DRAFT

Formation and Release of POP's in the Cement Industry

World Business Council for Sustainable Development
Cement Sustainability Initiative

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SINTEF

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Acronyms and abbreviations

AFR	Alternative fuel and raw material
APCD	Air pollution control device
ATSDR	Agency for Toxic Substances and Disease Registry
AWFCO	Automatic waste feed cut-off
BAT	Best Available Techniques
BEP	Best Environmental Practise
BHF	Bag House Filter
BIF	Boiler and industrial furnace
Btu	British thermal unit
^{o}C	Degree Celsius
CAA	Clean Air Act
CFR	Code of Federal Regulations
CKD	Cement Kiln Dust
Cl_2	Molecular chlorine
CEMS	Continuous emissions monitoring system
DL	Detection Limit
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DRE	Destruction and removal efficiency
Dscm	Dry standard cubic meter
EC	European Commission
EF	Emission Factor
e.g.	For example
EPA	U.S. Environmental Protection Agency
EPER	European Pollutant Emission Register
ESP	Electrostatic precipitator
EU	European Union
FF	Fabric Filter
g	Gram
GC-ECD	Gas Chromatography/Electron Capture Detector
GC-MS	Gas Chromatography/Mass Spectrometry

HAPs	Hazardous Air Pollutants
HCB	Hexachlorobenzene
HCI	Hydrogen Chloride
HF	Hydrofluoric acid
i.e.	That Is
IPPC	Integrated Pollution Prevention and Control
IUPAC	International Union of Pure and Applied Chemistry
J	Joules
kcal	Kilocalorie (1 kcal = 4.19 kJ)
kg	Kilogramme (1 kg = 1000 g)
kJ	Kilojoules (1 kJ = 0.24 kcal)
L	Litre
lb	Pound
LCA	Life cycle analysis
LOD	Limit of detection
LOl	Loss on ignition
LOQ	Limits of Quantification
m^3	Cubic Meter
MACT	Maximum achievable control technology
MJ	Megajoule (1 MJ= 1000 kJ)
mg/kg	Milligrams per kilogram
MS	Mass spectrometry
mol	Mole (Unit of Substance)
Na	Sodium
NA	Not Applicable
ND	Not Detected
NESHAP	National Emission Standards for Hazardous Air Pollutants
NR	Not Reported
NAAQS	National Ambient Air Quality Standards
ng	Nanogramme (1 ng = 10^{-9} gram)
Nm_3	Normal cubic metre (101.3 kPa, 273 K)
NH_3	Ammonia
NOx	Nitrogen oxides ($NO+NO_2$)
O_2	Oxygen

PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PCDD/F	Informal term used in this document for PCDDs and PCDFs
PIC	Product of incomplete combustion
pg	Picogram
PM	Particulate Matter
POHC	Principal organic hazardous constituent
POM	Polycyclic Organic Matter
ppb	Parts Per Billion
ppm	Parts Per Million
ppmv	Parts Per Million (Volume Basis)
ppq	Parts Per Quadrillion
ppt	Parts Per Trillion
ppt/v	Parts Per Trillion (Volume Basis)
ppm	Parts per million
ppmv	Parts per million volume
QA/QC	Quality Assurance/Quality Control
RACT	reasonably available control technology
RCRA	Resource Conservation and Recovery Act
RDF	Refuse derived fuel
RT	Residence Time
sec	Second
SINTEF	The Foundation for Industrial and Scientific Research of Norway
SNCR	Selective non-catalytic reduction
SiO_2	Silicon dioxide
SCR	Selective catalytic reduction
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SOx	Sulphur oxides
SQL	Sample quantification limit
SRE	System removal efficiency
t	Tonne (metric)

TCDD	2,3,7,8-tetrachlorobidenzo-p-dioxin
TCDF	2,3,7,8-tetrachlorobidenzofuran
TEQ	International toxicity equivalents (dioxins and furans)
TEQ/yr	Toxicity Equivalents per Year
THC	Total hydrocarbons
TOC	Total organic carbon
tpa	Tonnes per annum (year)
TRI	Toxics Release Inventory
TSCA	Toxics Substances Control Act
UK	United Kingdom
US EPA	United States Environmental Protection Agency
VDZ	Verein Deutscher Zementwerke e.V.
VOC	Volatile organic compounds
WBCSD	World Business Council for Sustainable Development
WHO	World Health Organization
yr	Year
% v/v	Percentage by volume
$\mu g/m^3$	Micrograms per cubic meter
µg	Microgram

Glossary

AFR	Alternative fuel and raw materials, often wastes or secondary products from other industries, used to substitute conventional fossil fuel and conventional raw materials.
Cementitious	Materials behaving like cement, i.e. reactive in the presence of water; also compatible with cement.
Co-processing	Utilisation of alternative fuel and raw materials in the purpose of energy and resource recovery.
Kiln inlet	Were the raw meal enters the kiln system.
Pozzolana	Pozzolanas are materials that, though not cementitious in themselves, contain silica (and alumina) in a reactive form able to combine with lime in the presence of water to form compounds with cementitious properties. Natural pozzolana is composed mainly of a fine, reddish volcanic earth. An artificial pozzolana has been developed that combines a fly ash and water-quenched boiler slag.
Pozzolanic cement	Pozzolanic cements are mixtures of Portland cement and a pozzolanic material that may be either natural or artificial. The natural pozzolanas are mainly materials of volcanic origin but include some diatomaceous earths. Artificial materials include fly ash, burned clays, and shale's.
Siliceous limestone	Limestone that contains silicon dioxide (SiO_2)

Executive summary

The newly ratified Stockholm Convention on POP’s aims to prevent and reduce unintentionally emissions of polychlorinated dibenzodioxins/-furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) from all potential source categories. Cement kilns firing hazardous waste are explicitly mentioned in the Stockholm Convention, Annex C part II, as “*industrial source having the potential for comparatively high formation and release of these chemicals to the environment*”.

The cement industry takes these potential emissions seriously, both because perceptions about these emissions have an impact on the industry's reputation, and because even small quantities of dioxin-like compounds can accumulate in the biosphere, with potentially long-term consequences.

The objective of this study is to compile data on POP’s emissions from the cement industry, to share state of the art knowledge about PCDD/F formation mechanisms in cement production possesses and how it is possible to control PCDD/F emissions from cement kilns by utilising primary measures, i.e. integrated process optimisation. This report is providing the most comprehensive data set available, collected from public literature, scientific databases and individual company measurements.

The report is based on more than 1,700 PCDD/F measurements, many PCB measurements and a few HCB measurements from the early 1990’s until recently. The data represents emission levels from both wet and dry kilns, performed under normal and worst case operating conditions, with and without the co-processing of a wide range alternative fuel and raw materials and with wastes and hazardous wastes fed to the main burner, to the rotary kiln inlet and preheater/precalciner.

The emissions from dry preheater/precalciner kilns seem to be frequently below 0.1 ng TEQ/m^3, and slightly lower than emissions from wet kilns. In most instances, the reported data from the dry kilns stems from co-processing of waste and alternative raw materials, which today is regarded to be normal practise. Two recent examples; a dry kiln in Colombia emits between 0.00023-0.0031 nanogram TEQ/m^3 when feeding pesticide contaminated soil to the raw meal kiln system. A UNEP managed project measured emissions between 0.0001-0.018 ng TEQ/m^3 from a dry kiln in Thailand replacing parts of the fossil fuel with tyres and hazardous waste; the lowest concentration was found when co-processing hazardous waste, 0.0002 ng TEQ/m^3. This conclusion is also drawn by the US EPA, which after many years of research and testing in 1999 stated "*that hazardous waste burning does not have an impact on PCDD/F formation; PCDD/F is formed post-combustion*".

Many national and international inventories use emissions factors published in the earlier literature; very few inventories have established emissions factors from actual measurements. The emissions factors found in many articles and reports are often outdated and the consequence of using those are often too high estimates of PCDD/F release from the cement industry. Experiences from inventories where emission factors are established by actual measurements, like Australia, shows that the cement industry contribution is insignificant compared to, for example, natural sources and is also lowest among industry sources.

The 6th Intergovernmental Negotiating Committee under the Stockholm Convention on POP's have given an expert group a mandate to develop guidelines for the application and implementation of best available techniques (BAT) and best environmental practices (BEP) for the prevention and reduction of unintentionally production of PCDD/Fs, PCBs and HCB in source categories.

The data presented and discussed in this report shows that:

1) most cement kilns can meet an emission limit of 0.1 ng TEQ/Nm^3;

2) co-processing of alternative fuels and raw materials, fed to the main burner or the preheater/precalciner does not influence or change the emissions of POP's;

3) cement kilns in developing countries presented here meet an emission level of 0.1 ng TEQ/Nm^3.

For new cement plants and major upgrades the best available technique for the production of cement clinker is a dry process kiln with multi-stage preheating and precalcination.

A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. Quick cooling of kiln exhaust gases to a temperature lower than 200°C is considered to be the most important measure to avoid PCDD/F emissions in wet kilns (process inherent in suspension preheater and precalciner kilns), as well as careful selection and control of substances entering the kiln through the raw material feed.

Primary measures have been shown to be sufficient to comply with an emission level of 0.1 ng TEQ/Nm^3 in existing suspension preheater and precalciner kilns under normal operating conditions.

1. Introduction

The Cement Sustainability Initiative CSI (launched in 1999 under the auspices of the World Business Council for Sustainable Development) was undertaken by 15 leading companies in the cement industry who collectively manufacture nearly 50% of the cement worldwide, outside of China, representing more than 100 countries. Their goal was to identify key sustainability issues for the industry over the next 20 years, and set up a credible, meaningful series of measures to address them. This is being accomplished through independent research, stakeholder consultation, business planning and specific joint and individual company actions. Key issues for the industry identified in this program are:

- Managing climate impacts.
- Responsible use of fuels and materials.
- Employee health and safety.
- Monitoring and reporting emissions.
- Local impacts on land and communities.
- Progress and communications.

The objectives of this present study, to compile data on POP's emissions from the cement industry, contribute significantly too many of the key issues listed above. Detailed information and descriptions of the initiative (along with current publications) may be found on the web site, www.wbcsdcement.org. In addition to providing the most comprehensive data set available, we hope this study will also improve current knowledge about normal dioxin/furan emissions from the industry and reveal possibilities for control measures where needed. Information presented here has been collected both from public literature, scientific databases, and individual company measurements.

In most scientific databases between 50 and 200 "hits" can be found on POP's emissions from cement kilns, but many of the hits are doublets. There is not much information about PCB releases and almost nothing on HCB emissions; these data mostly comes from the cement companies. The information on emissions levels and emissions factors used around the world is compiled and presented for the first time in this document.

One of the main routes towards sustainability in the cement industry is to reduce the use of fossil fuel and replace this energy by waste materials, which need to be treated anyway. The report gives an overview of production technologies for cement, and the practice of co-processing alternative fuels and raw materials. It describes how the cement industry verifies the performance of such practice, making sure that co-processing is done in an environmentally sound manner. The report also briefly presents the regulatory framework on POP's emissions for the cement industry and how it is possible to control PCDD/F emissions from cement kilns by utilizing primary measures, i.e. integrated process optimization. This report does not yet contain any data on PCDD/F release through cement kiln dusts or clinker - a subject for further investigation.

1.1 Stockholm Convention on POP's

The newly ratified Stockholm Convention on POP's aims to prevent and reduce unintentionally emission of polychlorinated dibenzodioxins/-furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) from all potential source categories. Cement kilns firing hazardous waste are explicitly mentioned in the Stockholm Convention, Annex C part II, as "*industrial source having the potential for comparatively high formation and release of these chemicals to the environment*" (Stockholm Convention, 2001).

The 6th Intergovernmental Negotiating Committee under the Stockholm Convention on POP's have given an expert group a mandate to develop guidelines for the application and implementation of best available techniques (BAT) and best environmental practices (BEP) for the prevention and reduction of unintentionally production and emission of POP's (Richter and Steinhauser, 2003). Cembureau, the European Cement Association, has served on this expert group, and represented the Cement Sustainability Initiative (CSI) in their discussions.

In terms of their contribution to the national environmental burden of dioxins and relative to other potential sources of emissions, cement kilns have not generally been regarded as significant emitters. For example, in the US and UK source inventories (Schaum et al, 1993; Eduljee and Dyke, 1996) cement kilns contribute less than 1% to the total dioxin releases to atmosphere. However, the perceptions that cement kilns substituting some of its fossil fuel with waste materials is a potential dioxin emitter is taken seriously by the industry.

1.2 What is PCDD/F?

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) comprise a family of 210 chemically related organic compounds containing from one to eight chlorine atoms, often collectively and colloquially denoted as ”dioxins” or PCDD/Fs (this document). Within the family of dioxins, 17 congeners are of particular concern, with the arrangement of chlorine atoms around the double-benzene molecular framework conferring a heightened toxicological response. The total weighted toxicological response of these congeners is conventionally expressed in units of International Toxic Equivalents, abbreviated to I-TEQ.

1.3 Toxicity equivalency factors for dioxins

Dioxins are always found in samples as a mixture of various congeners. The most toxic of the chlorinated dioxins is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The toxicity of other chlorinated dioxins is estimated relatively to 2,3,7,8-TCDD. Today only congeners with chlorine atoms in the 2,3,7,8-positions are considered to have toxic properties as TCDD.

Over the years a number of toxicity equivalency factor systems have been developed. The dominating system during the nineties has been the international system that was developed by a NATO-working group in the late eighties. This system replaced more or less the German UBA-system from 1985, the Nordic system from 1988 as well as older systems developed by US-EPA.

A new system was developed and published by WHO 1998 and by UNEP in 1999. This system gives in contrast to previous systems separate toxicity equivalency factors for humans/mammals, fish and birds.

It should be noted that the Nordic and the International systems are almost identical, whereas the German system as a very early system also assign toxicity to non-2,3,7,8-congeners. The new WHO-system differs strongly in the assessment of pentachloro- and octachlorodioxins. The knowledge of brominated dioxins is less developed. On an interim basis WHO suggests that the current toxicity equivalency factors for chlorinated dioxins are also applied to brominated dioxins (IPCS, 1998).

1.4 Properties and degradation of dioxins

Based on Jones and Sewart (1997), the properties of chlorinated dioxins may be briefly described as follows: Dioxins are non-polar, poorly water soluble, lipophilic and stable chemicals. Solubility in water decreases with increasing level of chlorination. E.g. the solubility of 2,3,7,8-TCDD is in the order of 20 ng/l, whereas the solubility of OCDD is about three orders of magnitude lower.

The octanol-water partition coefficient (log Kow) increases with chlorination and ranges from 6.80 for 2,3,7,8-TCDD to 8.20 for OCDD. These values are among the highest reported for environmental organic contaminants and means that dioxins will have a high affinity for organic matter, fats and oils. Dioxins are generally stable in the presence of strong acids and bases and remain stable at temperatures below 750°C.

Degradation mechanisms should be expected to include thermal, photochemical and biological degradation. Photo-degradation has been shown to favour the 2,3,7,8-positions for PCDFs and the 1,4,6,9-positions for PCDDs, leading to a decrease of 2,3,7,8-PCDF congeners and an increase in 2,3,7,8-PCDD congeners. Biological reactions in sediments are believed to cause a dechlorination of higher chlorinated dioxins like OCDD thereby transforming these into 2,3,7,8-TCDD and lower chlorinated dioxins (Albrecht et al, 1999).

However, all natural degradation processes apart from thermal degradation should be expected to be extremely slow. Preliminary estimates of degradation half-lives in nature indicate half lives in water and sediments ranging from around 30 years to around 200 years (Sinkkonen, 1998). In soil, it is generally accepted, that the half-life of 2,3,7,8-TCDD and other congeners is in the order of 10 years, which however may be due to physical loss processes like volatilisation, leaching of particles, oils and surfactants rather than degradation (Jones & Sewart, 1997). The fact, that dioxins have been detected in natural clay shows that dioxins is produced through natural processes and that they have the ability under appropriate conditions to persist for thousands and maybe even millions of years.

1.5 Basic assumptions for this investigation

It is recognised that dioxin formation is process specific. This means that the local conditions of the individual cement plants with respect to actual raw materials and process conditions, flue gas cleaning and in particular temperature patterns in the flue gas cleaning system and chimneys can affect the amount of dioxin created.

As a consequence, most confidence is generally placed with measurements from actual plants, no matter whether they are few and may be regarded as spot tests rather than thorough investigations. Still they represent actual conditions with respect to raw materials and process conditions. Less confidence is assigned to literature data available from reviews using emission factors only.

Whereas these considerations have guided the overall strategy for assessment of data reliability, basically a case by case assessment has been performed. In some cases, it has not been possible to be critical, as only a few data were available.

Although steps have been taken to improve the existing knowledge on dioxin formation and emissions by measurements, the number of analyses available is still limited. In adopting such figures it has been considered more correct to rely on average figures, as it is not known to what extent the maximum and minimum data available is representative. As can be seen frequently in this report, very low figures are reported.

1.6 Reliability of data

It's not possible to determine the accuracy of the sampling methods in use since no reference materials exist for PCDD/Fs in exhaust gases, only the external and internal variability can be evaluated (EN 1948, 1996).

It is reasonable to expect that earlier data are less reliable and accurate compared to recent data due to absence of standard procedures for sampling, extraction, clean-up and analysis. No scientific study can confirm this statement, but before the first European Standards on sampling, extraction and clean-up and identification and quantification appeared in 1996 (EN 1948, 1996) many different methodologies were used.

In a number of publicly available reports and articles there are gaps in the reported information which makes it impossible to evaluate the accuracy of the data. Often there is no information of which toxicity equivalency factor systems are used, or if and eventually how the referred data are corrected to normal conditions and oxygen concentration, and frequently, information about sampling methodology and spiking recoveries are missing. These uncertainties are impossible to eliminate and is also reflected in this document.

There will also be variability's in the formation process. A study performed by Alcock et al (1999) showed that I-TEQ concentrations in stack emissions collected within a few hours of each other on the same day could, in some cases, be very different. For example, the first sample collected from a cement kiln stack measured 4.2 and the second, collected 5 hours later, only 0.05 ng I-TEQ m^3. During the time stack gas was sampled the plant was running normally and spike recoveries of both samples were within the normal range. This suggest either a degree of variability within the process or a change in process operation mode and highlights the importance of quality control at all points within the process monitoring, sample collection/storage, extraction and analysis protocol. It also demonstrates the need for caution when extrapolating emissions from a single sample to providing emissions factors for a whole industrial sector.

1.6.1 Sampling

Today sampling of PCDD/Fs are in most cases undertaken by using one of two methods based on (or following that of) US EPA Method 23 or the EN 1948-1. The EN 1948 offer three possible options, the filter/condenser method, the dilution method and the cooled probe method.

In the US EPA Method 23, stack gases are sampled iso-kinetically through a sharp-edged nozzle, heated glass probe and particulates collected on a filter. From the filter, gases pass through a condenser and XAD-2 resin trap, then through two impingers connected in series. Sampling is usually conducted over a period of 4 to 6 hours in order to extract a volume of duct gas sufficient for reliable determination of all PCDD/F congeners.

In the EN 1948-1, gas is sampled iso-kinetically in the duct. The PCDD/Fs, both adsorbed on particles and in the gas phase, are collected in the sampling train. The collecting parts can be a filter, a condensate flask and a solid or liquid adsorbent appropriate to the sampling system chosen. The method offers three different sampling systems, filter/condenser method, dilution method or cooled probe method.

In the German VDI Dilution Method 3499 a known volume of flue gas is extracted iso-kinetically from the duct via a heated glass sampling probe. The sample is mixed in a glass chamber with a known volume of dried and filtered dilution air, lowering the temperature of the gas to below 50°C. The particulate fraction and condensates of the gas are collected on a glass fibre filter, with the vapour phase fraction passing through a pre-conditioned polyurethane foam filter.

In practice, iso-kinetic flue gas sampling conditions is not always achieved. This is primarily due to limitations imposed by the flue gas duct design and position of the sampling points, particularly in older installations. Uncertainties associated with the sampling and analytical procedures involved in sampling trace species such as PCDD/Fs have been estimated to have a 95% confidence limit of 65% to 200%, depending on duct gas concentrations (Alcock et al, 1999).

Since no reference materials are available for PCDD/Fs in exhaust gases, it’s not possible to determine the accuracy of the sampling methods, only the external and internal variability (EN 1948, 1996).

1.6.1.1 Development and validation of EN-1948

At the end of the 1980ies about 17 different sampling methods and a multitude of variants for clean-up and analysis existed in Europe (Bollmacher, 2001). Low and high resolution mass spectrometers (MS) were employed. Most of the measurement methods were not, or not well, validated. Only a few of them, e.g. Guideline VDI 3499, were partly validated for monitoring limit values of 0.1 ng TEQ/m^3. Therefore, EC and EFTA Secretariat asked CEN to establish a European Standard with reliable performance characteristics. Working Group 1 (WG 1) of CEN/TC 264 took over this task in 1991 and started with sampling pre-tests.

Three different sampling methods out of the 17 existing ones were chosen and tested in a comparative field test at a municipal waste incinerator. The analytical part was fixed and carried out by two laboratories. Due to the fact that there is no reference flue gas material the "true" PCDD/F emission concentration could only be checked by comparing the different measurement systems. The repeatability and reproducibility were determined by having three sampling teams, each of which representing one of the three sampling methods, perform duplicate measurements. The measurements were carried out at the same time with a sampling duration of eight hours. All tests were performed within one week. The results of the field test showed that all three sampling methods (filter/condenser method, dilution method and cooled probe method) gave equivalent results.

The sampling systems are as follows:

- The filter/condenser method: The filter is placed downstream of the nozzle (in the stack) or after the probe (out of the stack). The filter has to be kept below 125 °C, but above the flue gas dew point. Downstream, a filter (maximum abundance at a particle diameter of 0.3 µm) is attached. The sample gas is cooled below 20 °C and the condensate is collected in a flask. The gaseous and aerosol parts of the PCDD/Fs are captured by impingers and/or solid adsorbents. In a variant, a system with division of flow can be used.

- The dilution method: The sample gas is collected via a heated probe. The waste gas is cooled very rapidly to temperatures below 40 °C in a mixing channel using dried, filtered ambient air. After dilution a filter is used to collect the particulate PCDD/Fs contained in the waste gas stream. For the separation of the gaseous PCDD/Fs a solid adsorbent is linked downstream. The dilution avoids the temperature of the sampling gas falling below the flue gas dew point.

- The cooled probe method: The sample gas passes the nozzle and a water-cooled probe. The sample gas is cooled below 20 °C. The condensate is caught in a flask. Downstream, impingers and/or solid adsorbers are linked to collect the gaseous PCDD/Fs. Before the last impinger or adsorbent, there is a filter to separate particles and to break aerosols.

After showing the equivalency of the sampling methods, pre-tests for checking the variants of the analytical step were carried out and EN 1948 was drafted. According to the fixed procedure two validation field tests were performed at municipal waste incinerators to determine the performance characteristics. Three sampling teams, representing one of the sampling systems each, carried out the validation test at each of the incinerators. The samples were distributed to six analytical laboratories and to a seventh which performed cross checks for quality assurance. Each sample (extraction solution) was divided into two parts. One part was analyzed and the second one was retained for cross checking or in case of difficulties.

After the evaluation of the tests, several minimum requirements laid down in the draft EN 1948 had to be revised. This resulted in the withdrawal of several measurement results. A third field test at a municipal waste incinerator followed.

In the comparative and validation field test 19 laboratories in 11 European countries were involved. Huge efforts were made for the test because:

- Suitable incineration plants with PCDD/F emissions of nearly 0.1 ng TEQ/m^3 had to be found,

- In case of very low PCDD/F concentrations, e.g. in the range of the detection limits, it was impossible to obtain reliable performance characteristics,

- If the concentrations were above 0.1 ng TEQ/m^3, EC would not accept them because they were out of the monitoring concentration range,

- At that time, some laboratories were not well trained for this concentration range,

- The PCDD/F concentration in the cross section of the duct must be identical as, otherwise, the six sampling trains (two duplicate measurements by each of the three sampling teams) would collect different PCDD/F concentrations,

- Iso-kinetic sampling had to be carried out,

- Certified $^{13}C_{12}$-labelled standards had to be organized and checked for their applicability as sampling, extraction and syringe standards; it had to be tested and defined which of these standards was to be taken for the calculation of results,

- A minimum resolution of MS had to be fixed.

The field tests were sponsored by the EC, the EFTA Secretariat and the German Federal Environmental Agency. EN 1948 was finalized in time before mid-1996. It is subdivided in three parts. Part 1 describes sampling, Part 2 extraction and clean-up, and Part 3 identification and quantification. For each of the three steps, very stringent requirements are specified and illustrated by examples. EN 1948 have been accepted by all EU and EFTA states.

1.6.2 Analysis

PCDD/F analysis is carried out using high resolution mass spectrometry (GC-MS). Quality control procedures are required in each stage of the analysis and recovery spike concentrations associated with both sampling and extraction. The US EPA Method 23 specifies that all recoveries should be between 70% and 130%.

Spike recoveries of $^{13}C_{12}$ congeners (added before the sample is collected to monitor the collection efficiency during sampling) ranged from 30 to 110% in the UK emission inventory done in 1995-1997 (Alcock et al, 1999). The inventory collected 75 samples from different source categories and the analytical blanks for the analysis using Method 23 ranged from less than 0.005 ng to 0.1 ng TEQ.

1.6.3 Detection/quantification limits and interferences

The lower detection limits LOD measured during the validation test of EN 1948 at a municipal solid waste incinerator varied between 0.0001 - 0.0088 ng/m^3 for the 17 individual PCDD/F toxic congeners (EN 1948 -3, 1996).

In the new draft of EN 1948-3 of February 2004, Annex B, the uncertainty for the complete procedure is given to be 30 - 35 % and the external variability is estimated to be ± 0.05 ng I-TEQ/m^3 at a mean concentration of 0.035 ng I-TEQ/m^3. Taking into account the toxic equivalence factors for the individual congeners the resulting over all detection limit varies between 0.001 and 0.004 ng I-TEQ/m3, which means that this report contains figures which are below the overall detection limit. It's reasonable to assume that concentrations lower than 0.001 ng I-TEQ/m^3 should be considered as being not detectable.

In a Canadian study performed in 1999 the variability of sampling and analysis of 53 sets of PCDD/F emission data from 36 combustion facilities was investigated. The limit of quantification LOQ for PCDD/F was estimated to be 0.032 ng TEQ/m^3 (Environment Canada, 1999).

Interferences should be expected to occur from compounds that have similar chemical and physical properties to PCDD/Fs (EN 1948 -3, 1996).

2. Cement production process

In short, cement is made by heating a mixture of calcareous and argillaceous materials to a temperature of about 1450°C. In this process, partial fusion occurs and nodules of so-called clinker are formed. The cooled clinker is mixed with a few percent of gypsum, and sometimes other cementitious materials, and ground into a fine meal - cement.

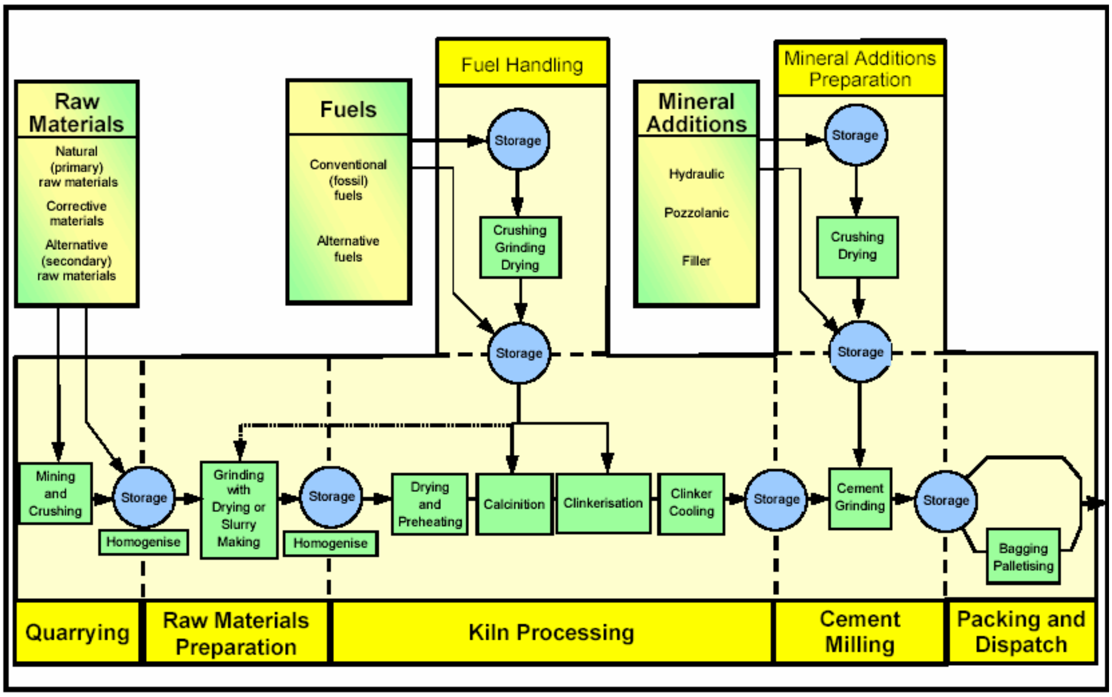


Figure 1 Processes identification and system boundaries of cement production (Environment Agency, 2001)

2.1 Quarrying and pyroprocessing of raw materials

The main components of clinker are lime (CaO), silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). The first stage in the industrial process of cement manufacture is the quarrying of raw materials.

