartz, magnetite, and mullite; unburnt and partially burnt coal; and small amounts of such alkali compounds as the chlorides and sulfates.

The properties of fly ash, especially the amount of unburnt and partially burnt coal, quartz, and other crystalline components are chiefly determined by the ash content of the
coal but also by the firing and combustion conditions; the quality of the fly ash increases with higher load of the steam generator and with combustion temperature.

**Burnt Oil Shale**

Another secondary constituent for the manufacture of cement is produced from oil shale. Oil shale is a lime-containing bituminous shale with ca. 11 wt % organic substances, 41 wt % calcium carbonate, 27 wt % clay minerals, and 12 wt % quartz. It is burnt at 800 °C in a fluidized bed furnace. The energy that is released when oil shale is burned is employed to generate electricity and the ash produced is ground with cement clinker to give oil-shale cement.

**Abatement technologies:**

The waste gases which contain particles are passed through an electrofilter in the mill-drying installation in combined operations. In direct operations, the waste gases are conditioned in an evaporation cooler upstream of the electrofilter to achieve an enhanced conductivity of the dust.

**Plant data/European situation**

About 300 plants belonging to 138 companies are told to be operated in Europe \(^1\). Detailed information on the plants can be taken from the World Cement Directory \(^2\). However, only few information is available regarding the applied production processes (wet/semi-dry/dry) and with respect to the extent of wastew burning.

**Activity data**

The activity data (shown in 030311—Table 4) were taken from the national inventories or from annual production statistics. There was quite good agreement between data from the national inventories and from production statistics.
European Dioxin Inventory - Results

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Emission factors

Emission factors for cement production as reported by the national dioxin inventories are shown in 030311—Table 4. Apparently most of them had been gained by measurements; only the Belgian value was adopted from literature data.

From these data the following default emission factors were taken for the following emission estimations:

<table>
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<th>Typical</th>
<th>Minimum</th>
<th>Maximum</th>
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<tr>
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<td>0.05</td>
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030311—Table 1 Default emission factor for cement production

[µg I-TEQ/t]

Emission estimation

On the basis of the default emission factors and the activity rates the following standardised annual PCDD/F emissions were derived. The values obtained were compared to those reported in the national inventories. For all 17 countries considered the following results were obtained (030311—Table 2):

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<thead>
<tr>
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<td>national inventories</td>
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<td>Re-evaluation, typical</td>
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030311—Table 2 Summary of re-evaluated typical PCDD/F air emissions

[g I-TEQ/a] for cement production

Concerning cement production the typical annual emissions obtained are higher for Austria, Germany, France and the United Kingdom than in the national reports. Only in the case of Belgium a significant decrease was observed. If all 17 countries are included into the total estimation, the European total emissions decreases compared to the sum of emissions reported by the inventories. This is mainly due to the much lower estimate for Belgium which compensates the additional contribution from those countries without
dioxin emission inventories. The maximum estimate is likely to be an overestimate since
(the very uncertain) emission factor reported in the Belgian inventory was taken into
account for the calculation of the maximum emission factor used for the re-estimation.

Conclusions/recommendations
In many cases cement production is of minor relevance for the total emission of
PCDD/F in Europe. Nevertheless, from the data reported in the surveyed document
follows that there is still substantial uncertainty concerning dioxin emissions. The reason
for this is the incineration of different kinds of waste in particular cement plants which
might contribute considerably to the national dioxin emission balance or to the local
immission situation.

Measurements may be recommended at some plants incinerating waste, in particular
hazardous waste with chlorinated compounds. In most other cases measurements at
cement producing plants do not appear to be necessary.
## European Dioxin Inventory - Results

### 030311

**Cement**

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<tr>
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<th>Flue gas conc. [ng I-TEQ/m³]</th>
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#### Table 3  PCDD/F air emission factors for cement production from national dioxin inventories
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030311—Table 4  Activity rates related to cement production
030311—Table 5  Comparison of PCDD/F air emission estimates [g I-TEQ/a] for cement production

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References to 030311

1. Panorama of EU Industry 95-96. Eurostat, Brussels