To obtain the proper composition of the raw mix, corrective ingredients normally have to be added to the quarried raw materials. Examples of corrective materials are sand, bauxite and iron ore; which compensate for deficiencies of silica, alumina and iron oxide, respectively. Fly ash, iron slag and other types of process residues can also be used as partial replacements for the natural raw materials.

The raw materials are ground in a mill into a fine powder – raw meal or raw mix – that is suitable for burning in a cement kiln. Typical compositions of raw meal and various raw materials are given in Table 1.

Based on the raw meal composition given in Table 1, the clinker would typically contain 66% CaO, 21% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 5% of other components. The four main oxides make up four major clinker phases, called alite, belite, aluminate and ferrite, see Table 2. To produce these phases, and to obtain them in right proportions, the raw meal is pyroprocessed (”burned”).

Table 1: Typical composition (% weight) of some raw materials and raw meal

Component	Limestone	Marl	Clay	Sand	Bauxite	Iron ore	Raw meal
LOI	40.38	24.68	7.19	0.2	15-20	5-12	35.8
SiO_2	3.76	27.98	67.29	99.2	16-22	20-25	13.2
Al_2O_3	1.10	10.87	8.97	-	44-58	3-9	3.3
Fe_2O_3	0.66	3.08	4.28	0.5	10-16	45-60	2.2
CaO	52.46	30.12	7.27	-	2-4	0.5-2.5	42.1
MgO	1.23	1.95	1.97	-	0.2-1-0	1.5-7	1.9
K_2O	0.18	0.20	1.20	-	-	0.3-0.6	0.6
Na_2O	0.22	0.33	1.51	-	-	-	0.3
SO_3	0.01	0.70	0.32	-	-	-	0.6
Sum	100.00	99.91	100.00	99.9	-	-	100.0

Table 2: Major phases in cement clinker

Name	Formula	Abbreviation
Alite	$3CaO \cdot SiO_2$	C_3S
Belite	$2CaO \cdot SiO_2$	C_2S
Aluminate	$3CaO \cdot Al_2O_3$	C_3A
Ferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

The standard reaction enthalpies for the most important reactions occurring are given in Table 3.

Table 3: Reactions and reaction enthalpies

Reaction	Reaction equation	Standard reaction enthalpy (kJ(kg)
I.Formation of oxides and decomposing reactions		
Evaporation of water	$H_2O(1) \rightarrow H_2O(g)$	2453
Decomposition of kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow$ $Al_2O_3 + 2SiO_2 + 2H_2O$	780
Oxidation of carbon	$C + O_2 \rightarrow CO_2$	-33913
Dissociation of $MgCO_3$	$MgCO_3 \rightarrow MgO + CO_2$	1395
Dissociation of $CaCO_3$	$CaCO_3 \rightarrow CaO + CO_2$	1780
II. Formation of Intermediates		
Formation of CA	$CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3$	-100
Formation of C_2F	$2CaO + Fe_2O_3 \rightarrow 2CaO \cdot Fe_2O_3$	-114
Formation of β-C_2S	$2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2$	-732
III. Sintering reactions		
Formation of C_4AF	$CA + C_2F + CaO \rightarrow C_4AF$	25
Formation of C_3A	$CA + 2CaO \rightarrow C_3A$	25
Formation of C_3S	β-$C_2S + CaO + C_3S$	59

Kåre Helge Karstensen
khk@sintef.no

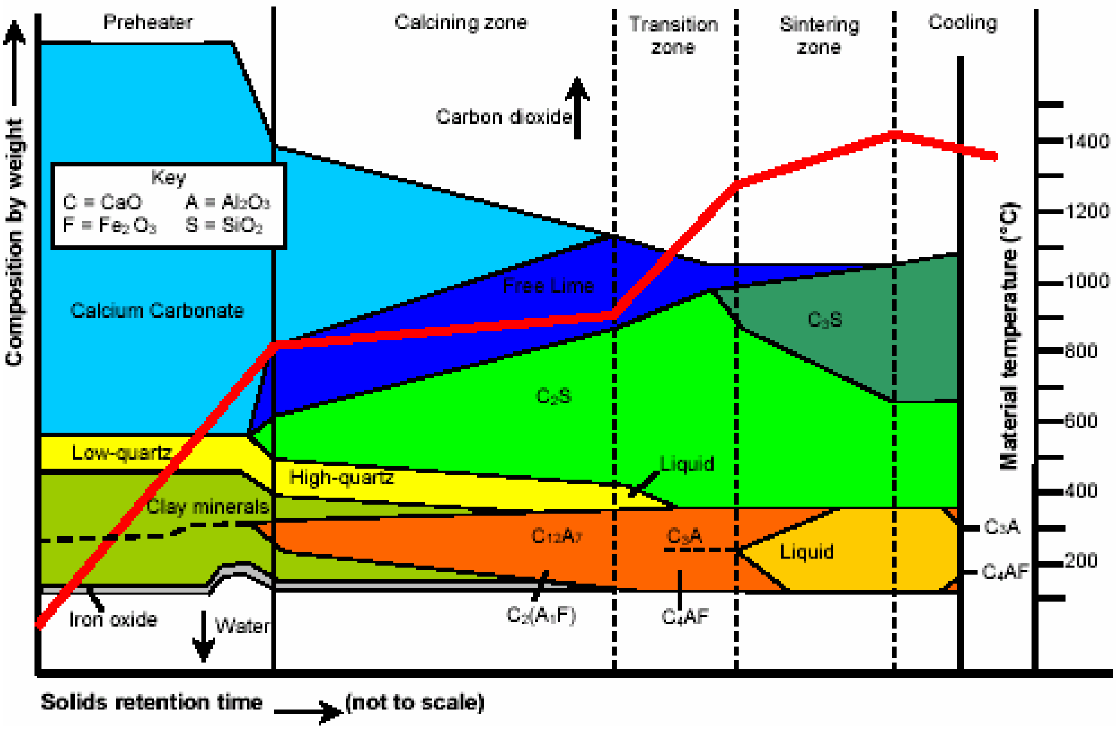


Figure 2 **Typical pre-heater kiln processing system (Environment Agency, 2001)**

The cooled clinker is mixed with cementitious materials such as gypsum, slag and flyash. Different clinker types and different types of additives are used, depending on what type of cement that is to be produced. The mix is ground simultaneously in cement mills and intermediately stored in cement silos. Finally the cement is packed in bags and dispatched, or in bulk.

2.2 Main process routes

There are four main process routes for the manufacture of cement; the dry, semi-dry, semi-wet and wet processes (IPPC, 2000):

1. In the dry process, the raw materials are ground and dried to raw meal in the form of a flowable powder. The dry raw meal is fed to the preheater or precalciner kiln or, more rarely, to a long dry kiln.

2. In the semi-dry process dry raw meal is pelletised with water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses.

3. In the semi-wet process the slurry is first dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate preheater or directly to a filter cake drier for raw meal production.

4. In the wet process, the raw materials (often with high moisture content) are ground in water to form a pumpable slurry. The slurry is either fed directly into the kiln or first to a slurry drier.

Typical kiln exhaust gas volumes expressed as m^3/ton 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 m^3/ton of clinker.

Kiln systems with 5 cyclone preheater stages and precalciner are considered standard technology for ordinary new plants, such a configuration will use 2900-3200 MJ/ton clinker. To optimise the input of energy in other kiln systems it is a possibility to change the configuration of the kiln to a short dry process kiln with multi stage preheating and precalcination. The application of the latest generation of clinker coolers and recovering waste heat as far as possible, utilising it for drying and preheating processes, are examples of methods which cut primary energy consumption.

Energy use will be increased by most type of end-of-pipe abatement. Some of the reduction techniques described will also have a positive effect on energy use, for example process control optimisation.

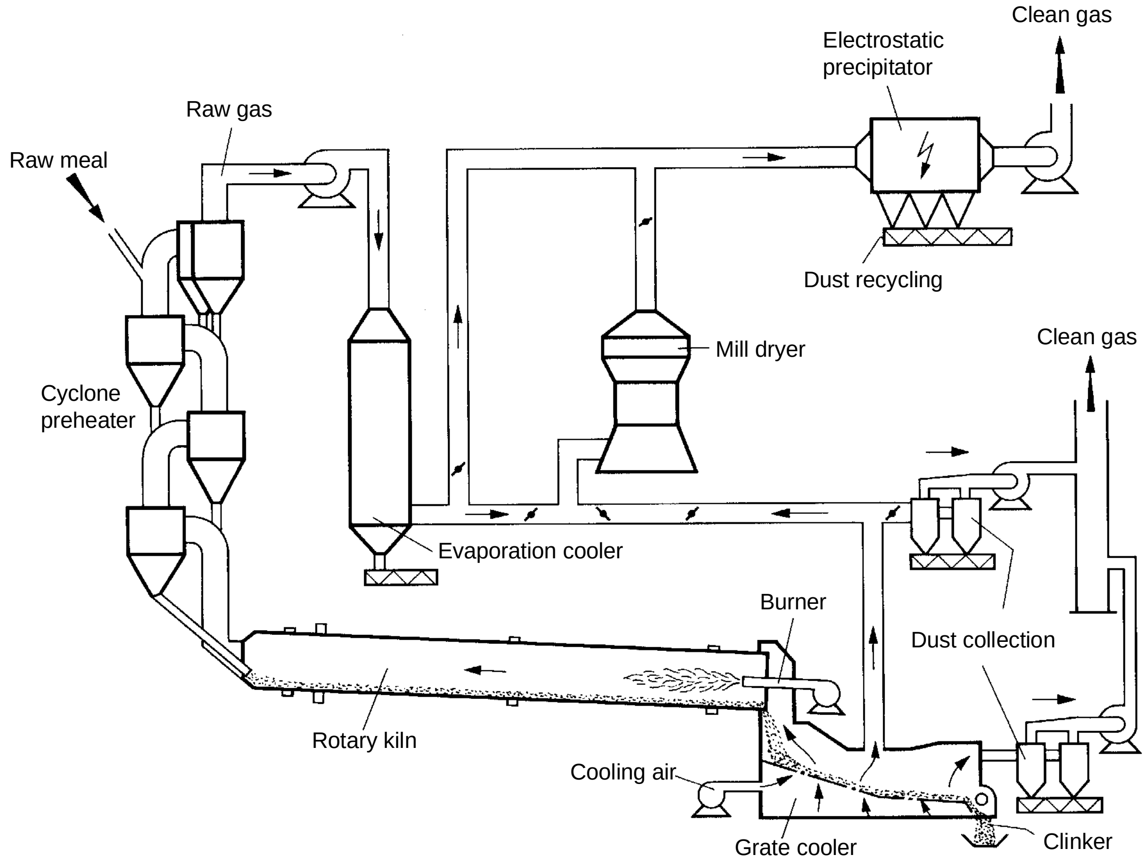


Figure 3: Rotary kiln with cyclone preheater and gas dust collection

2.3 Clinker burning

This part of the process is the most important in terms of emission potential and of product quality and cost. In clinker burning, the raw meal (or raw meal slurry in the wet process) is fed to the rotary kiln system where it is dried, pre-heated, calcined and sintered to produce cement clinker. The clinker is cooled with air and then stored.

In the clinker burning process it is essential to maintain kiln charge temperatures of between 1400 to 1500 °C and gas temperatures of about 2000 °C. Also, the clinker needs to be burned under oxidising conditions. Therefore an excess of air is required in the sintering zone of a cement clinker kiln.

Since the rotary kiln was introduced around 1895 it has become the central part of all modern clinker producing installations. The vertical shaft kiln is still used in a few countries for production of cement clinker, but only at small-scale plants.

The first rotary kilns were long wet kilns where the whole heat consuming thermal process takes place in the kiln itself. With the introduction of the dry process, optimisation led to technologies which allowed drying, preheating and calcining to take place in a stationary installation rather than in the rotary kiln.

The rotary kiln consists of a steel tube with a length to diameter ratio of between 10:1 and 38:1. The tube is supported by two to seven (or more) support stations, has an inclination of 2.5 to 4.5% and a drive rotates the kiln about its axis at 0.5 to 4.5 revolutions per minute. The combination of the tube's slope and rotation causes material to be transported slowly along it. In order to withstand the very high peak temperatures the entire rotary kiln is lined with heat resistant bricks (refractories). All long and some short kilns are equipped with internals (chains, crosses, lifters) to improve heat transfer.

Transient build-ups of material can occur around the inner surface of the kiln depending on the process and raw materials etc. These are known as rings and can occur at the feed end (gypsum rings), near the sintering zone (clinker rings) or the product exit end (ash rings). The cyclones and grates of preheater kilns may also be subject to build up of material which can lead to blockages.

2.3.1 Kiln firing

The fuel introduced via the main burner produces the main flame with flame temperatures around 2000 °C. For process-optimisation reasons the flame has to be adjustable within certain limits. In a modern indirectly fired burner, the flame is shaped and adjusted by the primary air (10-15% of total combustion air).

Potential feed points for supplying fuel to the kiln system are:

- via the main burner at the rotary kiln outlet end;
- via a feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- via secondary burners to the riser duct;
- via precalciner burners to the precalciner;
- via a feed chute to the precalciner/preheater (for lump fuel);
- via a mid kiln valve in the case of long wet and dry kilns (for lump fuel).

Coal/petcoke firing plants are of both indirect- and direct-firing types. Direct-firing plants operate without fine-coal storage and fine-coal metering. The pulverised fuel is blown directly into the kiln with the mill sweeping air acting as carrier and as (flame shaping) primary air. Direct firing plants have a number of drawbacks. In particular kiln-system heat losses are around 200-250 MJ/ton clinker (6 to 8% higher on modern kiln systems). Thus direct firing is seldom installed today.

Fuel oil is, at adequate viscosity and pressure, discharged via an atomiser nozzle into the kiln in order to form the main flame. Flame shaping is mainly accomplished via multi-primary air channel burners with the oil atomiser head in a central location.

Kiln burners for natural gas, too, are designed according to the multi-channel principle, the gas thereby replacing not only coal or fuel oil, but also primary air.

2.3.2 Use of waste as fuel

Preparation of different types of waste for use as fuel is usually performed outside the cement plant by the supplier or by waste-treatment specialist's organisations. This means they only need to be stored at the cement plant and then proportioned for feeding to the cement kiln. A reference document on best available techniques for pre-treatment of wastes is under preparation in the EU.

Wastes that are fed through the main burner will be decomposed in the primary burning zone at temperatures up to 2000 °C. Waste fed to a secondary burner, preheater or precalciner will be burnt at slightly lower temperatures but it is anticipated that the burning zone temperatures in the precalciner will be in the range of 900°C - 1200°C.

Types of waste most frequently used as fuels in the cement industry today are used tyres, waste oils, sewage sludge, rubber, waste woods, plastics, paper waste, paper sludge and spent solvents.

2.3.3 Long rotary kilns

Long rotary kilns can be fed with slurry, crushed filter cakes, nodules or dry meal and are thus suitable for all process types. The largest long kilns have a length-to-diameter ratio of 38:1 and can be more than 200 m long. These huge units produce around 3600 tonnes/day using the wet process. Long rotary kilns are designed for drying, preheating, calcining and sintering, so that only the feed system and cooler have to be added. The upper part of the long kilns is equipped with chain curtains and fixed installations to improve heat transfer.

Wet process kilns, used since 1895, are the oldest type of rotary kilns in use for producing cement clinker. Wet raw material preparation was initially used because homogenisation was easier with liquid material. Wet kiln feed typically contains 32 to 40% water. This is necessary to maintain the liquid properties of the feed. This water must then be evaporated in the specially designed drying zone at the inlet section of the kiln where a significant portion of the heat from fuel combustion is used. This technology has high heat consumption with the resulting emission of high quantities of combustion gas and water vapour.

Long dry kilns were developed in the US based on batch type dry homogenising systems for raw material preparation. Because of the high fuel consumption only a few have been installed in Europe.

2.3.4 Rotary kilns equipped with preheaters

Rotary kilns equipped with preheaters have a typical length-to-diameter ratio of between 10:1 and 17:1. There are two types' preheaters: grate preheater and suspension preheater.

2.3.4.1 Grate preheater technology

Grate preheater technology, perhaps better known as the Lepol kiln, was invented in 1928. It represented the first approach to letting part of the clinkering process take place in a stationary installation outside the kiln. This allowed the rotary kiln to become shorter and so reduced the heat losses and increased energy efficiency.

In the grate preheater nodules made from dry meal on a noduliser disc (semidry process) or from wet slurry filter cakes in an extruder (semi-wet process) are fed onto a horizontal travelling grate which travels through a closed tunnel. The tunnel is divided into a hot gas chamber and a drying chamber by a partition with an opening for the grate. A fan draws the exhaust gas from the rotary kiln into the top of the preheater, through the nodules layer in the hot gas chamber, and then through the cyclones of the intermediate dust collector. In these cyclones large dust particles, which would otherwise cause wear to the fan, are removed. The next fan then draws the gas into the top of the drying chamber, through the moist layer of nodules, and finally pushes it out into the dust collector. In order to achieve optimum thermal efficiency, the semi-wet grate preheaters can be equipped with triple-pass gas systems, and cooler waste air is used for raw material drying. The maximum unit size to have been built is 3300 tonnes/day for a semi-wet kiln system.

The rotary kiln exhaust gas enters the preheater with a temperature of 1000-1100 °C. As it flows through the layer of material in the hot gas chamber, the exhaust gas cools down to 250-300 °C, and it leaves the drying chamber at 90-150 °C. The material to be burnt reaches a temperature of about 150 °C in the drying chamber and 700-800 °C in the heating chamber.

2.3.4.2 Suspension preheater technology

The invention of the suspension preheater in the early 1930s was a significant development. Preheating and even partial calcination of the dry raw meal (dry/semi-wet processes) takes place by maintaining the meal in suspension with hot gas from the rotary kiln. The considerably larger contact surface allows almost complete heat exchange, at least theoretically.

Various suspension preheater systems are available. They usually have between four and six cyclone stages, which are arranged one above the other in a tower 50-120 m high. The uppermost stage may comprise two parallel cyclones for better dust separation. The exhaust gases from the rotary kiln flow through the cyclone stages from the bottom upward. The dry powdery raw material mixture is added to the exhaust gas before the uppermost cyclone stage. It is separated from the gas in the cyclones and rejoins it before the next cyclone stage. This procedure repeats itself at every stage until finally the material is discharged from the last stage into the rotary kiln. This alternate mixing, separation, and remixing at higher temperature are necessary for optimal heat transfer.

2.3.4.3 Shaft preheaters

A considerable number of shaft preheaters were built following the introduction of suspension preheater technology, given its theoretically superior heat exchange properties. However, the difficulty of ensuring an even distribution of meal to gas meant that actual performance was far worse than expected, and technology using shaft stages alone was eventually abandoned in favour of hybrid systems with cyclone stages or pure multi-stage cyclone preheaters. Some of those hybrids are still in operation, however most of them have been converted to pure cyclone preheaters.

A shaft stage is considerably less sensitive to build-up problems than a cyclone stage, which can be an advantage for the bottom stage in cases where excessive quantities of circulating elements (chlorides, sulphur, and alkalis) are present. Hybrid preheaters with a bottom shaft stage are still available for new plants.

Typical capacities of shaft preheater kilns were up to 1500 tonnes/day, whereas hybrid systems can produce 3000 tonnes/day or more.

2.3.4.4 Four stage cyclone preheater

The four-stage cyclone preheater kiln system was standard technology in the 1970s when many plants were built in the 1000 to 3000 tonnes/day range. The exhaust gas, which has a temperature of around 330 °C is normally used for raw material drying.

When the meal enters the rotary kiln, calcination is already about 30% completed. Severe problems have in the past been encountered with four stage preheaters in cases where inputs of circulating elements (chlorides, sulphur, and alkalis) from the feed and/or fuel were excessive. Highly enriched cycles of these elements lead to build-ups in cyclone and duct walls, which frequently cause blockages and kiln stops lasting several days. Kiln gas bypass, i.e. extraction of part of the particulate laden gas stream leaving the kiln so that it bypasses the cyclone system, is a frequently used solution to the problem. This bypass gas is cooled to condense the alkalis and then passed through a dust collector before discharge. Whilst in some regions it is necessary, for the control of clinker alkali levels, to send the bypass dust and part of the kiln dust to landfill, in all other cases it is fed back into the production process.

Almost all four-stage suspension preheaters operate with rotary kilns with three supports. This has been the standard design since around 1970. Kilns with diameters from 3.5 to 6 m have been built with length to diameter ratios in the range 13:1 to 16:1. Mechanically simpler than the long wet and dry kilns, it is probably the most widely used kiln type today.

2.3.5 Rotary kilns with preheater and precalciner

The precalcination technique has been available to the cement industry since about 1970. In this procedure the heat input is divided between two points. Primary fuel combustion occurs in the kiln burning zone. Secondary burning takes place in a special combustion chamber between the rotary kiln and the preheater. In this chamber up to 60% of the total fuel can be burnt in a typical precalciner kiln. This energy is basically used to calcine the raw meal, which is almost completely calcined when it enters the kiln. Hot air for combustion in the calciner is ducted from the cooler. Material leaves the calciner at a temperature above 900 °C, the burning zone temperature in the precalciner is expected to be up to 1 000 – 1 400°C.. In principle, secondary burning can also be applied in a kiln with a grate preheater. For a given rotary kiln size precalcining increases the clinker capacity.

Kiln systems with five cyclone preheater stages and precalciner are considered standard technology for new dry process plants.

The size of a new plant is primarily determined by predicted market developments, but also by economy of scale. Typical unit capacity for new plants today is from 3 000 to 5 000 tonnes/day. Technically, larger units with up to 15 000 tonnes/day are possible, and several 10 000 tonnes/day kilns are currently in operation in Asian countries.

Earlier precalciner systems had only four preheater stages with accordingly higher exhaust gas temperature and fuel consumption. Where natural raw material moisture is low, six-stage preheaters can be the preferred choice, particularly in combination with bag-filter dedusting.

Where excessive inputs of circulating elements are present, a kiln gas bypass is required to maintain continuous kiln operation. However, due to the different gas flow characteristics, a bypass in a precalciner kiln is much more efficient than in a straight preheater kiln.

In spite of the fact that the meal enters the kiln 75 to 95% calcined, most precalciner kilns are still equipped with a rotary kiln with a calcining zone, i.e. with an L/D ratio of 13:1 to 16:1 as in the case of the straight preheater kilns.

2.3.6 Raw material and air flows

The cold raw meal is injected into the gas flow between the upper two cyclone stages of the preheater. Flowing down the cyclone tower, the meal is dried and the clay minerals dehydrate and decompose. Also, any organic compounds present in the raw meal are oxidized, and magnesium carbonate is calcined. In this preheating process, the meal temperature is typically increased to about 700^{o}C, while the temperature of the counter flowing gas is reduced from about 900^{o}C to about 350^{o}C, depending on the preheater type. There may be four, five or six cyclone stages, resulting in different thermal efficiencies.

In the precalciner, the raw meal is calcined at a temperature of about 900^{o}C, i.e. a flame temperature of up to 1 200^{o}C is necessary. The solids residence time in the preheater is in the order of tens of seconds and up to minutes.

After precipitation in the lower cyclone stage (which is sometimes regarded as being part of the precalciner), the precalcined meal enters the rotary kiln. In the kiln, the meal is first completely calcined, where after the clinker formation reactions take place. The combination of the slight inclination and the revolution of the kiln cause the solid material to be transported slowly through it. Typically, the residence time in the rotary kiln is in the order of 30-60 minutes.

After reaching the maximum temperature of approximately 1450°C, the clinker is discharged from the kiln and cooled in the clinker cooler, the residence time in the cooler being about 15 minutes. The purpose of the cooler is both to recover heat from the hot clinker and to cool the clinker to a temperature level suitable for the downstream equipment.

The cooling air is generally divided into three: One part, the secondary air, is used as combustion air in the primary burning zone, in the rotary kiln. Another part, called the tertiary air, is drawn from the cooler to the precalciner through a separate duct – the tertiary air duct – and used as combustion air in the secondary burning zone, in the precalciner. The last part of the cooling air, which may be called excess cooling air, is drawn out of the cooler and released to the surroundings. The temperature of the excess cooling air discharged from the cooler is typically 200-300°C.

2.3.7 Shaft kilns

Shaft kilns consist of a refractory-lined, vertical cylinder 2-3 m in diameter and 8-10 m high. They are fed from the top with raw meal pellets and fine grained coal or coke. The material being burnt travels through a short sintering zone in the upper, slightly enlarged part of the kiln. It is then cooled by the combustion air blown in from the bottom and leaves the lower end of the kiln on a discharge grate in the form of clinker.

Shaft kilns produce less than 300 tonnes/day of clinker. They are only economic for small plants, and for this reason their number has been diminishing.

2.3.8 Releases from cement kiln systems

The main releases from the production of cement are to air from the kiln exhaust gases, the clinker cooler exhaust and any bypass gases. There may also be release of kiln dust to landfills depending on the alkali content of the raw materials used. Polluting releases result from the particular chemical composition of the raw materials and fuels used.

The production of cement clinker in kiln systems is characterised by cycles of components such as dust, chlorides, sulphur compounds and alkalis. These cycles may be internal to the system or partially induced by the recycling of kiln dust back into the system from abatement equipment. These cycles can influence the inherent releases from any kiln processing system. The cycles result from the variation in the capacity of the material within the kiln system to absorb or release substances. The absorptive capacity of material varies with its physical and chemical state, which in turn depends on its position within the kiln system. For instance, material leaving the calcination stage of the kiln process has high free lime content and therefore has a high absorptive capacity for acid species such as SO_2. However, when this same material passes to the sintering stage some of the absorbed sulphur will be released back to the gas phase. This variation, combined with the counter current nature of the air and solids flow through the system, results in the capture into the clinker of many of the pollutants that would otherwise potentially be released to air.

The type of kiln processing system also has a marked effect on the magnitude of releases to air. The pre-heater section on a dry cement kiln is a very efficient absorber of volatile or acid species such as sulphur oxides. This is due to the high gas-solid contact with the raw meal within the cyclone array, which acts as a dry scrubbing system.

The wet end (back end) of a wet cement kiln also acts as a pollutant absorber but it is not as efficient as a pre-heater kiln. Wet cement kilns can release more of some pollutants per tonne of clinker production compared with dry kilns due to their increased fuel requirements and larger gas flows.

2.3.8.1 Kiln dust, alkalis and kiln bypasses

In the cement industry levels of alkalis, sulphur and chlorides (volatile components) in the product clinker are controlled to achieve the required quality of the product cement. In some cases, construction standards impose an alkali specification of 3 kg/m^3 of concrete because of the risk of alkali-aggregate reactions and thus the alkali content of the cement is limited. Volatile components can also be a problem in the kiln system, as high levels can cause blockages in pre-heater cyclones or form rings in the in the rotary kiln inlet zone.

The cement industry has several options to control clinker alkali content. The careful control of the alkali content of raw materials can be used but the practicality of this depends on the availability of low alkali raw materials.

In wet cement kilns, some of the volatile components evaporate in the sintering section but condense in the drying zone on the fine particulate matter. Hence, if an electro static precipitator (ESP) is used for particulate arrestment, the finer proportion of the cement kiln dust (CKD) containing the highest concentration of volatile components can be removed whilst the remaining dust is recycled (by selecting the correct fields in the ESP). The recycle can be achieved by introducing CKD into the rotary kiln by using specially designed scoops in the cylindrical walls of the kiln or, more frequently by injecting CKD into the burning zone of the kiln (insufflations). In dry process kilns, CKD is always reintroduced into the raw meal or may be fed directly to the cement mill.

The inherent absorption capacity of pre-heater dry cement kilns can cause problems with blockages in the cyclone systems caused mainly by build-ups of volatile components. One option to curtail volatile component levels is by bypassing part of the particulate laden gas stream out of the kiln back end away from the cyclone system and condensing the volatiles by cooling. Bypasses of 10-30% of the kiln gas flow are typical (<10% of total flows). This bypass stream can be high in pollutants (particulates and sulphur oxides) and must be treated separately.

Both kiln dust and bypass dust can be completely returned to process providing clinker alkali levels are controlled. When this is not possible dust is sent to controlled landfills or sold as binder for waste stabilisation.

2.3.8.2 Kiln exhaust gases

In all kiln systems the exhaust gases are finally passed through an air pollution control device (electrostatic precipitator or bag filter) for separation of the dust before going to the main stack.

In the dry processes the exhaust gases have relatively high temperature and may provide heat for the raw mill when it is running (compound operation). If the raw mill is not running (direct operation), the gases are normally cooled with water sprays in a conditioning tower before going to the dust collector, both to reduce their volume and to improve their precipitation characteristics.

2.3.8.3 Gaseous and particulate emissions from cement kilns

Carbon dioxide, nitrogen oxides and sulphur oxides are the main gaseous emissions from cement plants.

About 60% of the CO_2 emissions originate from the calcination of carbonates; the remaining 40% comes from the oxidation of carbon in the fuels. Typically, 0.85 kg of CO_2 is emitted for each kg of clinker produced.

NO_x emissions from cement kilns mainly arise from oxidation of fuel-bound nitrogen and nitrogen in the combustion air. For precalciner kilns, emissions range from 0.4 to

3.2 grams per kg clinker produced. A number of techniques can be applied in order to reduce the NO_x emissions.

99% of the sulphur oxides emitted via the stack of cement kilns is in the form of SO_2. SO_2 mainly originates from sulphides and organically bound sulphur in the raw materials.

Table 4: Specific NOx (as NO_2) emission rates for different kiln types

Kiln type	Typical heat input requirement (MJ/kg clinker)	Range of NO_x emissions (g/kg clinker)
Long wet kiln	5.0-6.0	1.6-8.8
Long dry kiln	4.7	2.8-4.8
Preheater kiln	3.1-4.0	1.1-5.3
Precalciner kiln	3.0	0.4-3.2

Dust emitted from cement plant is mainly a local problem. Most cement plants have dedusting equipment installed, such as electrostatic precipitators (EPs), which effectively reduce the dust emissions (see principle below).

2.3.8.4 CO-trips

Carbon monoxide can arise from any organic content in the raw materials and, occasionally, due to the incomplete combustion of fuel. The contribution from the raw materials, due to preheating, will be exhausted with the kiln gases.

Control of CO levels is critical in cement kilns when EPs are used for particulate abatement, to ensure concentrations are kept well below the lower explosive limit. If the level of CO in the EP rises (typically to 0.5% by volume) then the electrical system is switched off to eliminate the risk of explosion. This leads to unabated particulate releases from the kiln. CO trips can be caused by unsteady state operation of the combustion system. This sometimes occurs when feeding solid fuels, so solid-fuel feeding systems must be designed to prevent surges of fuel into the burner.

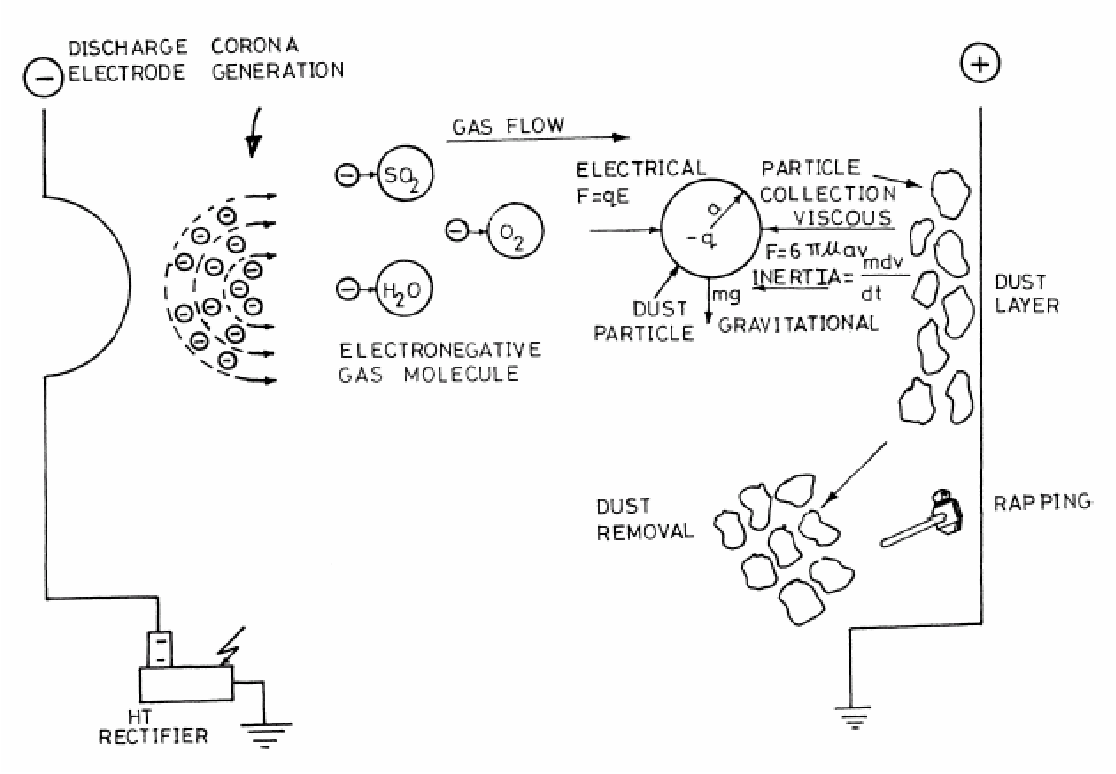


Figure 5 Principle of electrostatic precipitators

2.4 Cement production in developing countries

The global cement industry is more and more dominated by the bigger international companies, which is first of all expanding in emerging markets, i.e. developing countries. The bigger cement companies usually adopt their internal standards on business ethics, labour rights, corporate responsibility, health, safety and environment etc. throughout the world. When these companies build new plants in any country, with no exception the best available technologies BAT applies. This is also the most economic feasible option, which constitutes a competitive advantage and thereby contributes to raise the performance in developing countries. Older, polluting and less competitive technologies will gradually be phased out.

The bigger cement companies realises their challenges with regards to sustainability, reflected by the Cement Sustainability Initiative (CSI), which is a project spearheaded by 14 of the world's largest cement producers in association with the World Business Council for Sustainable Development (WBCSD).

Table 5 CSI companies

WBCSD CSI Companies	Home country	Approximate number of employees	Production of cement/clinker in approx. no. countries	Cement clinker plants	Cement production (million tons)
CEMEX	Mexico	26,000	30	70	81
Cimpor	Portugal	6,000	8		21
Heidelberg Cement	Germany	38,000	50	85	60
Holcim	Switzerland	48,000	40	90	95
Italcementi	Italy				
Lafarge	France	38,000	47	117	110
RMC	United Kingdom	30,000	26	21	20
Siam Cement	Thailand				
Taiheiyo Cement	Japan	18,770	6	23	51
Votorantim	Brazil	5,600		22	

3. Utilisation of alternative fuels and raw materials in cement production

Wastes and hazardous wastes in the environment represent one of our most challenging problems. The best hazardous organic waste disposal method is process combustion. Cement kilns have been used for burning hazardous industrial wastes all over. Existing cement kilns, when properly operated, can destroy all kinds of organic hazardous wastes in a safe and sound manner. Even the most complex chlorinated hydrocarbons can be completely destroyed during normal cement kiln operations. Burning hazardous wastes in cement kilns is mutually beneficial to both industry, which generates such wastes, and to society and government, who want to dispose properly of such wastes in a safe, environmentally acceptable manner. The added benefit of non renewable fossil energy conservation is important, since large quantities of valuable natural fuel can be saved in the manufacture of cement when such techniques are employed.

3.1 Theory of combustion

Combustion is a combination of pyrolysis and oxidation. Pyrolysis is a chemical change resulting from heat alone. Oxidation is the gross reaction of an organic species with oxygen and requires relatively low activation energies. Pyrolysis involves the breaking of stable chemical bonds, often resulting in molecular rearrangement, and higher molecular weight products. Pyrolysis occurs in a time scale of seconds, while oxidation occurs in milliseconds.

For efficient combustion, oxidation should be the dominant process, with pyrolysis occurring either incidentally to the oxidation or to put a material into a better physical form for oxidation.

To combust wastes effectively, pyrolysis must be efficient and complete before oxidation of the molecular chemical by-products can occur. This is why cement kilns are ideal; with kiln gas temperatures up to 2 000°C, long residence time of up to 6 seconds, or more, insures complete pyrolysis or breakdown of organic wastes. Complete oxidation can then easily follow.

Combustion temperature and residence time for mixed hazardous wastes cannot be readily calculated and are often determined empirically. Some common solvents such as alcohols and toluene can easily be combusted at about 1 000°C and one second residence time, while other more complex organic halogens require more stringent conditions such as the US EPA Toxic Substances Control Act (TSCA) PCB incineration criteria of 1 200°C and 2 sec residence time. In cement kilns, the gas temperatures will be up to 2000°C with residence time up to 10 seconds and the material temperature will be up to 1 450°C.

In order to burn hazardous wastes in cement kilns properly, it is important to know the parameters given in Table 6.

Table 6 Information needed for combustion of waste materials

Critical waste incineration parameters	Physical and chemical properties
Ultimate analysis	C, H, O, N, H_2O, S and ash composition
Metals	Na, K, Cu, V, Ni, Fe, Pb, Hg, Tl etc.
Halogens	Chlorides, bromides, fluorides
Heating value	Joule or cal/gram
Solids	Size, form and quantity
Liquids	Viscosity, specific gravity and impurities
Gases	Density and impurities
Organic portion	Percentage
Special characteristics	Corrosiveness, reactivity, flammability
Toxicity	Carcinogenicity, aquatic toxicity, etc.

3.2 Utilisation and co-processing of hazardous wastes

In Europe, cement kilns utilising wastes as co fuel must comply with the emission limit values laid down in the Council Directive 2000/76/EC on the Incineration of Waste.

Industrial facilities and cement kilns in the US combusting hazardous wastes must comply with emission limit values laid down in the NESHAPS (1999). In addition, they have to perform a Test Burn to demonstrate the incinerator performance on selected principal organic hazardous constituents (POHC). The rule requires that new and existing facilities demonstrate 99.99% destruction and removal efficiency (DRE) for POHC in the waste stream. Achieving this level of DRE "*will ensure that constituents in the waste are not emitted at levels that could pose significant risk*". On the other hand, a destruction and removal efficiency of 100% will never be possible to establish or demonstrate due to detection limits in the analytical instruments. This means that a demonstrated DRE of 99.99% is usually higher in reality.

The principal organic hazardous constituents should be representative of the compounds in the waste stream that are the most abundant and the most difficult to destroy. Accordingly, chlorinated and aromatic compounds are often chosen because they are difficult compounds to destroy.

3.2.1 Fate of the constituents in the hazardous waste fuel

The hazardous waste used as a fuel by the cement industry consists mainly of organic material, but may also contain trace amounts of metal components. To determine whether or not a cement kiln can burn hazardous waste fuel effectively, the fate of the organic constituents had to be determined. In other words, what happens to the components in the combustion process?

3.2.2 Organic constituents

Complete combustion of an organic compound composed only of carbon and hydrogen produces carbon dioxide and water. If the organic compound contains chlorine, then hydrogen chloride or chlorine gas is also produced, depending on the combustion conditions. In addition, if organic compound contains nitrogen or sulphur, then oxides of these elements (e.g., NO_x or SO_x) are produced. An organic compound is considered to be destroyed if the products mentioned above are the only ones formed.

If combustion conditions are not conductive to the complete destruction of the organic compounds, products of incomplete combustion (PICs) can be emitted from the combustion device. One of the steps in determining whether a cement kiln can burn hazardous waste effectively is the demonstration of the destruction of the organic components. It should however be emphasised that waste are not fed under kiln stops and start up or shut down.

Testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered. Lauber (1987), Ahling (1979) and Benestad (1989) describe some of these early tests on US, Swedish and Norwegian kilns, which confirmed the ability of cement kilns to destroy the organic component of a waste feed.

For example, the DRE for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and PCBs has typically been measured at 99.995% and better. Comprehensive emission studies have also been performed when a conventional fuel such as coal was burned, and when hazardous waste was introduced, and these have generally concluded that no significant differences could be measured between usages of the two fuels. For example, Branscome et al (1985) observed that ”*no statistically significant increase in emission rates were observed when the waste fuel (as opposed to coal) was burned*”. Early studies on dioxin emissions have also come to this conclusion (Branscome et al, 1985; Lauber, 1987;

Garg, 1990). In general, the level of dioxins emitted during the use of conventional fuel was similar to their concentration when hazardous waste was introduced into the kiln.

3.2.3 Results from trial burns conducted in the 1970s

In the mid-1970s, a series of tests were conducted at the St. Lawrence cement plant in Canada to measure the destruction of various chlorinated waste streams being fed into their wet process cement kiln. The overall DRE established for the chlorinated compounds was greater than 99,986%. This value is artificially low because the water used to slurry the raw feed was contaminated with low molecular weight chlorinated compounds (Mantus, 1992).

In 1978, a series of tests was conducted at the Stora Vika Cement Plant in Sweden to evaluate the efficiency of their wet process cement kiln in destroying various chlorinated waste streams. Although chloroform was found in the stack gas, the majority of the chlorinated compounds were not detected. A DRE greater than 99,995% was determined for methylene chloride and a DRE greater than 99.9998% was demonstrated for trichloroethylene (Mantus, 1992). The results from these tests confirm the ability of the cement kiln to destroy the organic components in the hazardous waste fuel as part of standard operations, even before U.S. regulations were in place requiring this level of destruction.

3.2.4 Results from trial burns conducted in the 1980s

Trial burns conducted in the 1980s continued to demonstrate that high DRE's could be obtained for the organic constituents in the hazardous waste fuel burned in cement kilns. The results of trial burns of one wet and one dry process cement kiln illustrate the typical values obtained for DRE's. The principle organic hazardous constituents selected for the trial burns were methylene chloride, 1,1,2-trichloro-1,2,2-

trifluoroethane (Freon 113), methyl ethyl ketone, 1,1,1-trichloroethane and toluene. As summarized in the table below, the majority of the DREs were greater than 99.99%. DREs less than 99.99% resulted from either laboratory contamination problems or improper selection of the POHCs (Mantus, 1992).

Table 7 **Average DREs[a] for a wet and a dry process cement kiln**

Selected POHCs	Wet process kiln	Dry process kiln
Methylene chloride	99.983%	99.96%
Freon 113	>99.999%	99.999%
Methyl ethyl ketone	99.988%	99.998%
1,1,1-Trichloroethane	99.995%	>99.999%
Toluene	99.961%	99.995%

Additional DREs were obtained in the trial burn for the dry process cement kiln. Since styrene, ethylbenzene, o-xylene, and benzaldehyde were also present in the waste stream, DREs were determined for each of these components, even though they were not specifically selected as POHCs. Similar to toluene, benzaldehyde was detected in stack emissions whether the fuel consisted solely of coal or a mixture of coal and hazardous waste. Regardless of this occurrence, a DRE of 99.998% was calculated for benzaldehyde. The other components were not detected in the stack gas and therefore the DREs were determined to be greater than 99.999% (Mantus, 1992).

3.2.5 Results from trial burns conducted in the 1990s

Trial burns conducted in the 1990s have focused on the selection of compounds as POHCs that would not typically be present as contaminants or generated as PICs from the combustion of conventional fuel. Use of this criterion has resulted in more accurate DREs being obtained.

In a DRE testing of a dry process cement kiln equipped with a preheater, carbon tetrachloride and trichlorobenzene were chosen as the POHCs. When hazardous waste fuel was fed to the burning zone of the kiln, DREs obtained were greater than 99.999% for carbon tetrachloride and greater than 99.995% for trichlorobenzene. To determine the limits of the system, DREs were also determined when these POHCs were fed to the entrance (i.e., cooler end) of the kiln along with tyres. DREs obtained were greater than 99.999% for carbon tetrachloride and greater than 99.996% for trichlorobenzene.

Recent DRE testing conducted at a cement kiln owned by United Cement supports the foregoing results. Sulphur hexafluoride was chosen as the POHC because of its thermal stability and ease of measurement in the stack gases. In addition, "contamination" problems and PIC interferences are unlikely with the use of this compound. DREs greater than 99.9998% were obtained in every case.

3.2.6 Results from newer trial burns conducted in the 2000d

In 2001 a test burn with pesticide contaminated soil fed into the kiln inlet was performed in a dry process kiln in Colombia. The test burn result showed a DRE of >99.9999% for all the introduced pesticides.

A test burn with two expired chlorinated insecticide compounds introduced at a rate of 2 tons per hour through the main burner was recently carried out in Vietnam. The destruction and removal efficiency for the introduced insecticides was >99.99999%.

3.2.7 Results from trial burns that focused on PCBs

The results of trial burns involving PCBs provide additional support for the ability of a cement kiln to destroy the organic constituents in the hazardous waste fuel. Because of their useful characteristics, such as thermal stability, exceptional dielectric properties, and non-flammability, PCBs were widely used in the U.S. PCB was banned by the U.S. Congress in 1976. At the same time, the TSCA, which regulated the disposal of PCBs, was passed. Incineration was recognized as the only acceptable method for the disposal of significant concentrations (i.e., greater than 500 ppm) of PCBs. A DRE of 99.9999% is required by TSCA for the incineration of these compounds.

The potential for using cement kilns to incinerate PCBs has been investigated. Since PCBs are such stable compounds, the ability of a cement kiln to destroy these compounds indicates the overall ability to destroy organic constituents in hazardous wastes. The DREs determined from several trial burns conducted in many countries indicate that cement kilns are effective at destroying PCBs. The majority of cement kilns burning hazardous waste as fuel have chosen not to burn PCB wastes for the reasons of perception and bad mention.

3.2.8 Trial burns – a summary

Earlier data which indicated cement kiln DRE results below 99.99% are either from outdated sources or improperly designed tests, or both. In the early years of development of this technology and the sampling and analytical techniques to evaluate its environmental performance, there were several instances where POHCs were selected that did not meet the necessary criteria's. For example, a major problem with many early tests was that the POHCs selected for DRE evaluation were organic species that are typically found at trace levels in the stack emissions from cement kilns that burn solely fossil fuel. While these products of incomplete combustion (PICs) were emitted at very low levels, they nonetheless greatly interfered with the measurement of POHC destruction. Practitioners quickly learned that DRE could not be properly measured if POHCs used in testing were chemically the same or closely related to the type of PICs routinely emitted from raw materials. For that reason, early DRE test results (i.e., before 1990) should always be treated with suspicion, particularly if the POHCs used were not in the group of four compounds listed above.

In a few cases, operational factors during the testing or sampling and analytical techniques contributed to the low DRE results. These typically were problems that occurred only in the earliest tests conducted during the developmental stages of this technology and should be disregarded as no longer representative of its performance.

Trial burns is a good way of demonstrating a kilns performance and ability to destroy wastes in an irreversible and sound way, but the design and the conditions of the trial is crucial.

4. Regulatory framework

Regulations on POP's emissions from cement kilns is only "recently" been adopted in developed countries and has so far been focusing on PCDD/F emissions. In many developing countries regulation and adequate legislation in not in place, were it is enforcement is usually lacking. However, the global cement companies are becoming more and more important in emerging economies and if present they normally make sure that they are in compliance with internationally accepted emission standards. The availability of PCDD/F data from developing countries is still rare.

4.1 Background for legislation on PCDD/F emissions in the European Union

In the early nineties the European Commission (EC) drafted the Directive 94/67/EC on the incineration of hazardous waste (Bollmacher, 2001). Due to the fact that this Directive was supposed to have a high level of environmental protection which requires the setting and maintaining of appropriate plant operating conditions and emission limit values, EC requested CEN (European Committee for Standardization) to prepare well-validated European Standards (ENs), so-called harmonized standards, to monitor several pollutants and special attention was paid PCDD/Fs. The directive entered into force on 16 December 1994. All member states of the European Union (EU) had to bring into force their laws, regulations and administrative provisions necessary to comply with this directive before 31 December 1996. In the directive a PCDD/F limit value of 0.1 ng TEQ/m^3 was set as an average value measured over the sample period of a minimum of six hours and a maximum of eight hours. The emission limit values had to be met from January 1997 at the latest unless, at least six months before that date, the availability of harmonized measurement methods had not been established at Community level. The standardization work was taken over by CEN/Technical Committee (TC) 264 "Air quality". Working Group 1 "Dioxins" of CEN/TC 264 established in time EN 1948 Parts 1 to 3 for monitoring a limit value of 0.1 ng TEQ/m^3 with sufficiently low detection limits and standard deviations to allow a meaningful result. EN 1948 was accepted by all member countries so that the emission limit value was mandatory in the EU as from January 1997. With respect to PCDD/Fs the following restrictions of the directive are of interest apart from the emission limit value of 0.1 ng TEQ/m3:

- Even under the most unfavourable conditions a temperature of > 850 °C has to be maintained for at least two seconds to destroy PCDDs/PCDFs and to avoid precursers (if more than 1 % of halogenated organic substances, expressed as chlorine, are incinerated, the temperature has to be raised to at least 1100 °C).

- Sampling and analysis of PCDDs/PCDFs shall be carried out as specified in EN 1948.

- At least two measurements per year shall be carried out (one measurement every two months for the first 12 months of plant operation). All measurements shall meet the emission limit values.

- The measurement results are based on standard conditions (273 K, 101.3 kPa, dry gas, 11 % O_2, or 3 % O_2 in case of waste oil).

- The determination of the emission limit values for co-incineration of hazardous waste must be calculated according to equation:

$$\frac{V_{waste} \times C_{waste} + V_{proc} \times C_{proc}}{V_{waste} + V_{proc}} = C$$

where V is the exhaust gas volume resulting from the incineration of hazardous waste or from the plant process, C is the total emission limit value, C_{waste} is emission limit value for plants to incinerate hazardous waste only (0.1 ng TE/m^3), $C_{process}$ is the emission limit value of the normal process laid down in the permit; in the absence of this data the mass concentrations are used.

- The emission limit value shall not apply to existing incineration plants before 31 December 2006.

- In accordance with Article 130t of the treaty any member state of the EU is allowed to maintain or introduce more stringent measures for the protection of the environment.

The co-incineration of hazardous waste in connection with the need to meet the emission limit value C_{waste} (0.1 ng TEQ/m³) makes high demands on the PCDD/F measurement technique. The PCDD/F emission values of the normal process and, in addition, the PCDD/F emission values of the process including the co-incineration have to be determined. In all EU member states EN 1948 is the official reference measurement method by law for monitoring PCDD/F emission limit values.

In addition to Directive 94/67/EG1 dealing with hazardous waste, a new Directive 2000/76/EC on the incineration of waste entered into force in December 2000. This directive includes the incineration of waste and hazardous waste as well as co-incineration of hazardous waste so that the existing two Directives on waste incineration – presenting a low level of environmental and human health protection – and the Directive on hazardous waste incineration shall be repealed as from December 2005. With respect to the PCDD/Fs the new Directive 2000/76/EC specifies the same requirements as those stated in Directive 94/67/EG and the following important items:

- If in a co-incineration plant more than 40 % of the resulting heat release come from hazardous waste, the complete emission limit value is 0,1 ng TE/m3,

- At least two PCDD/F measurements per year shall be carried out (one measurement at least every three months for the first 12 months of plant operation).

- EC shall decide, as soon as appropriate measurement techniques are available, the date from which on continuous measurements shall be carried out for PCDD/F monitoring.

- At least one PCDD/F measurement every six months (one at least every three months for the first 12 months of plant operation) shall be carried out for water discharges from the cleaning of exhaust gases at the point of the waste water discharge. The limit value is 0.3 ng TE/l. The measurements shall not exceed the limit value.

- The directive shall apply to existing plants as from December 2005.

As regards Directive 2000/76/EC5 it shall be emphasized that the Directive 96/61/EC concerning integrated pollution prevention and control (IPPC) in which all aspects of an installation environmental performance are considered in an integrated manner, shall be taken into account as well as the BREFs (Best Available Technique Reference Documents) established by the European IPPC Bureau, Sevilla, under the umbrella of the EC. BREFs are part of the Directive 96/61/EC and have to be taken into account by the authorities for IPPC permits. They describe the best available techniques for different fields of industry.

Moreover, it shall be stressed that the Protocol on persistent organic pollutants signed by the community within the framework of the United Nations Economic Commission for Europe (UN-ECE) Convention on long-range transboundary air pollutions sets the following legally binding PCDD/F emission limit values: 0.1 ng TEQ/m^3 for incinerating more than 3 tonnes per hour of municipal solid waste and 0.5 ng TEQ/m^3 for installations burning more than 1 tonne per hour of medical waste, and 0.2 ng TEQ/m^3 for installations incinerating more than 1 tonne per hour of hazardous waste.

4.1.1 PCDD/F emission limit values for cement kilns

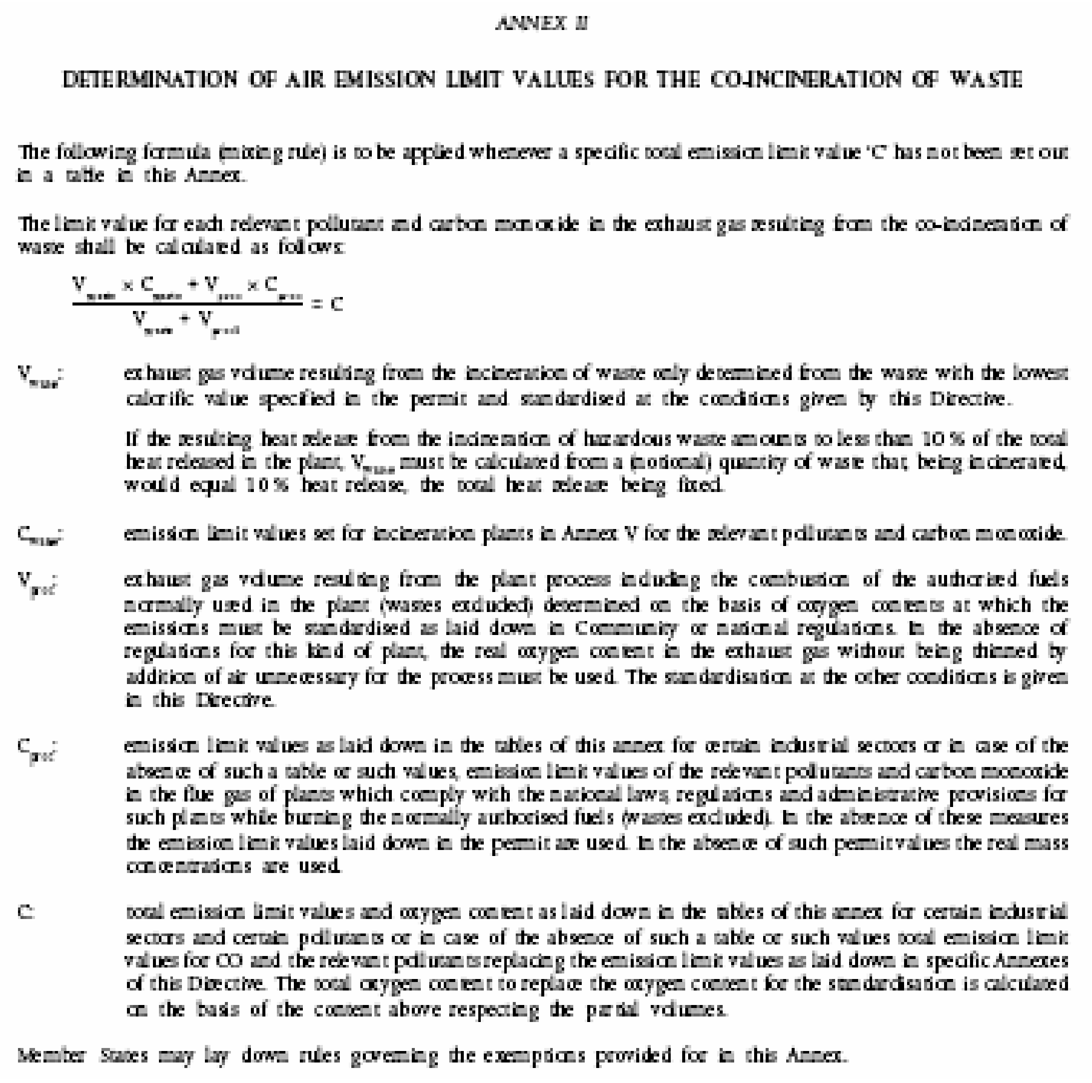
Gaseous emissions from cement kiln using conventional fuels are regulated within the European Union under the so-called Air Framework Directive 84/360/EEC on the combating of air pollution from industrial plants (Eduljee, 1998). A technical note defining Best Available Techniques (BAT) for the manufacture of cement was published in 2000 (IPPC), and includes the emission levels achievable when using conventional fuels within the kiln, but does not identify BAT achievable emission levels using secondary fuels. The cement industry has argued that prescriptive regulations designed to ensure combustion of these secondary fuels in dedicated waste incinerators are inappropriate for the regulation of fuel substitution in industrial furnaces such as cement kilns. The nature of the thermal processes governing cement manufacture is such that emissions arising from the combustion of the alternative fuel should be treated separately to emissions arising from the raw materials feeding the kiln.

This principle has been accepted by the EU and applied in Directive 2000/76/EC on the incineration of waste, regulating the use of hazardous waste as a alternative fuel in cement kilns, by recognising and providing for the practice of ”co-incineration”. Individual Member States have also accepted the need to take account of emissions from raw materials in setting emission controls on exhaust gases from cement kilns. For example, in France emission limits for sulphur dioxide are set according to the sulphur content in the raw materials. In Germany the national waste incineration regulation 17.BimSchV makes specific provision for the exemption of carbon monoxide and total organic carbon emissions from cement plants burning waste supplementary fuels on the grounds that the emission of these substances is not a function of the fuel used or the amount of waste burnt, and is also not a relevant parameter for ensuring the safe combustion of secondary fuels in such plants.

In general, the European cement industry has argued that regulatory decisions concerning the use of secondary fuels in cement plants are best taken at national level, thereby allowing regulators to take into account specific local conditions in writing permits. This position has been endorsed by the EU in Directive 96/61 EC on Integrated Pollution Prevention and Control, in which national regulatory authorities are requested to base operating permits on BAT, while taking into account the technical characteristics of processes, their geographic location and local environmental conditions. As a safeguard, permits must not allow any EC environmental quality standards to be breached.

Notwithstanding the derogations on emissions of substances such as sulphur dioxide and carbon monoxide, the cement industry has accepted that the emission standard for dioxins of 0.1 ng TEQ/m^3 generally applied throughout Europe to regulate dioxin emissions from municipal and hazardous waste incineration. Emission levels shall be corrected to 273 K, 101.3 kPa, 10%O_2 and dry gas.

The EU procedures for calculation of air emission limit values when co-incineration of waste in industrial facilities and the subsequent total emission limit values for cement kilns co-incinerating waste are given in figure 7 and 8 respectively.



ANNEX II

DETERMINATION OF AIR EMISSION LIMIT VALUES FOR THE CO-INCINERATION OF WASTE

The following formula (mixing rule) is to be applied whenever a specific total emission limit value 'C' has not been set out in a table in this Annex.

The limit value for each relevant pollutant and carbon monoxide in the exhaust gas resulting from the co-incineration of waste shall be calculated as follows:

$$\frac{V_{waste} \times C_{waste} + V_{proc} \times C_{proc}}{V_{waste} + V_{proc}} = C$$

V_{waste}: exhaust gas volume resulting from the incineration of waste only determined from the waste with the lowest calorific value specified in the permit and standardised at the conditions given by this Directive.

If the resulting heat release from the incineration of hazardous waste amounts to less than 10 % of the total heat released in the plant, V_{waste} must be calculated from a (notional) quantity of waste that, being incinerated, would equal 10 % heat release, the total heat release being fixed.

C_{waste}: emission limit values set for incineration plants in Annex V for the relevant pollutants and carbon monoxide.

V_{proc}: exhaust gas volume resulting from the plant process including the combustion of the authorised fuels normally used in the plant (wastes excluded) determined on the basis of oxygen contents at which the emissions must be standardised as laid down in Community or national regulations. In the absence of regulations for this kind of plant, the real oxygen content in the exhaust gas without being thinned by addition of air unnecessary for the process must be used. The standardisation at the other conditions is given in this Directive.

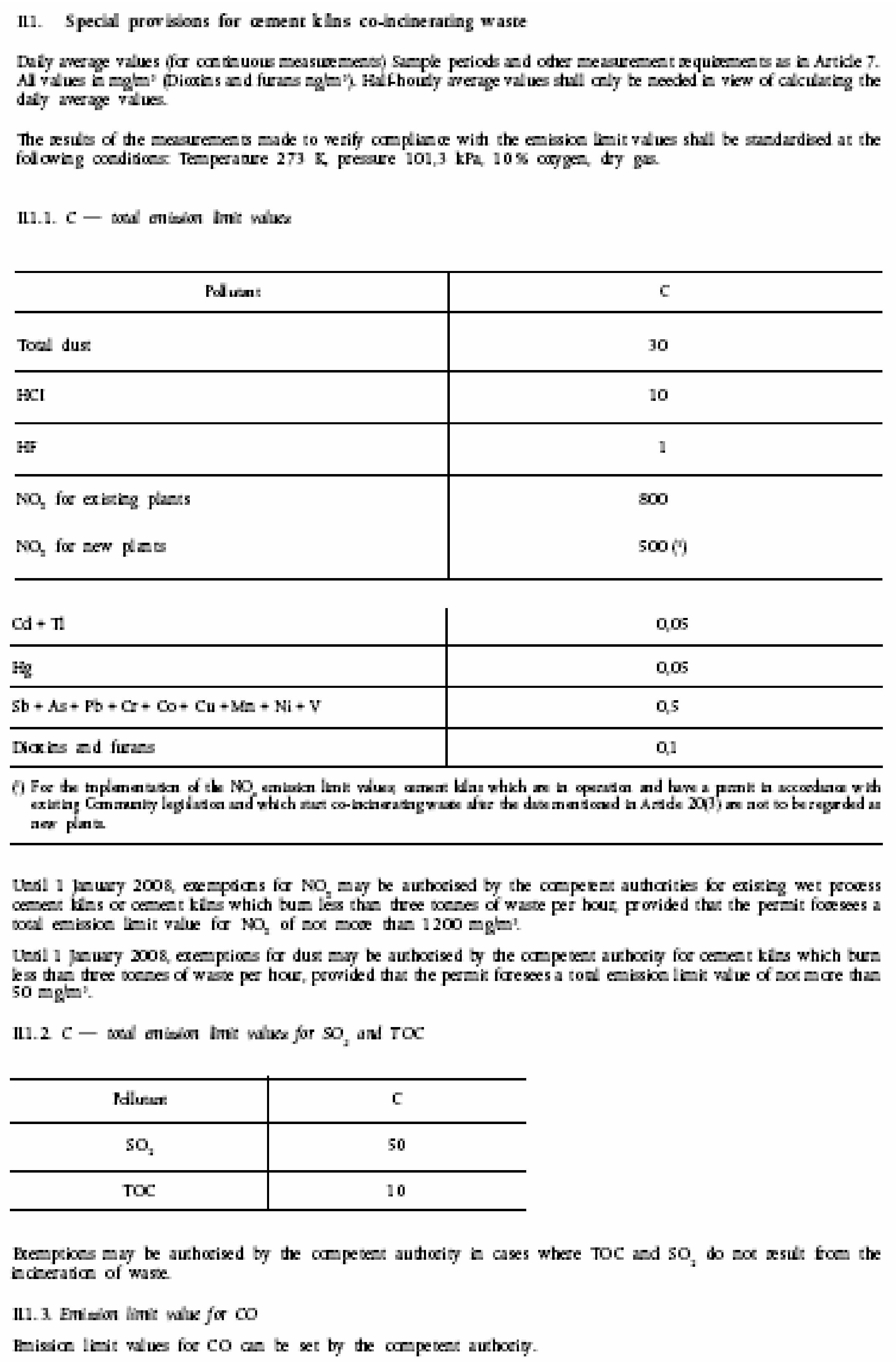
C_{proc}: emission limit values as laid down in the tables of this annex for certain industrial sectors or in case of the absence of such a table or such values, emission limit values of the relevant pollutants and carbon monoxide in the flue gas of plants which comply with the national laws, regulations and administrative provisions for such plants while burning the normally authorised fuels (wastes excluded). In the absence of these measures the emission limit values laid down in the permit are used. In the absence of such permit values the real mass concentrations are used.

C: total emission limit values and oxygen content as laid down in the tables of this annex for certain industrial sectors and certain pollutants or in case of the absence of such a table or such values total emission limit values for CO and the relevant pollutants replacing the emission limit values as laid down in specific Annexes of this Directive. The total oxygen content to replace the oxygen content for the standardisation is calculated on the basis of the content above respecting the partial volumes.

Member States may lay down rules governing the exemptions provided for in this Annex.

Figure 6 **Procedure given in the EU Directive 2000/76/EC on the incineration of waste for calculation of air emission limit values when co-incineration of waste in industrial facilities.**

Kåre Helge Karstensen
khk@sintef.no



II.1. Special provisions for cement kilns co-incinerating waste

Daily average values (for continuous measurements) Sample periods and other measurement requirements as in Article 7. All values in mg/m³ (Dioxins and furans ng/m³). Half-hourly average values shall only be needed in view of calculating the daily average values.

The results of the measurements made to verify compliance with the emission limit values shall be standardised at the following conditions: Temperature 273 K, pressure 101,3 kPa, 10 % oxygen, dry gas.

II.1.1. C — total emission limit values

Pollutant	C
Total dust	30
HCl	10
HF	1
NO_x for existing plants	800
NO_x for new plants	500 (1)
Cd + Tl	0,05
Hg	0,05
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V	0,5
Dioxins and furans	0,1

(1) For the implementation of the NO_x emission limit values, cement kilns which are in operation and have a permit in accordance with existing Community legislation and which start co-incinerating waste after the date mentioned in Article 20(3) are not to be regarded as new plants.

Until 1 January 2008, exemptions for NO_x may be authorised by the competent authorities for existing wet process cement kilns or cement kilns which burn less than three tonnes of waste per hour, provided that the permit foresees a total emission limit value for NO_x of not more than 1 200 mg/m³.

Until 1 January 2008, exemptions for dust may be authorised by the competent authority for cement kilns which burn less than three tonnes of waste per hour, provided that the permit foresees a total emission limit value of not more than 50 mg/m³.

II.1.2. *C — total emission limit values for SO_2 and TOC*

Pollutant	C
SO_2	50
TOC	10

Exemptions may be authorised by the competent authority in cases where TOC and SO_2 do not result from the incineration of waste.

II.1.3. *Emission limit value for CO*

Emission limit values for CO can be set by the competent authority.

Figure 7 **Special provisions for cement kilns co-incinerating waste given in the EU Directive 2000/76/EC.**

4.1.2 HCB

Hexachlorobenzene is not subject to regulatory monitoring in cement plants. However, some measurements have revealed very low levels or that HCB could not be detected, i.e. HCB emission is most probably not an issue for the cement industry.

4.1.3 PCB

PCBs are not subject to regulatory monitoring in cement plants, however 40 measurements done in 13 kilns in Germany in 2001 revealed a maximum concentration of 0.4 µg/Nm^3; in nine measurements, no PCB was detected.

4.2 PCDD/F emission standards in the US

The current PCDD/F emission standard for existing and new cement kilns co-processing hazardous waste in the US is either 0.20 ng TEQ/m^3 or 0.40 ng TEQ/m^3 and control of flue gas temperature not to exceed 200^{o}C at the inlet to the APCD. Emission levels shall be corrected to 25^{0}C, 7% O_2 and dry gas.

The US EPA regulations also require operators of US cement kilns that use hazardous waste as fuel to periodically demonstrate that the kilns achieve a minimum DRE of 99.99%. Based on the above criteria, the most common POHCs selected for these DRE tests are tetrachloroethylene, trichlorobenzene, 1,2-dichlorobenzene, and trichloroethylene. These chlorinated organic compounds are extremely thermally stable.

Reports that indicated cement kiln DRE results below 99.99% are either from outdated sources or improperly designed tests, or both. In the early years of development of this technology and the sampling and analytical techniques to evaluate its environmental performance, there were several instances where POHCs were selected that did not meet the four criteria listed below.

POHCs selected for DRE testing should possess the following characteristics:

1. The POHC should be representative of the hazardous waste feed composition.
2. The POHC should be easily distinguished from other organics that may be emitted from the stack.
3. The POHC should function within all operating, testing, and analytical limitations.
4. The POHC must demonstrate the unit's ability to destroy compounds that are difficult to destroy, including demonstration of both thermal and oxidation failure modes.

4.3 Regulatory framework in Developing countries

The degree to which developing countries have proper rules and regulations in place varies widely from country to country. As a rule, those developing countries that have put good infrastructures in place and who's economies on balance show strong growth tend to be more advanced. Typically in these more advanced developing countries, the population's primary needs are taken care of and the desire for a better environment and concerns for health and safety are more prominent. The poorer countries tend to focus on eradicating poverty and improving the living standards of their population as their first priority.

In many of the developing countries, even when rules and regulations are in place, enforcement of such regulations is weak. Few developing countries have proper rules and regulations for the combustion of hazardous wastes in cement kilns incorporated in their waste management master plan.

The development of a proper hazardous waste management infrastructure in developing countries is not only required to protect human health and the environment but it is also necessary to sustain further development of their economies. Continued poor management of hazardous waste will eventually destroy not only the environment but also the economy of a developing country.

The key word in this phrase is “proper”. There are examples of countries that have attempted to generate their own regulations through their internal staff or through the use of outside consultants that have little experience in waste management. They simply copy the rules of the US or the European Community and promulgate a carbon copy. There are also examples of countries that took the lowest numbers from the US, Japan and Swiss regulations and have simply adopted these with no further technical thought or justification. In other words, if a low number is good, then the lowest numbers of all in existence must be even better or safer.

The global cement industry is more and more dominated by the bigger international companies, which is first of all expanding in developing countries. When these companies build new plants, with no exception the best available technologies BAT applies. This is also the most economic feasible option, which constitutes a competitive advantage and thereby contributes to raise the performance in developing countries. Older, polluting and less competitive technologies will gradually be phased out.

5. Formation of PCDD/F

It is important to emphasise most of the research done on formation mechanisms is from studies of municipal solid waste incinerators or theoretical laboratory studies. PCDD/F formation involves many complex reactions and a complete understanding of the reaction chemistry behind may never be possible.

5.1 General theory of PCDD/F formation mechanisms in combustion

PCDD/Fs can result from a combination of formations mechanisms, depending on kiln and process design, combustions conditions, feed characteristics, and type and operation of air pollution control device (APCD) equipment. PCDD/F formation mechanisms have been studied since the late 1970's when PCDD/Fs were found in municipal waste combustor emissions. Lustenhouwer advanced three theories to explain the presence of PCDD/Fs (Lustenhouwer et al, 1980). The theories may now be described as:

1. If there is traces of PCDD/Fs in the fuel or raw materials, trace amounts can survive;

2. PCDD/F formation from gas-phase precursors which are chemically similar to PCDD/Fs, such as chloroaromatics, via

   a. Homogeneous (gas-gas phase) reactions, or
   b. Heterogeneous (gas-solid phase) condensation reactions between gas-phase precursors and a catalytic particle surface.

3. *De novo* synthesis of PCDD/Fs from carbon sources that is chemically quite different from the dioxin and furan ring structures. *De novo* synthesis involves heterogeneous, surface-catalyzed reactions between carbonaceous particulate and an organic or inorganic chlorine donor.

It is now generally accepted that Theory (1) cannot explain the levels of PCDD/Fs emissions which have been measured from combustors. Most combustors units do not burn PCDD/F contaminated wastes, and Schaub and Tsang have noted that the gas-phase thermal destruction efficiency for PCDD/Fs is high at the flame temperatures typically achieved in normal combustion units. PCDD/Fs have been found to decompose rapidly at temperatures above 925°C (Schaub and Tsang 1983). In cement kilns, the gas phase temperature will be up to 2000°C, which will ensure that any traces of PCDD/Fs in the fuel will be completely destroyed.

Theory (2a) is also believed to play a relatively minor role in the PCDD/F emissions from combustion facilities. An early kinetic model developed by Schaub and Tsang suggested that the homogeneous gas-phase rate of formation could not account for observed yields of PCDD/Fs. At the high temperatures in a combustion zone, the multi-step process necessary for PCDD/F formation cannot compete with destruction. Although Sidhu and others have subsequently demonstrated pure gas-phase formation of PCDD/F (Sidhu et al, 1994), the minor role of homogenous gas-phase formation is evidenced by numerous field measurements which show higher PCDD/Fs downstream of the combustion chamber than in the flue gases immediately exiting the combustion chamber (Gullett and Lemieux, 1994).

PCDD/F emissions from combustion devices are now believed to result primarily from heterogeneous, surface-catalyzed reactions in the post-furnace regions of the unit (Theories 2b and 3). Experimental evidence suggests that these reactions occur within a temperature range of approximately 200 to 450 °C or wider, with maximum formation occurring near 350 °C (Kilgroe et al, 1990).

Theories (2b) and (3) are both characterized by heterogeneous, surface-catalyzed reactions. Dickson summarizes the distinctions between the two heterogeneous formation pathways (Dickson et al, 1992). Theory (2b) can be distinguished by reactions involving gas-phase chloro-aromatic precursors which might already be present in the fuel, or which could be formed as products of incomplete combustion (Karasek and Dickson, 1987; Dickson and Karasek, 1987). Theory (3) does not require that chloro-aromatics precursors be present on fly ash or in the gas stream. Instead, both the chloro-aromatics precursors and PCDD/Fs may be synthesized *de* *novo* from gas-solid and solid-solid reactions between carbon particulates, air, moisture and inorganic chlorides in the presence of a metal catalyst, some suggest divalent copper (Stieglizt et al, 1989a and 1989b). Activated carbon has also been implicated as a catalyst.

Dickson has performed studies to quantitatively determine the relative predominance of the two heterogeneous formation pathways. Yields of polychlorinated dibenzo-*p*-dioxin from the precursor compound pentachlorophenol were 72-99,000 times greater than yields formed from reactions of activated charcoal, air, inorganic chloride and divalent copper catalyst under identical reaction conditions. Citing the kinetic work of Altwicker (Altwicker et al, 1990a), Dickson postulated the following:

> "*fast reactions involving chloro-aromatic precursors may be expected to predominate in the post-combustion and heat exchanger sections of a combustor, where the temperatures range from 600 to 250 °C and the residence time of the gas stream and entrained particulates is on the order if 1 second*",
>
> and
>
> "*slower processes such as de novo synthesis may influence PCDD/F emissions in dry pollution control equipment, where particulate residence times vary from 1 to about 1000 seconds.*"

Although both mechanisms may contribute to observed PCDD/F emissions, Gullett and Lemieux have shown that "in flight" formation alone (at residence times less than 5 seconds) is sufficiently rapid to explain the PCDD/F concentrations measured in the field (Gullett and Lemieux, 1994).

Molecular chlorine (Cl_2) appears to play a role in PCDD/F formation by chlorinating aromatics PCDD/F precursors through substitution reactions. Chlorination of phenol has been shown to be three orders of magnitude greater with Cl_2 than with HCl (Gullett et al, 1990). Although HCl does not directly participate in precursor chlorination to a significant degree, it can produce molecular chlorine via the Deacon reaction (Griffin 1986; Gullett et al, 1990):

Equation 1)

$2HCl + \frac{1}{2} O_2 \Longleftrightarrow Cl_2 + H_2O$, with copper or others metals serving as catalysts

The Deacon reaction depends on the presence of a metal catalyst to overcome kinetic limitations which would otherwise limit the production of Cl_2 from HCl (Griffin, 1986). However, the metal catalyst also serves another important function. Once the aromatic rings have been chlorinated, the metal catalyst supports condensation reactions to form the PCDD/F dual ring structure (Bruce et al, 1991; Gullett et al, 1992). Gullett has shown that formation of the dual ring structure (biaryl synthesis) is enhanced up to three orders of magnitude in the presence of metal catalysts, such as divalent copper (Gullett et al, 1992). Base upon testing with nine different metals and oxidation states, divalent copper appear to demonstrate the strongest catalytic activity (Gullett et al, 1992; Stieglitz et al, 1989a).

Radical Cl also appears to play a role in PCDD/F formation. Recent work by Gullett shows that radical Cl persists to temperatures where hydrocarbon chlorination occurs (Gullett et al, 2000a). This mechanism is a likely chlorination route, and is influenced by combustion conditions and their effect on Cl radical persistence.

Sulphur has been shown to decrease PCDD/F emissions. Substantially lower PCDD/F emissions have been observed from coal-fired power plants than from municipal waste combustors, even though coal-fired utilities operate under conditions that should generally be conductive to PCDD/F formation. The sulphur/chlorine ration of the fuel may explain the difference. The typical S/Cl ratio in a municipal waste combustor is about 0.2, which is approximately an order of magnitude lower than that found in coal combustion (Raghunathan and Gullett, 1996). Raghunathan and Gullett have demonstrated significant PCDD/F reduction at S/Cl ratios as low as 0.64 in a natural-gas-fired furnace, as low as 0.8 in a coal-fired furnace (expressed as uncorrected furnace concentrations of parts per million SO_2/HCl). Additional work has shown that PCDD/F formation is substantially inhibited when the S/Cl ratio is greater than about 1:1 (Gullett and Raghunathan, 1997).

Researchers have concluded that sulphur may interfere with PCDD/F formation by (1) SO_2 depletion of Cl_2 (Equation 2), and (2) SO_2 poisoning of copper catalysts (Equation 3) to prevent biaryl synthesis (Griffin 1986; Gullett et al 1992; Bruce 1993; Raghunathan and Gullett 1996):

Equation 2)

$$Cl_2 + SO_2 + H_2O <==> 2HCl + SO_3$$

and:

Equation 3)

$$CuO + SO_2 + \frac{1}{2} O_2 <==> CuSO_4$$

It is also possible that poisoning of the copper catalyst may interfere with the Deacon reaction.

From this background, it is clear that PCDD/F formation involves many complex reactions. A complete understanding of the reaction chemistry may never be possible. However, for units achieving good combustion, the most important reactions appear to depend on gas/solid chemistry in cooler zones downstream of the combustion chamber. Conditions conductive to downstream formation include (1) presence of particulate, which allow solid-catalyzed reactions, (2) post-furnace particulate residence time in the critical temperature window (approximately 200 to 450 °C), (3) presence of Cl and organic precursors, including chloro-aromatics, and (4) a shortage of formation inhibitors, such as sulphur. Poor combustion can substantially increase PCDD/F formation, possibly through increased soot formation (providing more catalytic reaction sites for PCDD/F formation), increased formation of PICs (which can serve as PCDD/F precursors), and increased gas-phase formation of PCDD/Fs, although sufficient oxygen also appears to be necessary. Approaches that have been successfully demonstrated in some full scale systems for controlling PCDD/F emissions include:

- Maintenance of good combustion conditions to limit organic precursors and soot;
- Rapid flue gas quenching or other measures to minimize post-furnace particulate residence time in the critical temperature zone;
- Use of formation inhibitors;
- End-of-pipe flue gas cleaning techniques for PCDD/F removal or catalytic decomposition.

The use of formation inhibitors and some end-of-pipe flue gas cleaning techniques will for the time being not be economical feasible in many industrial applications.

5.2 Formation of PCDD/F in Cement Kilns

Cement kilns utilise wastes commercially (i.e., they accept waste from off-site generators) for use as a fuel supplement in the production of Portland cement. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. For long kilns, this means that the solid waste is introduced mid-kiln, and for preheater/precalciner kilns it is introduced onto the feed shelf at the high temperature section.

All cement kilns are equipped with either electro static precipitator (ESPs) or fabric filters, or both, for particulate matter control. In some cases, the flue gases are cooled prior to the dry APCD. Acid gas pollution control devices are not used at cement kilns (except for SO_2 in some instances) since the raw materials are highly alkaline and provide acid gas control.

PCDD/F emissions data are available for most hazardous waste burning cement kilns in the US. Test condition averages are highly variable, ranging from 0.004 to nearly

50 ng TEQ/m^3 (EPA 1999d). The level of PCDD/F emissions from a cement kiln may potentially be affected by a number of factors. However, the inlet temperature to the particulate matter control device is one factor that has been shown to consistently affect PCDD/F formation, irrespective of fuel used (EPA 1999d).

Data presented in numerous documents (Harris et al, 1994; Lanier et al, 1996; EPA 1999d and 1999e) demonstrate that PCDD/F emissions from cement kilns increase exponentially with increases in inlet temperatures to the dry APCD within the PCDD/F formation window (200 to 450^{o}C). A number of wet kilns have recently added flue gas quenching units upstream of the APCD to reduce inlet APCD temperature, and these additions have significantly reduced PCDD/F emissions (EPA 1999d). This information suggests that maximum inlet temperature to the dry APCD system, as discussed previously, is the primary control parameter related to PCDD/F emissions for wet cement kilns.

Parameters related to combustion quality are generally less relevant for cement kilns than for incinerators and boilers. The operating envelope of cement kilns is dictated largely by standard specifications for their final product. Cement kilns operate at high temperatures (gas phase temperatures up to 2000 °C) to achieve material temperatures of 1450^{o}C, with typical gas residence times up to 6 seconds. These conditions are conducive to highly efficient organic destruction. Although some cement kilns operate at elevated carbon monoxide levels, these levels are not necessarily indicative of poor combustion. A portion of the carbon monoxide in cement kilns is due to the calcination process. The calcination process releases large quantities of carbon dioxide, which can subsequently decompose into carbon monoxide at the extremely high temperatures in the kiln. In addition, carbon monoxide may be formed at the kiln gas exit end where total hydrocarbons are volatilized from the raw materials and are partially oxidized.

Results from both kinetic modelling and field studies suggest that organics are efficiently destroyed when fed at the hot end of cement kilns (Dellinger et al, 1993). Destruction and removal efficiency (DRE) results confirm this. DRE failures at cement kilns are extremely limited, and can generally be explained by high blank or baseline levels of principal organic hazardous constituent (POHCs). In one instance, DRE failure has been attributed to poor atomizer design. However, facility-specific DRE testing should generally be sufficient to reveal design problems. For these reasons, control parameters related to combustion of liquid hazardous wastes introduced to the hot end of cement kilns is needless.

However, combustion control parameters can be useful when kilns feed batch waste at mid- or feed-end locations. Batch wastes injected at mid- or feed-end locations do not experience the same elevated temperatures and long residence times as liquid wastes introduced at the hot end. In a worst-case scenario, volatile compounds may be released from the charge so rapidly that they are not able to mix with oxygen and ignite before they cool below a critical temperature, forming products of incomplete combustion (PICs) (Dellinger et al, 1993). Increased PICs, or precursor organics, may enhance formation of PCDD/Fs.

In cement kilns, main stack emissions of total hydrocarbons are dominated by organics that are volatilized from the raw materials prior to entering the high temperature regions of the kiln (Schreiber and Strubberg, 1994). The chlorination of these hydrocarbons is a potential source of PCDD/F precursors, such as mono-chloro-benzene. Bench-scale, as well as full-scale, tests by the industry has confirmed that hydrocarbons from raw materials play a significant role in governing the production of PCDD/Fs (Sidhu and Dellinger, 1997).

Although the operating conditions necessary for achieving high total hydrocarbon emissions may vary by facility, maximum volatile organic carbon levels are likely to be achieved by some combination of high production rate, high gas temperatures at the raw material feed end of the kiln, and low oxygen at the raw material feed end of the kiln. It must be emphasised that cement production is always done with excess oxygen; one expectance is the production of white cement. Dellinger observed an inverse relationship between total hydrocarbons and stack oxygen concentrations (Dellinger et al, 1993), and Schreiber and Strubberg observed that raw-material-generated hydrocarbons decrease as kiln oxygen increases (Schreiber and Strubberg, 1994). The organic content of the raw material can also significantly influence hydrocarbon levels. However, raw material characteristics are largely dictated by quarry location and are not easily controlled.

In the context of PCDD/F and other organic testing, total hydrocarbon levels are recommended for use as a control parameter indicating levels of organics within raw materials that may be chlorinated from any fuel source.

Contradictory information exists regarding the significance of waste fuel chlorine. It has been proposed that the highly alkaline environment in a cement kiln scavenges available chlorine, making it unavailable for chlorination of organics. Data presented by Lanier from testing conducted at a full-scale facility showed 97% acid gas capture by the alkali material, and no effect on PCDD/F emissions due to variations in chlorine feed rate (Lanier et al, 1996). However, equilibrium calculations show lower chlorine capture at high temperatures and conversion of HCl to Cl_2, suggesting that even a highly basic chemical species such as calcium hydroxide would not always be expected to effectively control chlorinated hydrocarbon formation (including PCDD/Fs) at temperatures above 200°C (Dellinger et al, 1993). It must be emphasised that chlorine levels usually are strictly controlled in cement production due to operational or quality considerations.

The need for metal catalysts for PCDD/F formation is discussed by many scientists, but spiking wastes with copper was not observed to affect PCDD/F emission rates during full-scale testing of a cement kiln (Lanier et al, 1996). Also, other metals that have been identified as PCDD/F catalysts (iron and aluminium) are major ingredients in cement kiln raw materials.

PCDD/P precursors are expected to be dominated by precursors in the cement kiln raw materials, rather than precursors in the waste.

Naturally occurring PCDD/F inhibitors, such as sulphur, is expected to be present in the coal used for firing a cement kiln. In cement kilns, where the alkali raw materials provide some control of acid gases, the S/Cl molar ratio in the stack may be more relevant than the ratio in the feed. Other potential PCDD/F inhibitors, such as calcium, are already being present in the raw materials.

In some cases, sulphur or other PCDD/F inhibitors have been intentionally added to a cement kiln to achieve PCDD/F control. Schreiber documented PCDD/F emissions reductions after sulphur was added to the raw materials to increase the stack concentrations of SO~ from less than 20 ppm to above 300 ppm (Schreiber et al, *1995).* Schreiber also documented PCDD/F emissions reductions when Na_2CO_3 was injected at the fuel feed end to react with chlorine in the system (Schreiber, 1995).

There is currently no cement kilns utilizing carbon injection for sole PCDD/F control. For a cement kiln to effectively utilize carbon injection, the carbon injection system may have to be installed after the APCD, along with a second APCD to collect the carbon.

5.2.1 Prerequisite for formation in cement kilns

PCDD/F formation and subsequent emission requires the simultaneous presence of the following factors of influence:

- Particulate surfaces/catalytic sites; some reports suggest that Cu_2^+ (and Fe_2^+) have a enhanced catalytic effect;
- Hydrocarbons and chlorides;
- Appropriate temperature window: between 200°C and 450°C with a maximum at around 350°C;
- Appropriate residence time > 2 seconds.

In addition, molecular O_2 has to be present in the gas stream.

5.2.2 Effect of fuel composition

More systematic studies on the effect of changing fuels, substitute raw materials and kiln conditions were conducted from the late 1980s. As an example, Krogbeumker (1994) and Kuhlmann et al (1996) describe the results of tests conducted on 16 cement kilns in Germany since 1989. In one study, the following wastes were introduced into the kiln:

- used tyres
- refuse derived fuel
- solvents with varying amounts of chlorine

When compared against the burning of coal, the use of substitute fuels resulted in an increase in dioxin emissions, from a very low base of 0.002-0.006 ng I-TEQ/m^3 to 0.05 ng I-TEQ/m^3 for solvents, and to 0.08 ng I-TEQ/m^3 in the case of used tyres. Even if these latter emission levels fall below the target emission limit of 0.1 ng I-TEQ/m^3, it is questionable if the difference is real or within the normal variability of that particular kiln.

A broad range of other and more recent studies (see chapter 6) concludes that the use of alternative fuels and raw materials doesn't influence or affect the emissions of PCDD/Fs.

The UNEP Standardized toolkit for identification and Quantification of Dioxin (2003) and Furan releases summarised this issue very clearly:

"*In the USA, tests have indicated that higher emissions were found for some kilns where hazardous wastes were fired. More detailed investigation suggested that – provided combustion is good - the main controlling factor is the temperature of the dust collection device in the gas cleaning system. The plants equipped with low temperature electrostatic precipitators appear to have well controlled emissions with or without waste fuels. It is thought that the raw materials themselves can have a considerable influence on the emissions and the presence of high levels of organic matter in the raw materials has been associated with elevated emissions of PCDD/F. It should be noted that the higher emissions measured in the USA were from wet kilns whereas the lower emissions (several hundred measurements) from European cement kilns were obtained from plants using the dry process*".

In general, however, the ranges of dioxin emission concentration resulting from the use of conventional fuels such as coal and pet coke overlap with the ranges obtained with the use of secondary fuel, regardless of the type of secondary fuel.

5.2.3 Effect of feeding alternative fuels to the preheater/precalciner

In a report by Lafarge (Chahine, 2003 b) the feeding of different alternative fuels to the preheater/precalciner is investigated (see table below).

Table 8 Feeding of alternative fuels to the preheater/precalciner and influence on PCDD/F emissions

Plant	Year	Type of alternative fuel	PCDD/F emissions in ng I-TEQ/Nm^3	N
1	2002	Animal meal, plastics and textile	0.0025	4
2	2002	Animal meal and impregnated saw dust	0.0033	4
3	2001	Coal, plastic and tyres	0.0021 & 0.0041	2
4	2002	Tyres	0.002 & 0.006	2
5	2002	Petcoke, plastic and waste oil	0.001	1
6	2002	Petcoke, sunflower shells and waste oil	0.012	1
7	2002	Tyre chips	0.004 & 0.021	2
8	2002	Solvents	0.07	1
9	2002	Impregnated saw dust and solvents	0.00003 & 0.00145	2
10	2002	Solvents	0.00029 & 0.00057	2
11	2002	Sludges	<0.011	1
12	2002	Car waste and sludges	0.0036 & 0.07 & 0.0032	3

The concentration level of PCDD/F is low in all the measurements and doesn’t seem to be influenced by the feeding of different alternative fuels to the preheater/precalciner.

The same results was shown in a recent study in Colombia were pesticide contaminated soil was fed to the kiln inlet; see chapter 6.

In the figure below (VDZ, 2003) approximately 160 PCDD/F emission measurements of German cement kilns carried out between 1989 and 1996 is presented. The measurements are carried out under baseline conditions and when feeding alternative fuels and secondary raw materials.

The substitution of fossil fuel and normal raw materials with alternative fuel and raw materials (AFR) increased in German cement kilns from 23 % (1999) to nearly 35 % (2002) (see figure 17). When suspension preheater cement kiln increases its use of alternative fuel, it's normal to feed more to the preheater/precalciner.

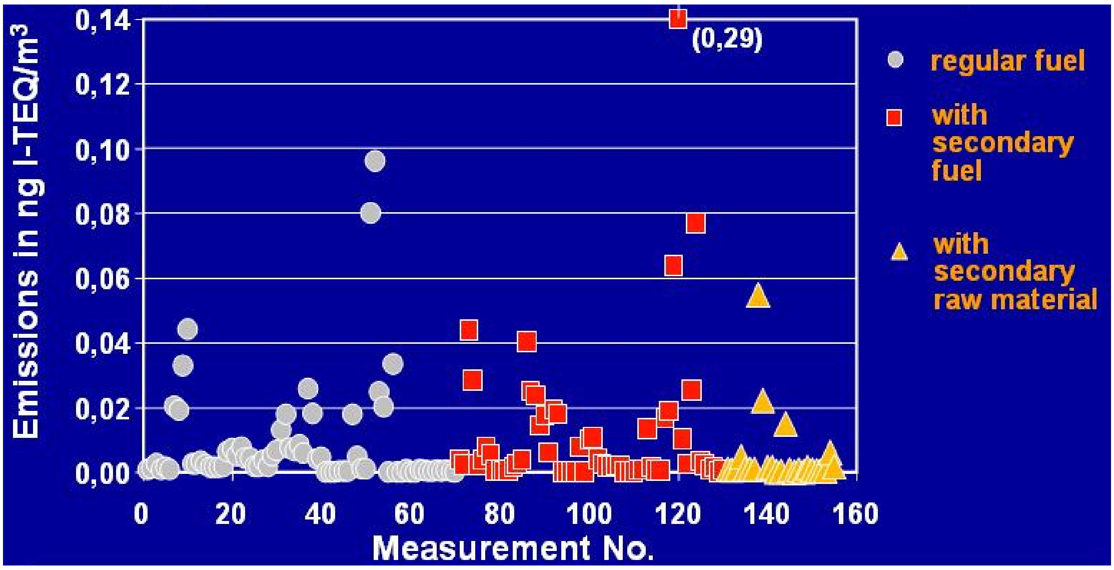


Figure 8 **PCDD/F-emissions of German cement kilns between 1999 and 2002**

In a report from Holcim (Lang, 2004) the effect of increasing the total thermal substitution rates on the emissions of PCDD/F, PCB and HCB were investigated in one suspension preheater/precalciner kiln.

In the figure below the total thermal substitution rate increased from 23% in 1997 up to 60% in the period 2001-2003. The thermal substitution rate to the precalciner increased in the same period from approximately 14% up to near 50%. The thermal substitution rate to the main burner remained more or less stable around 10%.

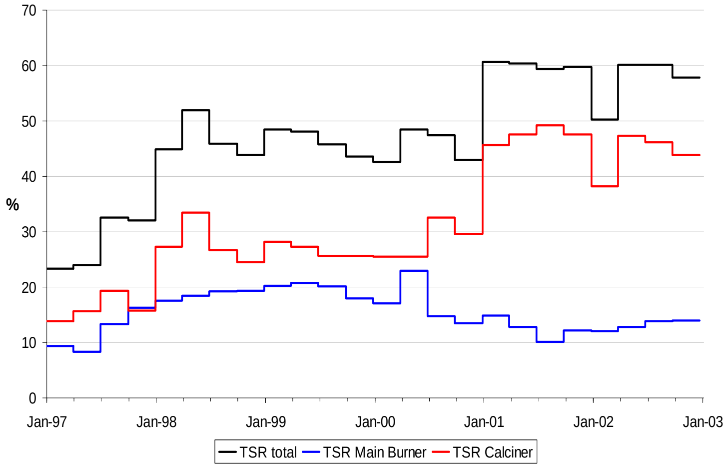


Figure 9 **Thermal substitution rate of alternative fuel in a Holcim precalciner kiln**

In the figure below the different alternative fuels used is presented.

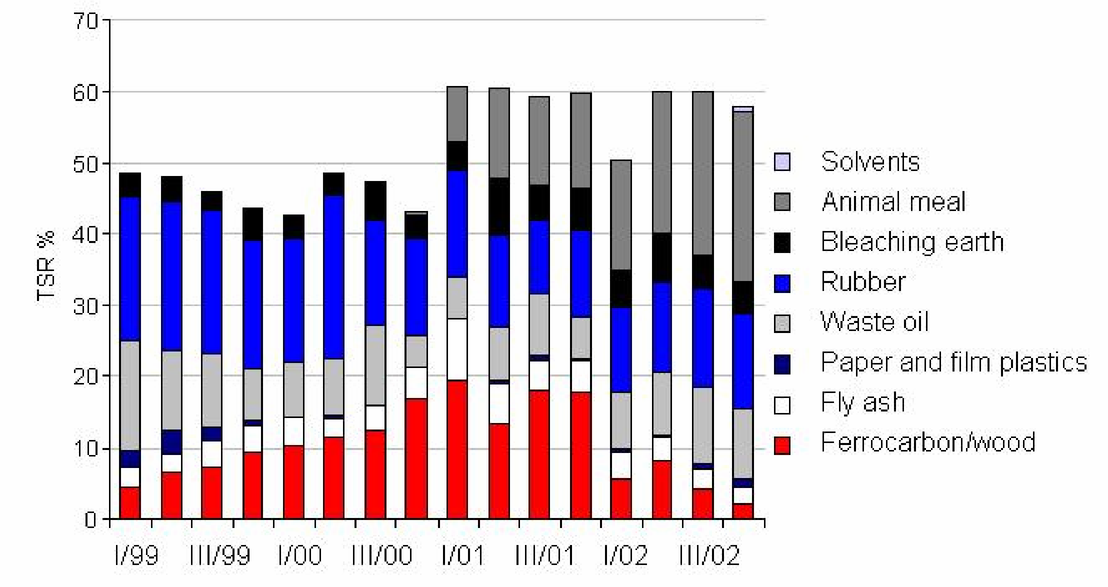


Figure 10 **Alternative fuel used in the Holcim study**

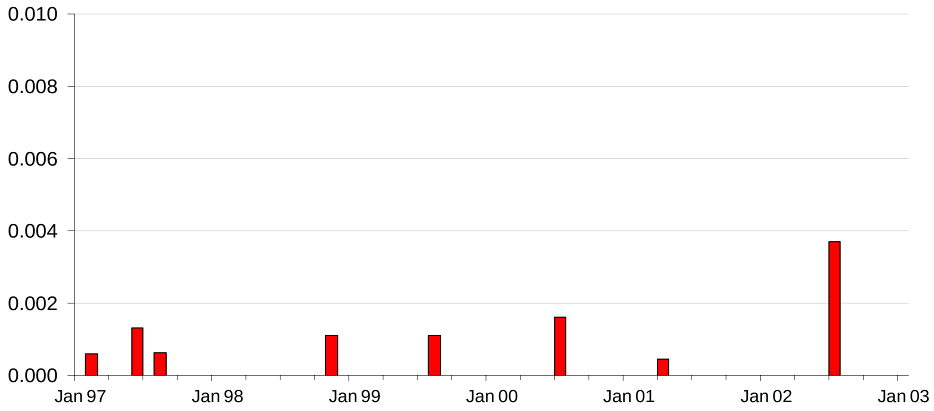


Figure 11 PCDD/F levels measured in the Holcim study (ng TEQ/Nm^3)

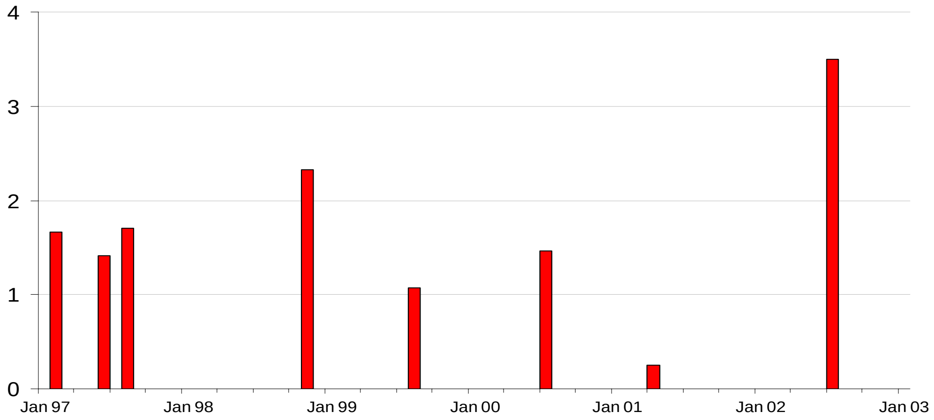


Figure 12 PCB levels measured in the Holcim study (µg/Nm^3)

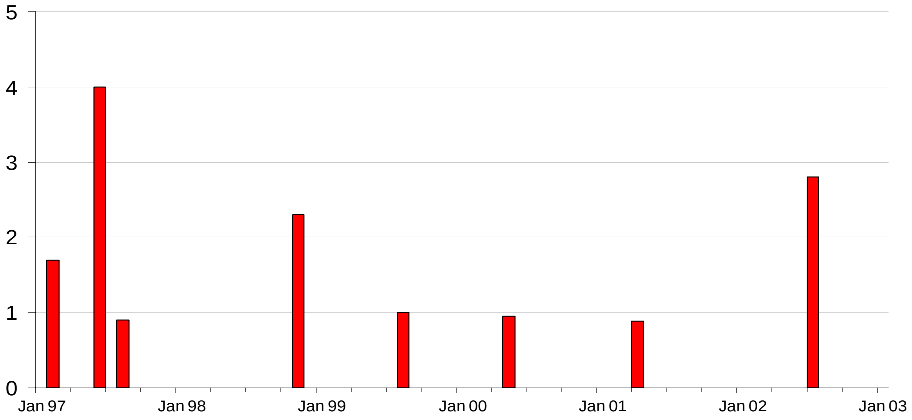


Figure 13 HCB levels measured in the Holcim study (ng /Nm^3)

When the substitution rates are compared with the emission values for PCDD/F, PCB and HCB in the three figures above it is evident that the emission levels are very low and seems to be independent of feeding waste materials to the precalciner and the main burner.

The presented data in this chapter indicates that feeding of different alternative fuels to the preheater/precalciner does not influence the emissions of PCDD/Fs.

5.2.4 Effect of operating variables

The most detailed studies examining the influence of kiln design and operating conditions during the combustion of hazardous waste have been undertaken by US EPA (1994). Data from 14 separate facilities on 23 separate kilns (predominantly wet kilns with ESP pollution abatement equipment, comprising 86 data points) has been analysed for correlations against various emissions and operational parameters. There was *no* correlation between PCDD/F emissions and:

- stack HCl emissions;
- stack total hydrocarbon emissions;
- stack oxygen concentration.
- stack particulate concentrations

for the same type of pollution abatement equipment (ESPs). Comprehensive data do not exist to compare the effect of different types of particulate arrestment systems on dioxin emissions from cement kilns.

One positive correlation identified both in the US and German studies were that between PCDD/F emission concentration and ESP/stack temperature, at high temperatures. In the US tests at one facility (Schreiber, 1993) the ESP temperature recorded between 255°C and 400°C. The dioxin emissions were highest at 400°C, and decreased 50-fold at 255°C. This correlation was generally observed across all facilities tested.

At temperatures lower than 250°C in the ESP/stack inlet there is no correlation between temperature and dioxin emissions. This is consistent with known mechanisms of dioxin formation within municipal waste incinerator systems.

6. POP's releases from cement kiln systems

The general releases from the production of cement are to air from the kiln exhaust gases, the clinker cooler exhaust and any bypass gases. There may also be release of kiln dust to land depending on the alkali content of the raw materials used. Any release through clinker is doubtful but will be investigated further.

In the following paragraphs, available data on releases of POP's are presented for different countries and cement companies in an alphabetically order. In chapter 6.3 data from international and national inventories are summarised and in chapter 6.4 the presented data is discussed.

Since PCDD/F is the only group of compounds currently being regulated, there are fewer data measurements available for PCB and almost none for HCB.

The available information is divided into three main categories:

1) Publicly available reports and articles which have included actual measurements from cement kilns, often trial burns, and with complete references;

2) Data on actual measurements from cement companies and individual cement plants especially gathered for this study (not all the cited information is properly referenced at this stage);

3) National or regional inventories which present POP's contribution estimates from the cement industry, mostly based on emission factors found in literature.

In many of the available reports there are gaps in the reported information which makes it impossible to evaluate the accuracy of the data. Often there is no information of which toxicity equivalency factor systems are used, or how the referred data are corrected to normal conditions and oxygen concentration, or lacking information about sampling methodology and/or spiking recoveries. These uncertainties are impossible to eliminate and should be kept in mind when evaluating the data in this report.

The report may also contain duplication of some data, for example data from cement companies will in some instances also be included in country reports and inventories. This is unavoidable.

6.1 PCDD/F and PCB levels established by actual measurements

In this chapter public available reports and articles are referred. Most of these studies have included actual measurements from cement kilns, often in trial burns under worst case scenario conditions.

When searching for studies performed in cement kilns most scientific databases between 50 and 200 "hits" can be found on POP's emissions from cement kilns, but many of the hits are doublets. There is not much information about PCB releases and almost nothing on HCB emissions.

6.1.1 Australia

PCDD/F emissions have been measured from a range of Australian cement plants representing different operating and process conditions, different fuel sources and different raw materials. Both wet and dry process are represented, as are plants using gas and coal as primary fuels sources as well as some plants using waste-derived fuels. No significant difference in dioxin emissions due to use of waste derived fuels was observed within plants (Environment Australia, 2002).

Results of repeated measurements over a decade show that levels of dioxin emissions from Australian cement manufacturing are consistently below 0.1 ng I-TEQ/m^3. Based on emissions factors from the total industry, the cement industry represents one of the lowest contributions in Australia. Comparison with all sources, places cement manufacturing as an "insignificant" contributor to overall PCDD/F emissions in Australia.

The 55 measured concentrations of dioxins in stack gases cover the range 0.001-0.07 ng I-TEQ/Nm^3. The subsequent emissions factors cover the range 0.0032-0.216 µg I-TEQ/t cement (42 data points).

6.1.2 Belgium

The Belgium Cement Association Febelchem reported PCDD/F measurements for all Belgian kilns (23 values from measurements at 5 kilns) performed in 1999-2000. All measurements was below 0.1 ng TEQ/Nm^3 and were performed during the combustion of PCB contaminated animal meal and fat.

6.1.3 Canada

In an effort of establishing a virtual elimination target of PCDD/Fs and HCB, the Environment Canada (November, 1999) suggested to use the level of quantification (LoQ) as a baseline. The study assessed the variability of sampling and analysis of 53 sets of PCDD/F emission data from 36 combustion facilities and the LoQ for PCDD/F was estimated to be 0.032 ng/m^3 TEQ.

30 PCDD/F measurements from 8 cement kilns burning hazardous and non-hazardous waste was included in the study and covered the range 0.0054 - 0.057 ng I-TEQ/Nm^3 at 11% O_2.

6.1.4 Denmark

Cement is manufactured by one plant only in Denmark. The plant operates 7 kilns, of which 3 including the largest are used for grey cement and the rest for white cement. The raw materials for grey cement are sand, chalk and fly ash from power stations, whereas chalk, sand, kaolin and spent catalyst are used for white cement (Danish EPA, 2000.

The largest kiln (produced 1.5 million tonnes cement in 1999) is heated by a mixture of petcoke, coal and industrial waste including plastic and sludge from paper manufacturing and textiles from tyres. The air emission from this kiln is cleaned in an electrostatic filter at 130° C before directed to the chimney.

Measurements of dioxin emissions to air from the large kiln has shown values of <0.6-2.7 pg I-TEQ/Nm^3 equalling an emission of 0-9.5 mg I-TEQ/year. The figures reflect normal operation, and should thus be representative of 98-99% of the total production time.

6.1.5 Europe

In a recent survey performed by CEMBUREAU (van Loo, 2004) 230 PCDD/F measurements from 110 cement kilns and 11 countries were presented. The countries covered by the survey were Belgium, Czech Republic, Denmark, France, Germany, Hungary, Italy, Norway, Spain, The Netherlands and United Kingdom. The measurements were performed under standard conditions (dry gas, 273 K, 101.3 kPa and 10% O_2) and showed that the average concentration was 0.017 ng I-TEQ/m^3 for all measurements. The lowest and highest concentration measured was <0.001 and 0.163 ng I-TEQ/m^3 respectively; see figure below.

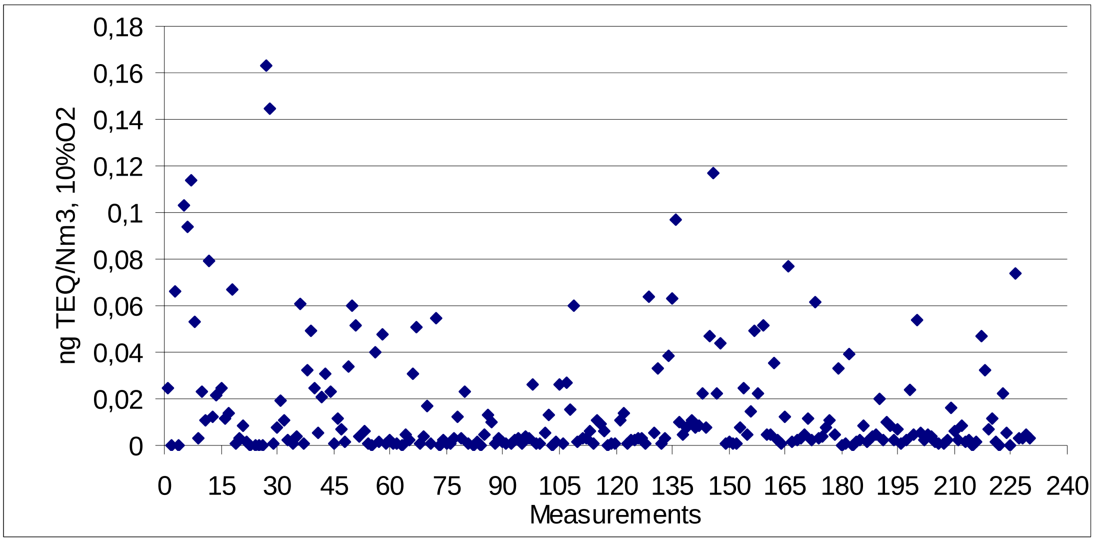


Figure 14 230 measurements in 110 kilns and 11 European countries

The concentration distribution of the 230 measurements is given in the figure below. The graphics show that 98% of the measured kilns have a PCDD/F exit gas concentration below 0.1 ng TEQ/m^3 and that the majority of the kilns emit very low concentrations, i.e. lower than 0.01 ng TEQ/m^3.

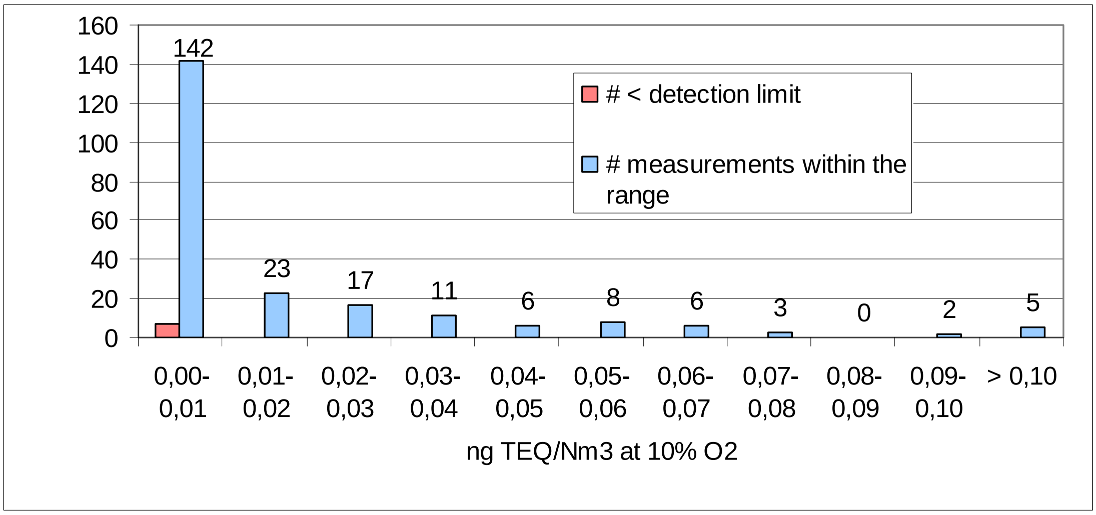
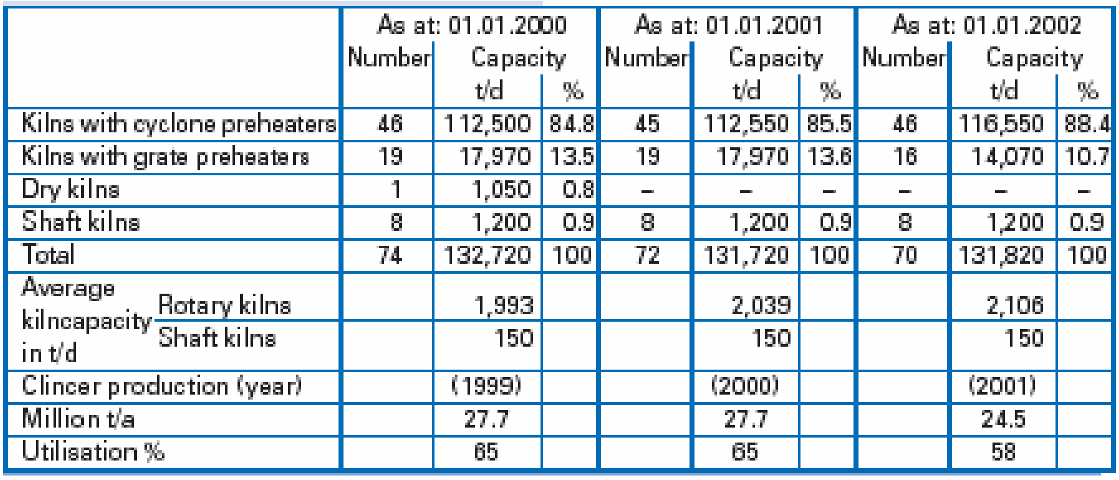


Figure 15 Concentration distributions of 230 measurements in 110 kilns and 11 European countries

6.1.6 Germany

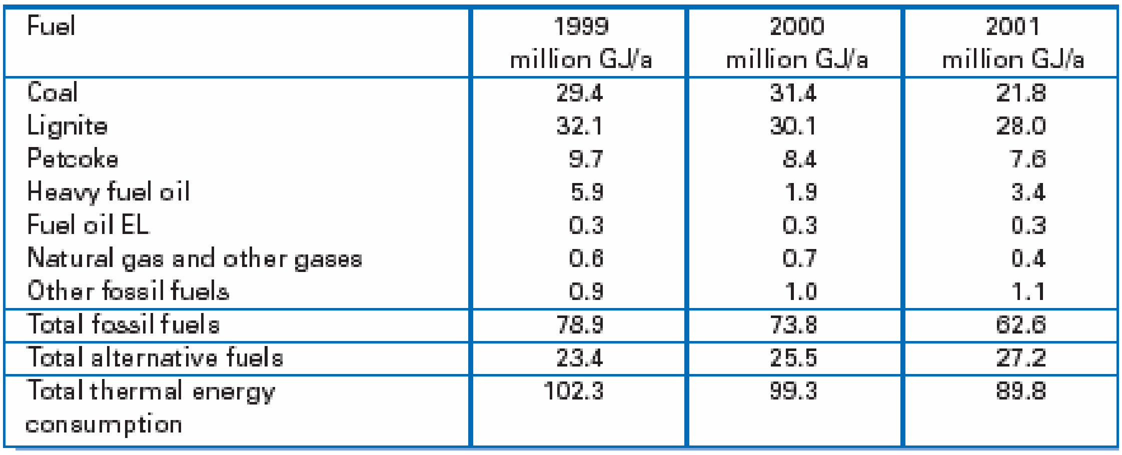
Germany is probably the country in Europe which has performed most PCDD/F measurements in the cement industry. In 2001 38 cement companies produced approximately 32 million tons of cement in 64 plants. Most of the cement clinker is produced in dry kilns with preheaters and precalciner; se table below (VDZ, 2001).



	As at: 01.01.2000			As at: 01.01.2001			As at: 01.01.2002		
	Number	Capacity		Number	Capacity		Number	Capacity	
		t/d	%		t/d	%		t/d	%
Kilns with cyclone preheaters	46	112,500	84.8	45	112,550	85.5	46	116,550	88.4
Kilns with grate preheaters	19	17,970	13.5	19	17,970	13.6	16	14,070	10.7
Dry kilns	1	1,050	0.8	–	–	–	–	–	–
Shaft kilns	8	1,200	0.9	8	1,200	0.9	8	1,200	0.9
Total	74	132,720	100	72	131,720	100	70	131,820	100
Average kilncapacity in t/d – Rotary kilns		1,993			2,039			2,106	
Shaft kilns		150			150			150	
Clincer production (year)		(1999)			(2000)			(2001)	
Million t/a		27.7			27.7			24.5	
Utilisation %		65			65			58	

Table 9 Process types and capacity in Germany 2000-2002 (VDZ, 2001).

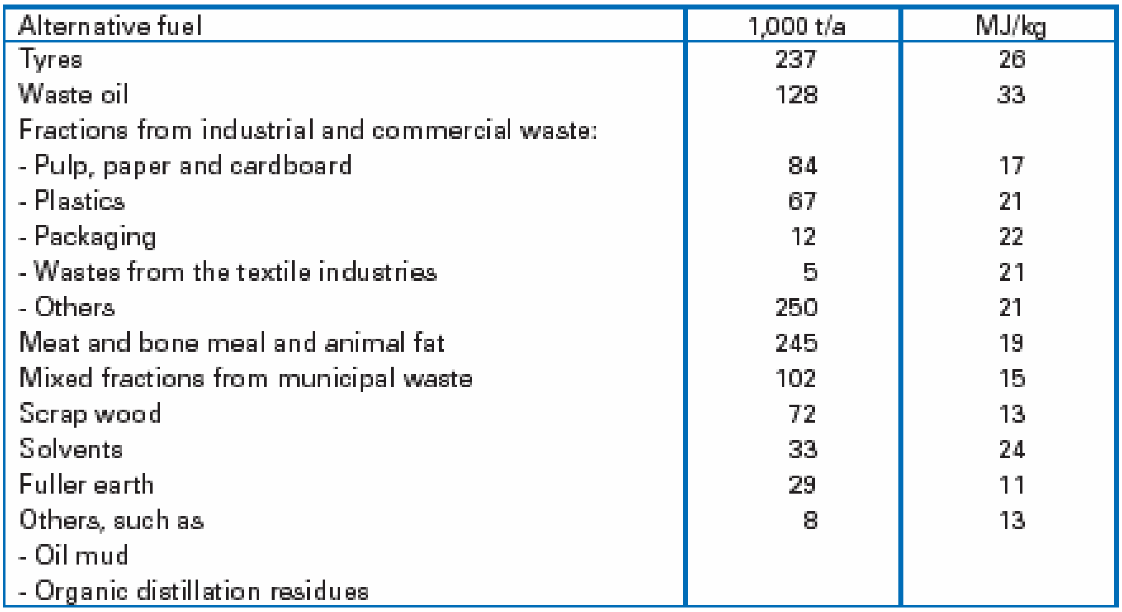
The use of traditional fuel coal and lignite is decreasing in the German cement industry and is more and more replaced with different kinds of alternative fuel; see tables below (VDZ, 2001).



Fuel	1999 million GJ/a	2000 million GJ/a	2001 million GJ/a
Coal	29.4	31.4	21.8
Lignite	32.1	30.1	28.0
Petcoke	9.7	8.4	7.6
Heavy fuel oil	5.9	1.9	3.4
Fuel oil EL	0.3	0.3	0.3
Natural gas and other gases	0.6	0.7	0.4
Other fossil fuels	0.9	1.0	1.1
Total fossil fuels	78.9	73.8	62.6
Total alternative fuels	23.4	25.5	27.2
Total thermal energy consumption	102.3	99.3	89.8

Table 10 Fuel types and energy consumption in Germany 2000-2002 (VDZ, 2001).

The substitution of fossil fuel with waste fuel increased from 23 % in 1999 to nearly 35 % in 2002.



Alternative fuel	1,000 t/a	MJ/kg
Tyres	237	26
Waste oil	128	33
Fractions from industrial and commercial waste:		
- Pulp, paper and cardboard	84	17
- Plastics	67	21
- Packaging	12	22
- Wastes from the textile industries	5	21
- Others	250	21
Meat and bone meal and animal fat	245	19
Mixed fractions from municipal waste	102	15
Scrap wood	72	13
Solvents	33	24
Fuller earth	29	11
Others, such as - Oil mud - Organic distillation residues	8	13

Table 11 Alternative fuel types used in Germany 2001 (VDZ, 2001).

6.1.6.1 PCDD/F results before 1996

In 1996 Schneider from the Research Institute of the German Cement Industry (VDZ) reported PCDD/F data from more than 150 single emission measurements at German cement clinker kilns done in the period 1989 – 1996. The measurements covered 16 different dry preheater kilns, i.e. suspension preheater kilns and Lepold kilns, all equipped with electrostatic precipitator for dedusting. Gas temperatures in the ESP typically ranged from 95 to 205^{o}C (suspension preheater kiln) and 120 to 150^{o}C (Leopold kilns).

All PCDD/F emission samples were collected by using the filter/cooler sampling method according to the VDI Guideline. Sampling ports were always downstream from the ESP where the flue gas had been dedusted. Sampling time was about 6 hours; a total of 20-25 m^3 flue gas was extracted from the stack gas. During sampling the respective kiln was in a representative mode of operation, i.e. the raw feed was at least 70% of kiln capacity. Secondary fuels such as used oil, bleaching earth, used car tyres or waste-derived fuels were used in some kilns. In some cases secondary raw material substitutes like e.g. fly ash, or old sand were used as corrective ingredients.

The average concentration amounts to about 0.02 ng I-TEQ/m^3 at 11 % O_2. No significant difference is indicated from the type of fuel being burnt. For the reported measurements the ESP temperatures were from about 95 to 205^{o}C. At this temperature range there is no indication that temperature correlates with the PCDD/F concentration in stack. Detailed examinations also showed that the oxygen content as well as the dust concentration in stack did not correlate with the reported emission concentrations.

6.1.6.2 PCDD/F results for 2001

In the VDZ report, Environmental Data of the German Cement Industry of 2001, 106 PCDD/F measurements at 37 kilns are reported. All values are below 0.065 ng I-TEQ/m^3 at 11 % O_2. In seven cases no PCDD/F was detected.

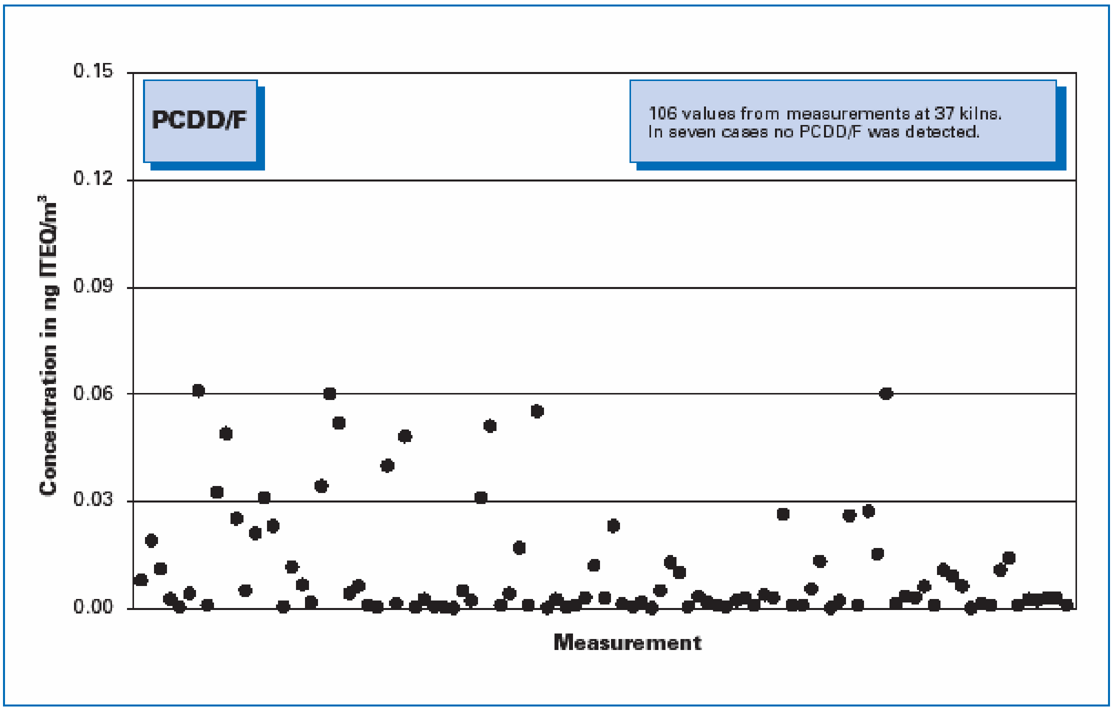


Figure 16 PCDD/F levels in 37 cement kilns in Germany 2001 (VDZ, 2001).

A summary of all PCDD/F-emissions of German cement kilns done in the period 1999 to 2002 is presented in the figure below (VDZ, 2003). The substitution of fossil fuel with waste fuel increased in this period from 23 % (1999) to nearly 35 % (2002). The data clearly show that there is no impact of the use of alternative fuels on the emissions of PCDD/F.

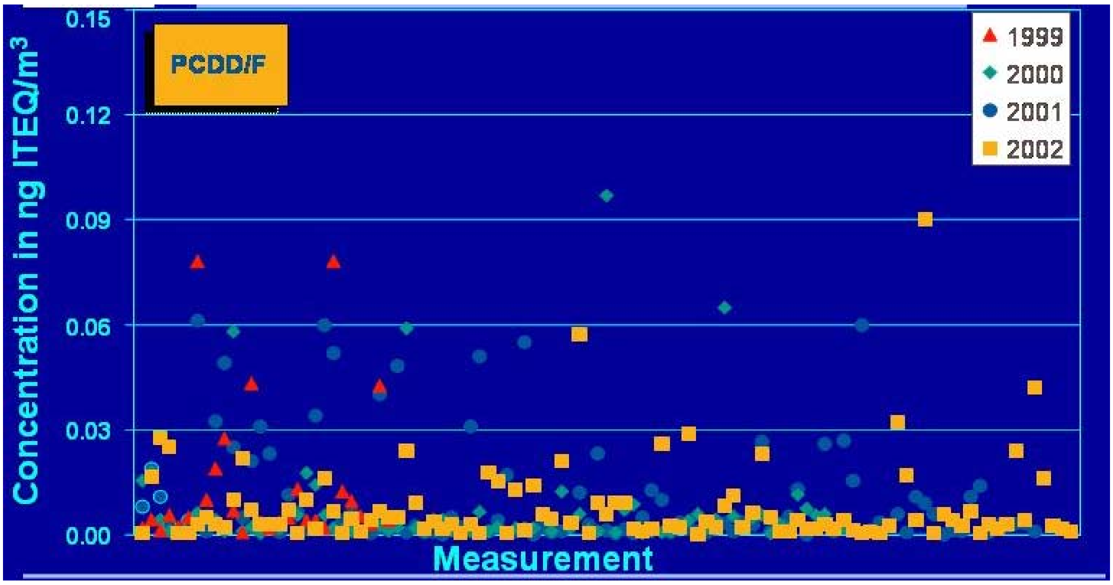


Figure 17 PCDD/F-emissions of German cement kilns between 1999 and 2002

6.1.6.3 PCB results for 2001

In the VDZ report, Environmental Data of the German Cement Industry of 2001, 40 PCB measurements at 13 kilns are reported. All values are below 0.40 µg/m^3, in nine cases no PCB was detected.

A summary of all PCB-emissions of German cement kilns done in the period 1999 to 2002 is presented in the figure below (VDZ, 2003). The substitution of fossil fuel with waste fuel increased in this period from 23 % (1999) to nearly 35 % (2002). The data show that there is no impact of the use of alternative fuels on the emissions of PCB.

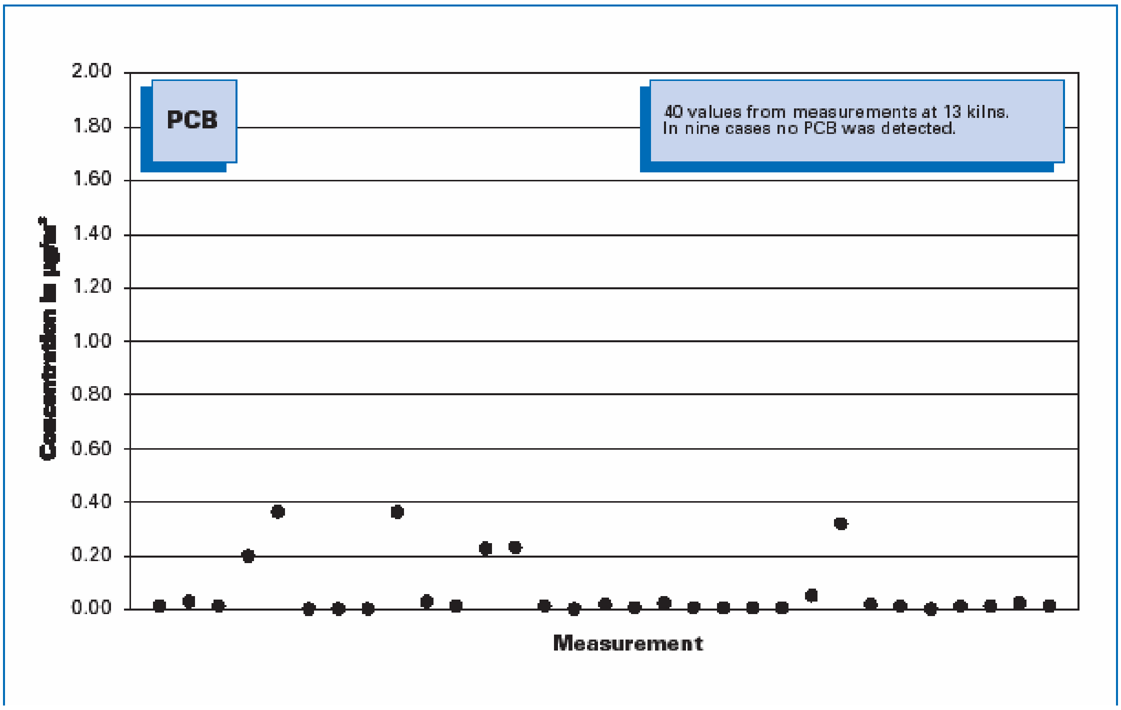


Figure 18 PCB levels in 13 cement kilns in Germany 2001 (VDZ, 2001).

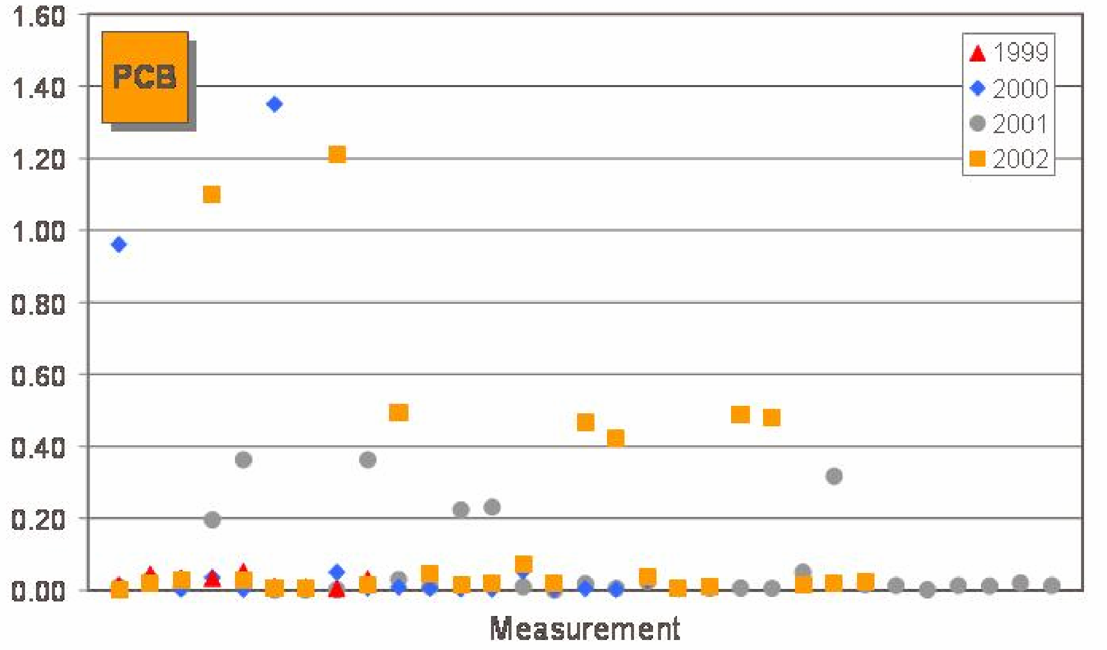


Figure 19 PCB-emissions of German cement kilns between 1999 and 2002

6.1.7 Japan

In 2003 approximately 78 million tonnes of clinker were produced in total 62 dry suspension preheater kilns in Japan (Sakai, 2003). 54 measurements performed in 2000 uncovered that all kilns were below 0.0941 ng TEQ/m^3; 53 measurements performed in 2001 showed that all kilns were below 0.126 ng TEQ/m^3 and 57 measurements performed in 2002 showed that all kilns were below 0.096 ng I-TEQ/m^3 at 11 % O_2 (Japan Ministry of Environment, 2003). The Japanese cement industry utilise a broad range of alternative fuels and raw materials.

6.1.8 Poland

In an attempt to investigate if co-processing of inorganic and organic hazardous waste had an influence on the PCDD/F emissions from a Polish cement kin Dudzinska et al carried out a test in 1998. There are no details about the process type, operating conditions used or waste composition used in the test. The article claims that Polish cement plants are mostly using high content sulphur coal as fuel and that this probably disturb the formation of PCDD/F. The wastes introduced during the test consisted of 10% (of the raw feed?) “inorganic wastes” from metal finishing processes containing 0.08% copper (earlier believed to be a crucial catalyst in the formation of PCDD/F) and 10% “organic waste” without copper. The kiln was operated at 6% oxygen (kiln inlet?) and the PCDD/F emissions was 0.0515 ng I-TEQ/Nm^3 with coal only and 0.0819 and 0.0698 ng I-TEQ/Nm^3 when feeding inorganic and organic waste respectively.

In another Polish test recently reported by Stobiecki et al (2003) different mixes of 12 obsolete pesticides (DDT, HCH, metoxychlor, fenitrotion, fention, endosulfan, dichlorobenzene, esfenwalerat, DONC, deltametrine and carbosulfan) were introduced into a cement kiln (no details about the process type or operating conditions) over a period of three days. The different pesticide mixtures were blended into three batches of alternative fuel with light heating oil; the pesticide content represented 11.5, 29.4 and 30.5 percent of the alternative fuel mix respectively. The mixes were fed through the main burner (?) together with the coal in an introduction rate of approximately 400 kg/h (?). None of the pesticides were detected in the exit gas and the PCDD/F emissions was 0.009 ng I-TEQ/Nm^3 with coal only and 0.015, 0.053 and 0.068 ng I-TEQ/Nm^3 when feeding the three alternative fuel mixes with pesticides respectively.

6.1.9 Spain

In the framework of the Spanish PCDD/F inventory 20 cement kilns (18 dry and 2 wet processes, i.e. 40% of the Spanish cement industry) were measured for PCDD/F emissions under normal operating conditions (Fabrellas et al, 2002). The mean emission value was 0.00695 ng I-TEQ/Nm^3 and the mean emission factor 0.014464 µg I-TEQ/ton cement

Spain has 36 cement plants with 58 kilns, whereas 6 wet, 4 semi-dry and 48 dry processes. The industry produced 32 million ton of clinker and contributed in total with an estimated 0.578 g I-TEQ in 2001, which was regarded to be very low.

6.1.10 Thailand

In 1997 the Pollution Control Department (PCD) of the Ministry of Science, Technology and Environment of the Government of Thailand initiated a dioxin program which included an emission inventory of PCDD/Fs. Seven facilities representing different sectors where selected for stack gas emission and residue sampling (liquid, sludge and solid) and analysis (UNEP/IOMC, September 2001). Among the facilities, a dry process cement plant with two kilns with and without co-processing of liquid hazardous waste and/or tyres where selected for sampling.

Details of the production process and operating conditions are not revealed in the report, but dioxin measurements were performed at both kilns under normal operation at full load (kiln A, 270 t/h, and kiln B, 330 t/h, raw material) when fuelled with a blend of lignite and petroleum coke as primary and secondary fuel and with waste tyres (kiln A) or liquid hazardous waste (waste oils and contaminated solvents in kiln B) to replace a certain percentage of the secondary fuel at the calciner in the high temperature zone.

All stack sampling was performed in compliance with EN 1948 and VDI 2066. The concentrations measured were all below 0.02 ng I-TEQ/m^3 and as low as 0.0001 ng I-TEQ/m^3; the means were 0.0105 ng I-TEQ/m^3 and 0.0008 ng I-TEQ/m^3 for the normal operation conditions and 0.003 ng I-TEQ/m^3 and 0.0002 ng I-TEQ/m^3 for the test performed with substitute secondary fuels, respectively (see table below). The following sentence is quoted from the report: "*2,3,7,8-Cl_4DD was not detected in any of the samples and results clearly revealed that the addition of tyres and/or liquid hazardous waste had no effect on the emission results…*".

The industrial facilities investigated in the Thai inventory exhibited a broad spectrum of different activities and the PCDD/F concentrations ranged over six orders of magnitude; the cement kiln was lowest and a hospital waste incinerator highest with 33.8 ng I-TEQ/m^3, i.e. 113,000 times more. The subsequent mean emission factor was 0.0046 µg I-TEQ/t cement. The emission factors for the kilns co-processing waste was one third of those run without waste.

Table 12 Cement kiln emission measurements in Thailand

Cement kiln/measurement	Fuel replacement	Concentration of PCDD/F in ng I-TEQ/m^3 at 11 % O_2	Emission factor µg I-TEQ/t cement
1-1	No	0.018	
1-2	No	0.009	
1-3	No	0.005	
Mean kiln 1	**No**	**0.0105**	**0.0136**
2-1	Tyres	0.004	
2-2	Tyres	0.003	
2-3	Tyres	0.001	
Mean kiln 2	**Tyres**	**0.0029**	**0.0045**
3-1	No	0.0018	
3-2	No	0.0004	
3-3	No	0.0001	
Mean kiln 3	**No**	**0.0008**	**0.0008**
4-1	Hazardous waste	0.0001	
4-2	Hazardous waste	0.0001	
4-3	Hazardous waste	0.0006	
Mean kiln 4	**Hazardous waste**	**0.0002**	**0.00024**

6.1.11 United Kingdom

Alcock et al presents in 1999 an improved atmospheric emission inventory for UK of PCDD/F and PCB. The inventory was based on emissions measurement program were 5 cement plants was investigated. 14 measurements were performed and covered the range 0.012 - 0.423 ng N-TEQ/Nm^3 at 11% O_2.

The study does not reveal any information of the cement production process type, air pollution control device, operating conditions or fuel sources. Based on the 14 measurements the UK cement industry is estimated to contribute with between 0.29-10.4 grams TEQ per year, which constitute 0.04-4.7% of the total emissions.

The study also included sampling and analysis of dioxin-like PCBs, those with the highest toxicological significance, at one single cement kiln site in the UK. The three measurements were generated during a test burn with substitute liquid fuel; see table below.

Table 13 PCB emission ng TEQ/m^3 for a UK cement plant

Congener	**TEQ**	**Day 1**	**Day 2**	**Day 3**
Non-ortho-PCB				
PCB 77	0.0005	0.0003	0.0005	0.0002
PCB 126	0.1	0.019	0.023	0.012
PCB 169	0.01	Nd	Nd	Nd
Mono-ortho-PCB				
PCB 105	0.0001	0.00007	0.00007	0.00006
PCB 114	0.0005	Nd	Nd	Nd
PCB 118	0.0001	0.0004	0.0002	0.0002
PCB 123	0.0001	0.00003	0.0000	0.00000
PCB 156	0.0005	0.0015	0.0006	0.0005
PCB 157	0.0005	0.0002	0.00009	0.00008
PCB 167	0.00005	0.00005	0.00002	0.00002
PCB 189	0.0001	0.00007	Nd	Nd
PCB Σ TEQ		0.025	0.024	0.013
PCDD7F Σ TEQ		0.017	0.040	0.018
% of Σ TEQ attributable to PCBs		60	38	42

The range in measured TEQ emission for PCBs was small (0.013 to 0.025 ng/m^3), suggesting a consistent sampling method and stable process. PCB 126, PCB 77 and PCB 156 contributed most to the Σ TEQ-PCB, accounting for between 80 and 96% of Σ PCB.

6.1.12 USA

Most of the data regarding PCDD/F emissions from cement kilns in the US is gathered in trial burns with hazardous waste. The US Environmental Protection Agency (EPA) has done numerous studies on the influence of co-processing hazardous wastes in cement kilns. Cement kiln operators in the US began recovering energy from organic waste materials, including chlorinated compounds, as early as 1974. That practice became commonplace by 1987 and since 1991 US cement kilns have used roughly 1,000,000 tons per year of hazardous waste as fuel. Some of these kilns replace up to 100% of their conventional fuels with waste-derived fuels (Cement Kiln Recycling Coalition Comments CKRC, 2002).

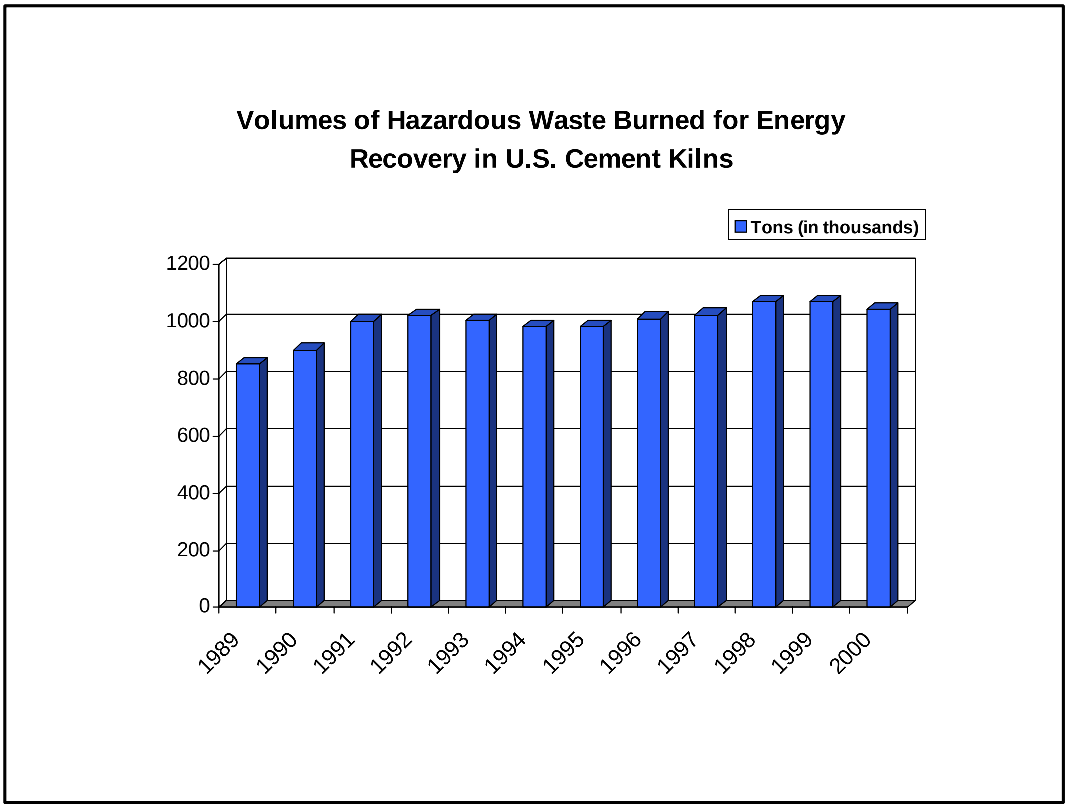


Figure 20 Hazardous waste use in cement kilns in the USA 1989-2000

These kilns operate in compliance with stringent and comprehensive US EPA regulation (Federal Register, 2002a and 2002b) and they have undergone multiple stack emissions tests in accordance with those regulations. As a result, there now exists within US EPA a large, publicly available database that completely describes the environmental performance of cement kilns that recover energy from waste materials, including PCDD/Fs (HWC MACT Data Base NODA Documents, 2002). A majority of the hazardous waste burning cement kilns in operation in the US uses a wet process.

Data from several kilns show PCDD/F emissions as high as 1.76 ng TEQ/m^3 when operating their air pollution control device APCD in the range of 200^{o}C to 230^{o}C. In establishing the emission standards, hazardous waste burning and nonhazardous waste burning cement kilns are considered together because the data sets are representative of general PCDD/F behaviour and control in either type of kiln. The similarity between the two types is judged on engineering bases "*that hazardous waste burning does not have an impact on PCDD/F formation, PCDD/F is formed postcombustion*" (Federal Register, 1999). The highest PCDD/F emissions data from maximum achievable control technology (MACT) operating conditions, i.e. less than 200^{o}C, is 0.28 and 0.37 ng TEQ/m^3 for hazardous waste and nonhazardous waste burning cement kilns respectively. US EPA estimates that approximately 70 percent of hazardous waste burning cement kilns is emitting less than 0.4 ng TEQ/m^3, irrespective of temperature in the APCD, and approximately 50 percent of all kilns will emit less than 0.2 ng TEQ/m^3.

The US cement industry has conducted comprehensive testing to investigate the specific origins of PCDD/F emissions, identified emissions reduction opportunities, and voluntarily implemented modifications to realize these reductions. As a result, cement kilns that burn hazardous waste have decreased their PCDD/F emissions by 97% since 1990; see figure nelow (Federal Register, 1999).

Many of EPA's early publications on this subject severely over-estimated PCDD/F emissions from cement kilns that burn hazardous wastes for energy recovery because they were based on information that was inaccurate and/or outdated. For example, in 1990, when EPA began developing MACT standards for hazardous waste burning cement kilns, EPA estimated an 860 g TEQ/year contribution for this sector. The Cement Kiln Recycling Coalition (CKRC) cooperated with EPA to improve the accuracy of the emissions database and, as a result, exposed numerous errors. After making the appropriate corrections to its database, EPA revised its hazardous waste burning cement industry PCDD/F emissions estimate to 431 g TEQ/year for 1990.

In 1996, EPA further revised its PCDD/F emissions estimate for hazardous waste burning cement kilns to 23 g TEQ/year. In the final MACT rule published on September 30, 1999, EPA recognized the "*significant reduction in national dioxin/furan emissions achieved over the past several years by hazardous waste burning cement kilns due to emissions improving modifications*" and stated that "*the hazardous waste burning cement kiln national dioxin/furan emission estimate for 1997 decreased by nearly 97% since 1990, from 431 g TEQ/yr to 13.1 g TEQ/year*." See figure below.

The PCDD/F emissions from these facilities will diminish even further as hazardous waste burning cement kilns achieve compliance with the limits in the recently published Interim Standards for Hazardous Air Pollutants from Hazardous Waste Combustors (Federal Register, 2002b).

The figure below shows EPA's estimated contributions from cement kilns co-processing hazardous waste in the USA from 1990 until 1997 and illustrate clearly the great uncertainties introduced by solely rely on emission factors (columns for 1990). When the cement industry started to provide actual measurement data to EPA the estimates reduced significantly (column 1996 and 1997) and the cement industry contribution to the total PCDD/F release in the USA was suddenly regarded to be "insignificant".

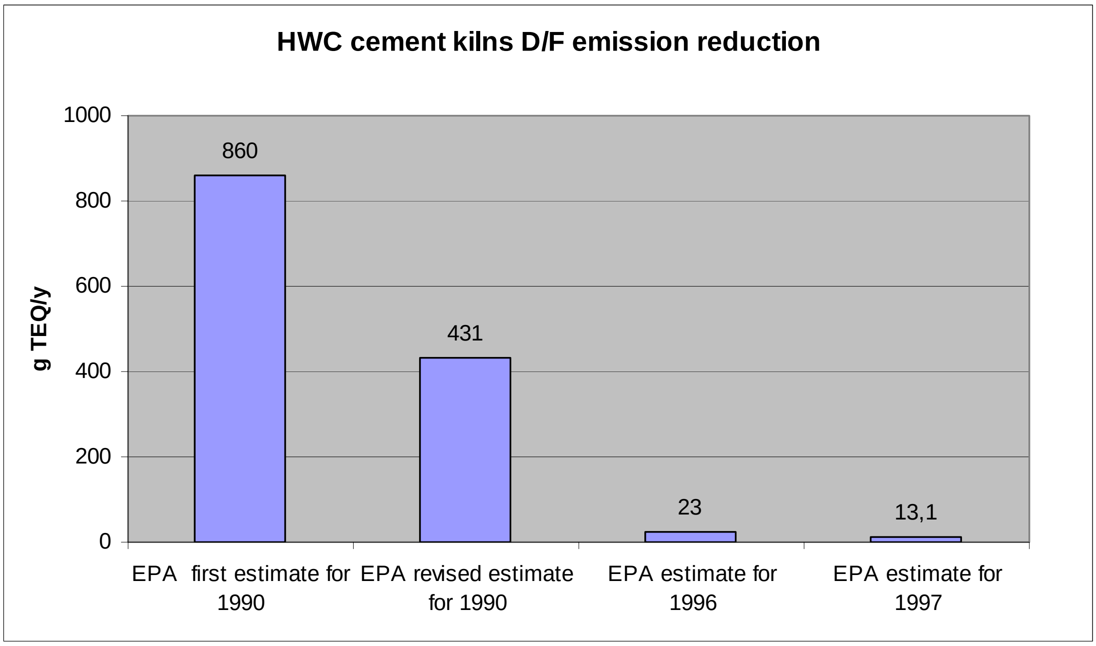


Figure 21 **US EPA PCDD/F contribution estimates for cement kilns co-processing hazardous waste.**

In a joint Canadian and US project on PCDD/F reduction options from the Great Lakes Binational Toxics Strategy (GLBTS, 2000) the following conclusions are given on cement kiln contributions:

I. *"EPA reports that although studies show some inconsistencies, results tend to indicate that cement kiln dioxin emissions are more a result of the combustion process rather that the type of waste inputs, and that the burning of hazardous waste in cement kilns generally does not have an impact on dioxin/furan emissions".*

II. *"Regarding ash from HWC (co-processing hazardous waste) cement kilns (i.e. cement kiln dust); industry reported that because facilities are controlling dioxin stack emissions by preventing formation in the first place, this type of strategy also prevents the accumulation of dioxins/furans in the ash".*

III. *"GLBTS work group reached agreement that cement kilns should be assigned a low GLBTS priority status, based on progress already made in emissions reductions, voluntary activities by the industry, and adequate management that will be in place regarding cement kilns dust".*

6.2 PCDD/F data from cement companies

Data on actual measurements is especially gathered for this study from the CSI cement companies and individual cement plants. The data is reported as received.

6.2.1 Cemex Cement Company

The Mexican cement company Cemex recently reported 16 PCDD/F measurements done in Mexico, Venezuela and Spain in the period from 1999 – 2003 (Quiroga, 2004); see table below.

6.2.1.1 Cemex - Mexico

Three measurements are reported from one cement kiln in Mexico (Quiroga, 2004). The measured concentration was 0.00049, 0.0013 and 0.024 ng/m^3 TEQ at 10% O_2.

6.2.1.2 Cemex - Spain

Five measurements are reported from five dry cement kilns in Spain (Quiroga, 2004). The measured concentration varied between 0.0013 and 0.016 ng/m^3 TEQ at 10% O_2.

6.2.1.3 Cemex - Venezuela

Five measurements are reported from two wet cement kilns in Venezuela (Quiroga, 2004). The measured concentration varied between 0.0001 and 0.007 ng/m^3 TEQ at 10% O_2.

Table 14 PCDD/F measurements in Cemex kilns

COUNTRY	RESULTS PCDD/F (ngEQT/Nm3)	LIMIT (ng/Nm3) 10% O2	DATE
MEXICO	0.00113	0.2	1999
	0.024	0.2	2000
	0.00049	0.2	2001
VENEZUELA	0.007	0.1	2003
	0.006	0.1	2003
	0.005	0.1	2003
	0.0001	0.1	2003
	0.0002	0.1	2003
	0.0002	0.1	2003
	0.0003	0.1	2003
	0.0001	0.1	2003
SPAIN	0.01603	0.1	2001
	0.00131	0.1	2001
	0.00217	0.1	2001
	0.00512	0.1	2001
	0.00424	0.1	2001

6.2.2 Cimpor Cement Company

The Portuguese cement company Cimpor recently reported 14 PCDD/F measurements done in Portugal, Spain and South Africa in the period from 1997 – 2003 (Leitao, 2004); see table below.

Table 15 PCDD/F measurements in Cimpor kilns

Country	Plant	Kiln	Date	ng I-TEQ/m3	Production process / type of kiln	Air pollution control system	Gas
				10 % O_2			T (ºC)
Portugal	Souselas	2	16.07.2001	0,0008	Dry kiln; cyclone preheater	Electr. precip. / bag filter	117
		3	13.12.1997	0,0009	Dry kiln; separated SLC-D precalcinator	Electr. precip. / bag filter	106
	Alhandra	6	08.12.1997	0,0009	Dry kiln; cyclone preheater	Electr. precip. / bag filter	122
		7	06.12.1997	0,0006	Dry kiln; separated RSP precalcinator	Bag filter	110
Spain	Oural	2	31.05.2000	0,02	Dry kiln; in line precalcinator	Electrostatic precipitator	-
			03.12.2002	0,0009			-
			13.02.2003	0,00039			-
			11.06.2003	0,039			-
			26.11.2003	0,02			-
	Toral de los Vados	5	07.03.2002	0,00078	Dry kiln; in line ILC-E precalcinator	Electrostatic precipitator	-
	Cordoba	1	06.06.2001	0,0243	Dry kiln; cyclone preheater	Bag filter	90
	Niebla	1	2001	0,006	Semi-dry; Lepol preheater	Bag filter	117
South Africa	Simuma	1	11.07.2002	0,00053	Dry kiln; cyclone preheater	Electrostatic precipitator	113
				0,001			114

6.2.2.1 Cimpor - Portugal

Four measurements are reported from 4 dry preheater kilns in Portugal (Leitao, 2004). The concentrations are very low, 0.0006 – 0.0009 ng/m^3 TEQ at 10% O_2. All kilns are equipped with electro precipitators and bag-house filters and has a exit gas temperature between 106 – 122°C.

6.2.2.2 Cimpor - Spain

Eight measurements are reported from 4 dry preheater/precalciner kilns in Spain (Leitao, 2004). The concentrations vary between 0.00039 – 0.039 ng/m^3 TEQ at 10% O_2. All kilns are equipped with electro precipitators or bag-house filters and has an exit gas temperature between 90 – 117°C.

6.2.2.3 Cimpor – South Africa

Two measurements are reported from one dry preheater kiln in South Africa (Leitao, 2004). The measured concentration was 0.00053 and 0.001 ng/m^3 TEQ at 10% O_2. The kiln is equipped with electro precipitator and has a exit gas temperature of 113°C.

6.2.3 Holcim Cement Company

In the Holcim Environment Report for 2000 the average emissions for the measured plants are reported to be 0.05 ng TEQ/Nm^3. The measurements cover 43% of their kilns (Holcim, 2001).

In a recent report from Holcim (Lang, 2004) the average PCDD/F value for 2001, 2002 and 2003 are 0.041 ng TEQ/Nm^3 (71 kilns), 0.030 ng TEQ/Nm^3 (82 kilns) and 0.025 ng TEQ/Nm^3 (91 kilns) respectively. The average emission factor was 0.104 µg TEQ, 0.073 µg TEQ and 0.058 µg TEQ pr ton clinker, representing a clinker production of 35.1, 46.7 and 57.6 million ton respectively.

120 of the measurements performed in 2001 and 2002 were from OECD countries with an average value of 0.0307 ng TEQ/Nm^3; the minimum and maximum value measured was 0.0001 and 0.292 ng TEQ/Nm^3 respectively, with 9 long wet kilns being above 0.1 ng TEQ/Nm^3.

29 of these measurements performed in 2001 and 2002 were from non-OECD countries with an average value of 0.0146 ng TEQ/Nm^3; the minimum and maximum value measured was 0.0002 and 0.074 ng TEQ/Nm^3 respectively, with no measurements being above 0.1 ng TEQ/Nm^3.

In the table below, 244 kiln measurements of PCDD/F performed by Holcim around the world are presented. The data are representing a total production of 140 million tons of clinker with various process technologies, with and without waste feeding and in developing and developed countries.

Table 16 Summary of PCDD/F levels measured in 244 Holcim kilns (wet and dry) world wide 2001-2003.

Year	No. of kilns	Clinker production	Average PCDD/F ng TEQ/Nm^3	Minimum PCDD/F ng TEQ/Nm^3	Maximum PCDD/F ng TEQ/Nm^3	Emission factor µg TEQ pr ton clinker
2001	71	35.1	0.041	0.0001	0.2395	0.104
2002	82	46.7	0.030	0.0001	0.292	0.073
2003	91	57.6	0.025	0.0003	0.169	0.058

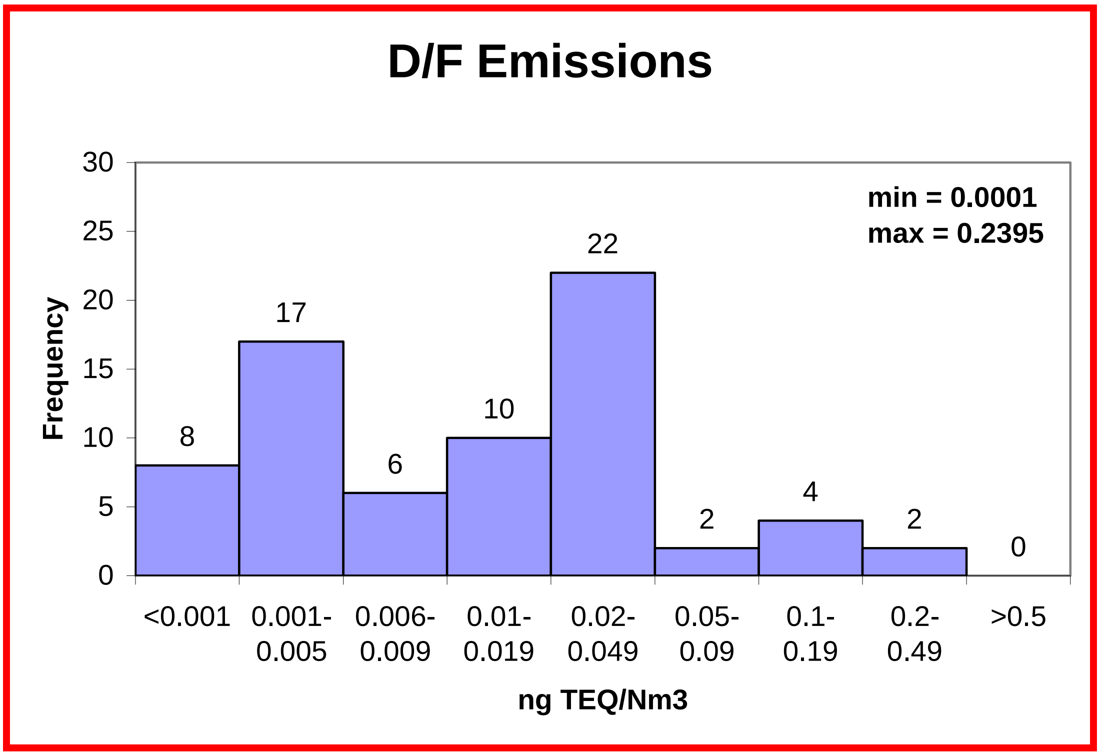


Figure 22 Holcim PCDD/F data from 2001 representing 71 kilns

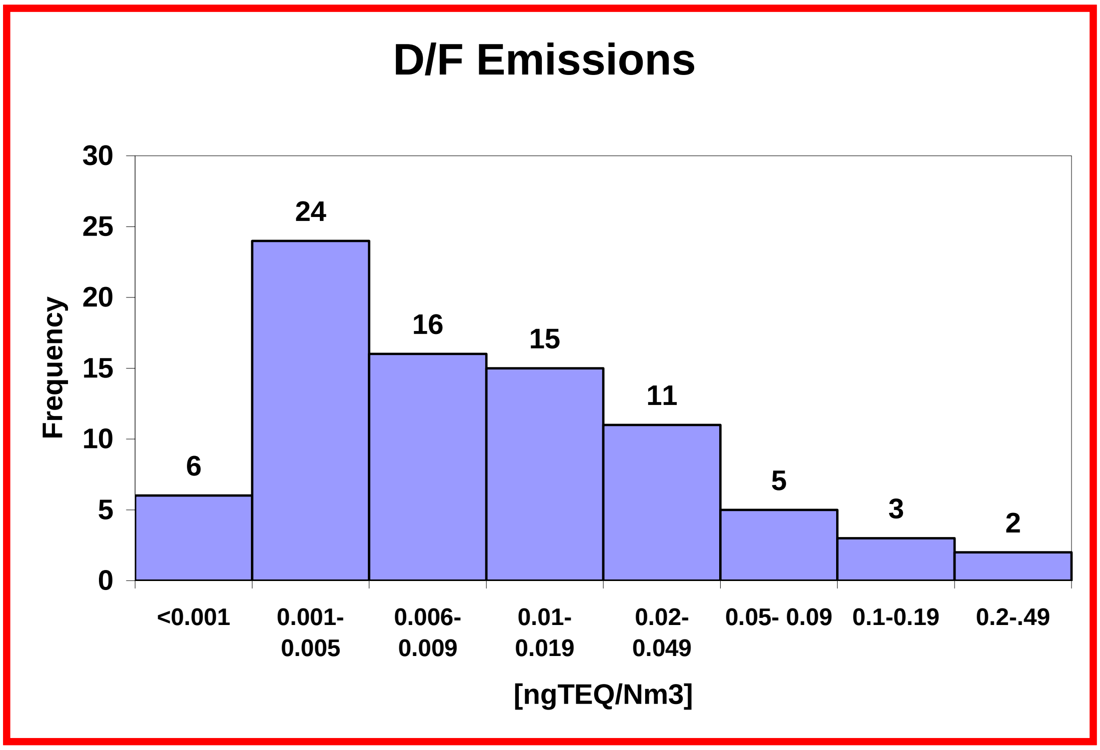


Figure 23 Holcim PCDD/F data from 2002 representing 82 kilns

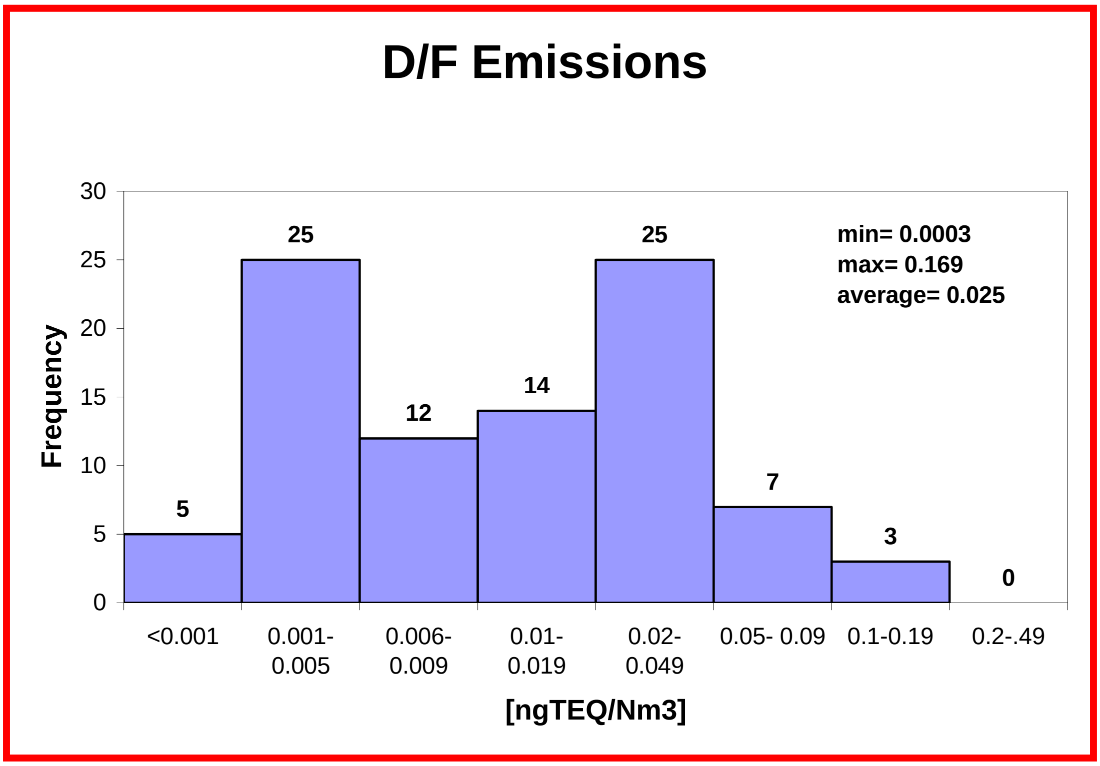


Figure 24 Holcim PCDD/F data from 2003 representing 91 kilns

6.2.3.1 Holcim Chile

Five PCDD/F measurements are recently reported from cement manufacturer in Chile, done in the period 1998 – 2003. Two measurements are done with 25% Petcoke and 75% coal showing a concentration of 0.0059 and 0.0194 ng I-TEQ/Nm^3 at 10% O_2; one measurement is done with coal only, showing 0.0100 ng I-TEQ/Nm^3 at 10% O_2, and two measurements are done when introducing liquid alternative fuel: one with 20% liquid alternative fuel, 6% tyres, 18.5% Petcoke and 55.5% coal showed a PCDD/F concentration of 0.0036 ng I-TEQ/Nm^3 at 10% O_2, and another test with 12% liquid alternative fuel and 88% coal showed a PCDD/F concentration of 0.0030 ng I-TEQ/Nm^3 at 10% O_2. The current emission limit value for Chile is 0.2 ng I-TEQ/Nm^3.

6.2.3.2 Holcim Colombia

In 2001 a test burn with pesticide contaminated soil fed into the kiln inlet was performed in a dry process kiln. The 58 meter long five stage preheater kiln with a clinker production capacity of 3.350 ton per day was fired with bituminous coal. The exit gas was cleaned in a bag filter system with 2592 bags. The three PCDD/F measurements performed during the test burn, including one blank measurement under normal operation, covered the range 0.00023 - 0.0031 ng I-TEQ/Nm^3 at 11% O_2. The test burn result showed a DRE of 99.9999% for all the introduced pesticides. There is currently no emission limit value for PCDD/F in Colombia.

6.2.3.3 Holcim Egypt

A test burn with used industrial solvents was recently carried out in Egypt. A baseline test was carried out before and after the test burn and all three results showed a PCDD/F concentration less than 0.001 ng TEQ/Nm^3.

6.2.3.4 Holcim Philippines

In a very recent study, four dry cement kilns were measured for PCDD/F in the Philippines (5 measurements). The concentration measured was 0.0073, 0.0093. 0.0059, 0.013 and 0.011 ng N-TEQ/Nm^3 at 11% O_2.

6.2.3.5 Holcim Vietnam

A test burn with two expired chlorinated insecticide compounds introduced at a rate of 2 tons per hour through the main burner was recently carried out in Vietnam. A baseline test without insecticide introduction was carried out the day before the test burn; PCDD/F results for both days were below the detection limit for all 17 TEQ congeners. A summary of half the detection limit values, gave 0.0095 and 0.014 ng TEQ/Nm^3 for the baseline and the test burn respectively.

HCB were measured to be below the detection limit, <31 and <35 ng HCB/Nm^3 for the baseline and the test burn respectively. All the non-ortho and mono-ortho PCB congeners were also below the detection limit, see table below.

Table 17 PCB concentration measured during a test burn in Vietnam

ng PCB/Nm^3		**Baseline study**	**Test burn**
Total "dioxin-like" PCB's	Excluding LOD values	0.00	0.00
	Including half LOD values	0.78	0.78
Toatl PCB TEQ (WHO-98)	Excluding LOD values	0.00	0.00
	Including half LOD values	0.00058	0.00086

The destruction and removal efficiency for the introduced insecticide was >99.99999%.

6.2.4 Heidelberg Cement Company

Data from the German cement company Heidelberg is also included in the information presented under Europe chapter 6.1.5 and Germany chapter 6.1.6. In addition to these data, several reports have been received from HeidelbergCement (Haegermann, 2004).

Data of 152 PCDD/F measurements from 43 kilns, 37 plants, in 2001-2004 showed an average value of 0.020 ng TEQ/Nm^3 (see figure below). A comparison made between kilns using a high substitution rate of alternative fuels and kilns only using fossil fuel showed that the use of alternative materials had no influence on the PCDD/F emissions (see figure below). Nine plants with a substitution rate of minimum 40 % had an average value of 0,007 ng TEQ/Nm^3 (minimum 0,001, maximum 0,016 ng

TEQ/Nm³) while the average of eight kilns not using any secondary fuels was 0.016 ng TEQ/Nm³ (minimum 0,002, maximum 0,031 ng TEQ/Nm³).

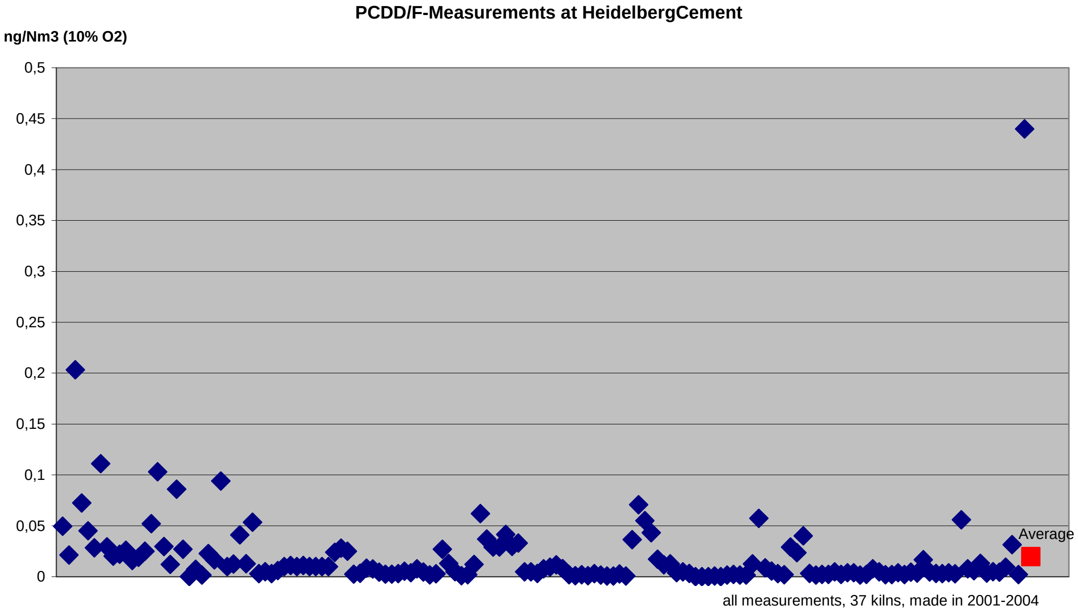


Figure 25 **152 PCDD/F measurements from 43 Heidelberg kilns in 2001-2004**

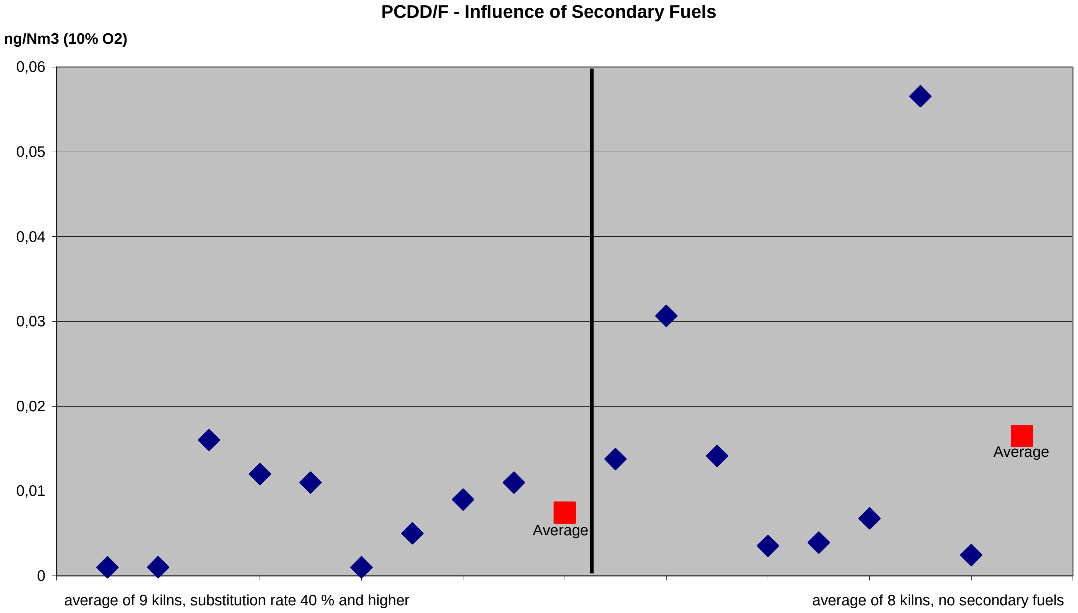


Figure 26 **Heidelberg kilns using more than 40% alternative fuel compared with kilns using fossil fuel only**

The highest value of 0.44 ng TEQ/Nm³ was measured at the stack of a long wet kiln.

Five PCDD/F emission measurements from two German preheater kilns feeding a mix of coal and plastics to the main burner and tyres to the kiln inlet showed the following concentrations:

Kiln 1: 0.0057, 0.0041 and 0.0018 ng TEQ/Nm^3;

Kiln 2: <0.0041 and <0.0021 ng TEQ/Nm^3.

There is clearly no influence by feeding waste to the kiln inlet.

Measurements from 5 European dry kilns done in 2001 and 2003 are presented in the table below.

Table 18 PCDD/F emission data and emission factors from 5 dry European kilns using waste fuel or tyres.

	Dry Kiln	Dry Kiln	Dry Kiln	Dry Kiln	Dry Kiln
Alternative fuel to kiln inlet (t/h)	3	3	3	0	0
Tyres with raw material (t/h)	3	2	2	1.7	1.8
PCDD/F ng I-TEQ/Nm^3 at 10% O_2	0.005	0.001	0.003	0.012	0.062
Emission factors PCDD/F µg TEQ/t clinker	0.011	0.002	0.007	0.025	0.016

In another report from Heidelberg measurements from 3 dry kilns are presented.

Plant 1

Operates two dry kilns and five measurements were made in 2003; the concentration measured in ng PCDD/F I-TEQ/Nm^3 at 10% O_2 was: 0.0099 , 0.0125, 0.041, 0.0128 and 0.0535 ng/Nm^3.

Plant 2

Operates a double-string 4-stage preheater kiln with planetary coolers and a production capacity of 2 000 tons per day. The concentration measured in ng PCDD/F I-TEQ/Nm^3 at 10% O_2 has varied in the range off 0.03-0.05 ng/Nm^3.

Plant 3

Operates two kilns; one long dry kiln with a capacity of approximately 410 tons per day and one long dry with 2-stage preheater with a capacity of approximately 430 tons per day. The concentration measured in ng PCDD/F I-TEQ/Nm^3 at 10% O_2 has varied in the range off 0.03-0.06 ng/Nm^3.

6.2.4.1 Heidelberg Norway

There is only on cement manufacturer in Norway which operates two cement plants with precalciner kilns, one in the south and one in the north of Norway. The total production capacity is about 1.8 million tons clinker per year and the company has for almost twenty years utilised different types of liquid and solid wastes as a co-fuel in one of their preheater/precalciner kiln.

The emission measurements are carried out in compliance with the requirements of the European Directive on the Incineration of Hazardous Wastes and are usually done twice a year.

The kiln in the southern plant produces about 3500 tons clinker/day. The exit gases from the kiln pass through an identical twin-type and four-stage preheater. After the preheater system the exit gases are diverted to two dedusting systems called String 1 and String 2. String 1 is directly operated and the exit gases are cooled in a cooling tower from about 370ºC to about 150ºC before dedusting in an electrostatic precipitator and a bag house filter. The temperature of the exit gases from String 2 is reduced in a cooling tower to about 220ºC before pre-dedusting and utilization for drying in the raw mill department where after a repeated dedusting takes place at about 100ºC in an electrostatic precipitator and a bag house filter before the exit gases leaves the stack.

Annual PCDD/F measurements have been performed in the two strings of kiln no. 6 since 1992; see table below. The kiln has been fired with a mix of coal, liquid and solid hazardous waste, refuses derived fuel, petcoke and used oil fed through the main burner and kiln inlet.

Table 19 **Mean PCDD/F concentration in a Norwegian cement plant using a wide range of alternative fuel and raw materials (ng PCDD/F N-TEQ/ Nm^3 at 11% O_2)**

Year	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
ng/ Nm^3	0.055	0.133	0.092	0.071	0.011	0.025	0.078	0.107	0.064

The PCDD/F level is given as the Nordic Toxicity Equivalent N-TEQ. The difference in applying Nordic Toxicity Equivalency Factor N-TEFs or the International I-TEFs is negligible as the two schemes differ only in a single congener; in the N-TEF scheme 1,2,3,7,8-Cl_5DF is given a TEF of 0.01 whereas in the I-TEF scheme a value of 0.05 is assigned to this specific congener.

6.2.4.2 Heidelberg UK

The Heidelberg plant in the UK operates three kilns, two long wet kilns and one dry process precalciner kiln. The PCDD/F emission of the dry precalciner kiln is approximately 0.001 ng/Nm^3. The results of 8 measurements of the two long wet kilns covered the showed a maximum concentration of 0.44 ng I-TEQ/m^3. The current authorized limit for the kilns is 0.8 ng TEQ/Nm3.

6.2.5 Lafarge Cement Company

In a recent report from Lafarge 64 individual PCDD/F measurements are reported (Reiterer, 2004), covering the period from 1996 to 2003, 6 different kiln configurations covering long wet kilns, long dry kilns, semi dry grate kilns, suspension preheater kilns and precalciner kilns. Almost all measurements are done under alternative fuel and raw material feeding. The average value of all these measurements was 0.0207 ng TEQ/m^3 at 11 % O_2, covering the range 0.003 – 0.231 ng TEQ/m^3 at 11 % O_2. The data is representing the production of approximately 37 million tons of clinker (see table below).

6.2.6 RMC Cement Company

RMC Cement Company operate 4 cement kilns in the UK using wet, semi-wet and semi- dry process technology. Raw materials are primarily chalk and clay and alternative fuels in the form of liquid waste have been used in one location for nearly 10 years. 13 measurements were carried out the last 4 years and covered the range 0.0014 - 0.0688 ng N-TEQ/Nm^3 at 11% O_2.

Table 20 64 PCDD/F measurements from Lafarge Cement Company

	Data from	Main kiln type	Filter type	AF & ARM	Clinker production [t/year]	Stack emissions [ng/Nm^3]
Plant						PCDD/F
Plant 1 K1	1996	KGSD	ESP	Tyres	130 000	0,002
Plant 1 K2	1996	KGSD	ESP	Tyres	305 000	0,001
Plant 1 K1	1997	KGSD	ESP	Tyres	130 000	0,002
Plant 1 K2	1997	KGSD	ESP	Tyres	305 000	0,003
Plant 1 K1	1998	KGSD	ESP	Tyres	130 000	0,004
Plant 1 K2	1998	KGSD	ESP	Tyres	305 000	0,002
Plant 1 K1	1999	KGSD	ESP	Tyres	130 000	0,008
Plant 1 K2	1999	KGSD	ESP	Tyres	305 000	0,01
Plant 1 K1	2000	KGSD	ESP	Tyres	130 000	0,014
Plant 1 K2	2000	KGSD	ESP	Tyres	305 000	0,004
Plant 1 K1	2001	KGSD	ESP	Tyres, MBM	130 000	0,028
Plant 1 K2	2001	KGSD	ESP	Tyres, MBM	305 000	0,004
Plant 1 K1	2002	KGSD	ESP	Tyres, MBM	70 000	0,021
Plant 1 K2	2002	KGSD	ESP	Tyres, MBM	305 000	0,004
Plant 2 K3	22.11.1999	KSPH	ESP	Waste Oil	575 000	0,078
Plant 2 K3	11.05.2000	KSPH	ESP	Waste Oil	575 000	0,059
Plant 2 K3	2001	KSPH	ESP	Waste Oil, MBM	575 000	0,034
Plant 3	mai.00	KSPH	ESP, Wet Scrubber	Tyres, Plastics	384 692	0,007
Plant 3	2002	KSPH	ESP, Wet Scrubber	Tyres, Plastics, MBM,	377 000	0,002
Plant 4	mai.00	KPAS	ESP	Waste Oil, Plastics	660 071	0,003
Plant 4	2002	KPAS	Bag filter	Plastics, MBM,	657 000	0,0015
Plant 5	mai.01	KSPH	ESP	MBM	263 111	0,002
Plant 5	2001	KSPH	ESP		263 000	0,017
Plant 6	jul.00	KPAT	ESP	Tyres, Kormul	543 100	0,01
Plant 6	2001	KPAS	ESP	Tyres, Kormul, plastics	543 000	0,059
Plant 7 K5		KPAT	ESP	no	622 500	b.d.
Plant 7 K6		KPAS	ESP	no	707 400	b.d.
Plant 8	2002	KLDR	ESP	yes	180 000	0,042
Plant 9	2000	KPAS	ESP	yes	746 000	<0,012
Plant 10	2002	KPAT	ESP	yes	337 120	b.d.
Plant 11	1999	KPAS	ESP	no	1 085 032	0,007884
Plant 12	1999	KPAS	ESP	no	1 790 000	0,008813
Plant 13 K4	1999	KPAS	ESP	no	604 060	0,004519
Plant 13 K1	1999	KPAS	ESP	no	1 598 790	0,004683
Plant 14	2002	KLDR	baghouse	no	2 200 000	0,0257
Plant 15	2002	KSPH	baghouse	yes	900 000	0,0209
Plant 16	2000/2002	KPAS	ESP	no	1 100 000	0,008
Plant 17	2002/1995	KLWT	ESP	yes	400 000	0,003
Plant 18	1998/1999	KLWT	baghouse	yes	450 000	0,1714
Plant 19	2002/1997	KLDR	baghouse	no	1 650 000	0,015
Plant 20	1999/2003	KPAS	baghouse	no	1 100 000	0,0012
Plant 21	2002	KSPH	baghouse	no	700 000	0,0029
Plant 22	2002/1996	KLWT	ESP	no	350 000	0,231
Plant 23	2002	KLDR	baghouse	yes	600 000	0,005
Plant 24	2002	KSPH	baghouse	yes	850 000	0,0094
Plant 25	2001	KPAS	ESP	YES	448 780	0,07
Plant 26	2001	KGSD	ESP/FB	YES	368 800	0,0003
Plant 27 K1	2001	KPAS	ESP	NO	707 583	0,0031
Plant 27 K2	2001	KPAS	ESP	NO	758 550	0,0008
Plant 28	2001	KPAS	ESP	NO	542 499	0,0009
Plant 29	2001	KSPH	ESP	NO	965 644	0,0016
Plant 30	2001	KSPH	ESP	NO	457 756	0,015
Plant 31 K1	2000	KGSD	ESP	YES	283 877	0,0128
Plant 31 K2	2000	KGSD	ESP	YES	311 906	0,0179
Plant 32	2000	KSPH	ESP	YES	500 388	0,0465
Plant 33	2000	KPAT	ESP	YES	806 459	0,0443
Plant 34	2000	KGSD	ESP	YES	344 457	0,0017
Plant 35	2000/01	KGSD	ESP	YES	236 070	0,0498
Plant 36 K1	2000	KLDR	ESP	YES	247 557	0,004
Plant 36 K2	2001	KLDR	FB	YES	324 491	0,003
Plant 37	2001	KPAS	FB	YES	649 113	0,0192
Plant 38	2000	KGSD	ESP	YES	316 300	0,00192
Plant 39	2002	KSPH	ESP	YES	905 960	0,0036
Plant 40		KPAS	ESP	YES	1 115 726	0,0041

Kåre Helge Karstensen
khk@sintef.no

6.2.7 Siam Cement Company

A summary of a recent report from Siam Cement Company in Thailand is given in the table below.

Table 21 PCDD/F measurements from Siam Cement in Thailand

Plant location	**Date of measurement**	**Process type**	**Clinker production t/d**	**Type of alternative fuel and raw material**	**ng TEQ/Nm^3 at 10% O_2**
Saraburi	May 2003	Dry	10,000	Petcoke & mixed solid waste	0.0158
Saraburi	May 2003	Dry	3466	Mixed solid and liquid wastes	0.0006
Nakhorn Sri Thamarat	April 2003	Dry	5510	Palm shell & fibers	0.0184
Nakhorn Sri Thamarat	April 2003	Dry	7296	Saw dust	0.0222

6.2.8 Taiheiyo Cement Company

Taiheiyo Cement operates currently 8 cement production plants with 16 kilns spread around on all the Japanese main islands. The company has officially published their environmental targets, key priority measures and subsequent performance since 1999.

Taiheiyo Cement was established in October 1998 and has been measuring PCDD/F emission levels in all their kilns since 1999; see table below (Taiheiyo, 2003).

Table 22 Emission levels Taiheiyo Cement (ng PCDD/F TEQ/Nm^3 at 12% O$_2$)

Year	1999	2000	2001	2002
Number of kilns	18	17	16	16
Average concentration	0.0066	0.017	0.011	0.012
Total emissions in gram TEQ/year		0.9	0.7	0.7

Taiheiyo Cement produced 23.59 million tons of cement in 2001 and emitted approximately 0.7 grams TEQ, compared to the 2200 grams TEQ discharged throughout Japan in year 2000. These emissions would be equivalent to an emission factor of approximately 0.03 µg TEQ/t of cement for the year 2001.

6.2.9 Uniland Cement Company

In a recent report from the Spanish cement company Uniland Cementera (Latorre, 2004) the measurements from two dry preheater kilns were reported. The 3100 ton clinker/day kiln had a PCDD/F concentration of 0.006 ng I-TEQ/Nm^3 at 10% O$_2$ in a measurement conducted in 2000. The 2100 t clinker/day kiln had a PCDD/F concentration of 0.002 ng I-TEQ/Nm^3 at 10% O$_2$ in a measurement conducted in

2002. The calculated emission factors was 0.011 and 0.005 µg I-TEQ/t clinker, respectively.

6.3 PCDD/F levels established by estimations

In many instances measured data are not available and many inventories are solely based on emission factors (micrograms of PCDD/F emitted under production of one ton of cement or clinker) established by other studies. With a broad range of variability in raw material composition, process technology, operation etc. such transference of emission factors is questionable, especially because many recent inventories haven't looked up the latest and most updated information. There are many examples of uncritical use of emission factors which has lead to exaggerated estimates.

6.3.1 Europe

In the final results of the European Dioxin Air Emission Inventory project (Quaβ et al, 2003) the maximum emission estimates of year 1985 is compared with projections for year 2005 for all industrial sources. The purpose is to evaluate if the EU 5th Action Programme's goal of 90% reduction of dioxin emissions until 2005 is achievable. The upper estimate contribution of the European Cement Industry was 21 grams in 1985, i.e. 0.15% contribution of the considered sources. In 2005 the cement industry is projected to emit minimum 14 and maximum 50 grams TEQ, i.e. between 0.37% and 2.55% of total emissions.

The typical dioxin contribution of the cement industry in European inventories is about 0.5%. In some inventories, the cement industry is even not mentioned (Eduljee, 1996). It is important to highlight that these contributions are often calculated on the basis of an estimated emission factor, not an actual measurement. Emissions factor generally used range from 5 to 0.001 µg/t cement. The European dioxins inventory is based on an emission factor of 0.15 µg/t cement.

The European Cement Association CEMBUREAU argues that this emission factor is too high (van Loo, 2003). CEMBUREAU consider the an average PCDD/F concentration in the flue gas of a dry kiln to be 0.02 ng TEQ/Nm3 and assume an exhaust-gas volume of 2300 Nm^3/ton clinker and a clinker/cement ratio of 0.8. This calculation gives an emission factor of 0.037 µg TEQ/ t cement, i.e. one fourth of the value used in the European inventory.

6.3.2 Italy

In a PCDD/F emissions inventory in the Lombardy region of Italy, Caserini and Monguzzi uses the emission factors for the cement industry proposed by US EPA 1998, i.e. 16.7 µg I-TEQ/ton cement and 0.216 µg I-TEQ/ton cement produced for cement kilns burning and not burning hazardous waste respectively. In the study cement kilns not burning hazardous waste are estimated to release 1.5 grams I-TEQ per year, i.e. approximately 4.48% of the total emissions in the region.

6.3.3 UK Inventory 1995

In an inventory of PCDD/F sources in UK, Eduljee and Dyke 1996, uses emissions factors of 0.025-1.08 µg I-TEQ/t product to estimate the release from the cement industry. The emission factors are provided by the British Cement Association BCA in 1995. The UK Public Register gave emissions factors of 1.2 and 0.9 µg I-TEQ/t product for two wet kilns burning both fossil fuel and waste derived fuel and emphasised that there was no difference between emissions measured when the kilns were fired with coal only, or with the coal and supplementary fuel mixture. The inventory doesn't say what is meant by product, clinker or cement.

Based on the emission factors the UK cement industry were estimated to contribute with 0.2-11 grams I-TEQ per year in 1995, which would constitute 0.018-1.96% of total emissions.

6.3.4 Newly Independent States (NIS) countries and Baltic countries

Parties of the Protocol to the 1979 Convention on Long Range Transboundary Air Pollution are obliged to present national emissions information on POP's. In the report by Kakareka and Kukharchyk of June 2002 the emissions of PCDD/F and PCB from industrial sources are estimated for the Newly Independent States (NIS) countries and the Baltic countries. For the cement industry an emission factor of 0.2 μg TEQ/t are used (see also Kakareka 2002). In the table below the estimated annual emissions of PCDD/F from the cement industry is compared with the total emissions for the NIS and the Baltic countries.

Table 23 Estimated annual emissions of PCDD/F from the cement industry compared with the total emissions for the NIS and the Baltic countries.

Country	Emission factor used	Emission of PCDD/F from the cement industry (gram TEQ/y) in 1997	Percentage of total National emissions
Azerbaijan	0.2 μg TEQ/t	0.06	4.1%
Armenia	0.2 μg TEQ/t	0.059	5.4%
Belarus	0.2 μg TEQ/t	0.375	2.3%
Estonia	0.2 μg TEQ/t	0.085	0.8%
Georgia	0.2 μg TEQ/t	0.02	0.07%
Latvia	0.2 μg TEQ/t	0.049	0.4%
Lithuania	0.2 μg TEQ/t	0.14	2.3%
Moldova	0.2 μg TEQ/t	0.024	1%
Russia	0.2 μg TEQ/t	4.04	0.9%
Ukraine	0.2 μg TEQ/t	1.02	0.2%

6.3.5 Hong Kong

In an assessment of PCDD/F emissions in Hong Kong, the Environmental Protection Department (March 2000) estimated an annual release of 0.32 gram I-TEQ from Green Island Cement in 1997. The estimate was based on an assumption of a maximum exit gas concentration of 0.1 ng I-TEQ/m^3, 7680 hours of operation per year and a flow rate of 7000 m^3/min. The contribution from the cement industry would constitute between 0.96-1.39 percent of total emissions.

6.3.6 United Nations Environment Programme UNEP PCDD/F inventories

The United Nations Environment Programme UNEP prepared in 1999 a national and regional inventory of PCDD/F emissions (UNEP, 1999). The intention of the publication was to serve as the first guide on available PCDD/F inventories established for countries and regions. The information in the report was taken from the published scientific literature, from government reports, from internet and personal communication.

The report categorizes the PCDD/F sources to air into nine major sectors, whereof cement production is covered as a subcategory under Mineral Products Production. Its worth to notice that cement production is not mentioned neither among the primary sources nor among the combustion sources.

The report underline that there are no harmonised methods on generation and evaluation of data for PCDD/F inventories and that the immediate purpose of the report was to "…*assist countries in the identification of national sources of PCDD/F releases by promoting access to the information on available sources of PCDD/Fs*…".

Table 24 UNEP estimates (UNEP, 1999)

Country	**Year**	**Emission factor used µg I-TEQ/t cement**	**Emission of PCDD/F from the cement industry (gram I-TEQ/y)**	**Percentage of total National emissions**	**Total National emission gram I-TEQ/y**
Austria	1994				28.7
Belgium	1985		16.1	1.9	850
	1990		19.7	2.2	892
	1995		20.8	3.1	662
Czech Republic	1995				30.2
Denmark	1995		0.08 – 1.5	0.16 – 2.4	50
Germany	1990				1210
	1995	0.0448	0.19	0.06	291
	2000				70
Hungary	1996				103.5
Slovak Republic	1993		0.023	0.05	42
Sweden	1993		0.07 – 1.3	0.3 – 1.5	21.6 - 88
Switzerland	1990		0.8	0.3	242
	1995		0.7	0.38	180
	2000		0.7	0.97	72
The Netherlands	2000				58
United Kingdom	1993		0.2 – 11		559 – 1099
	1997 low estimate		0.29	0.13	219
	1997 high estimate		10.4	1.56	663
European Inventory (17 countries)	1993 - 1995				3273 - 5750
European Atmospheric Emission Inventory (38 countries)			19.1	0.17	11314
Canada	1990		2.6	0.74	353
	1997		2.8	0.96	290
	1999		2.8	1.4	199
USA	1987		117 (hazardous waste burning)	0.97	12000
	1987		14 (non HW)	0.12	12000
	1995		153 (hazardous waste burning)	5.57	2745
	1995		17.8 (non HW)	0.65	2745
Australia	1998		0.12 – 153	0.08 – 102*	150 - 2300
Japan	1994				3981 - 8351
Global Emission Inventory	1996	2600	680 kg (hazardous waste burning)	4.9 - 6.07	12500±1300 kg PCDD/F
Global Emission Inventory	1996	200	320 kg (non HW)	2.3 - 2.86-	12500±1300 kg PCDD/F

6.3.7 UNEP Standardized Toolkit

The United Nations Environment Programme UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases (UNEP, 2003) is designed to cover all source categories and processes that are listed in Annex C, Parts II and III of the Stockholm Convention. The Toolkit can be used where there are no measured data available and provides default emission factors for all source categories.

The Toolkit states that "*obtaining PCDD/F data is analytically challenging and that locally obtained data should be used only if it is of adequate quality and is representative and trustworthy*". The Toolkit recommends to use its default emission factors rather than using own measured data of questionable quality.

6.3.7.1 UNEP Standardized Toolkit default emission factors for cement production

With relevance to the provisions of the Stockholm Convention Article 5, Annex C, Part II, the source category "*Cement kilns firing hazardous waste*" is explicitly mentioned as a potential source of PCDD/F emissions to air and release in residues (cement kiln dust).

The UNEP Standardized Toolkit has developed three classes of default emission factors for cement production, differentiating between type of kiln and ESP temperature. The Toolkit has realised that the US EPA in 1999 changed their conclusions from the tests done in the eighties and the nineties and "*that hazardous waste burning does not have an impact on PCDD/F formation, PCDD/F is formed post combustion*" (Federal Register, 1999).

The Toolkit emphasis that the more detailed investigations of the US EPA study has suggested that provided combustion is good, the main controlling factor is the temperature of the dust collection device in the gas cleaning system, and says further “*the plants equipped with low temperature electrostatic precipitators appear to have well controlled emissions with or without waste fuels*”.

Further it says “*It is thought that the raw materials themselves can have a considerable influence on the emissions and the presence of high levels of organic matter in the raw materials has been associated with elevated emissions of PCDD/F. It should be noted that the higher emissions measured in the USA were from wet kilns whereas the lower emissions from European cement kilns were obtained from plants using the dry process.*”

Further: “*The low results found in most of the modern European plants have been confirmed by the recent PCDD/F sampling and analysis program in Thailand (UNEP, 2001), were the results demonstrated that the addition of tyre and/or liquid hazardous waste had no effect on the emissions results*”.

Table 25 UNEP default emission factors for cement production

Classification	**Emission factors - µg TEQ/t of cement**				
	Air	Water	Land	Product	Residue
1. Wet kilns with ESP temperature >300°C	5.0	ND	ND	ND	1.0
2. Wet kilns with ESP temperature 200-300°C	0.6	ND	NA	ND	0.1
3. Wet kilns with ESP temperature <200°C **Dry kilns with APC (all types)**	0.05	ND	NA	ND	0.003

The Toolkit claims that the concentration of PCDD/F in the flue gases seems to be influenced by the temperature of the ESP. Low temperature (<200°C) seems to indicate that typical concentrations will be under 0.1 ng TEQ/Nm^3, temperatures over 300°C increase the likelihood of finding higher emissions, typical concentrations would be 0.3 ng TEQ/Nm^3 and above. In some cases much higher emissions may be found and these seems to be linked to high dust collector temperatures, high levels of organic matter in the raw materials and may be linked to use of certain wastes under inappropriate conditions.

An average emission factor of 5 µg TEQ/t of product, i.e. clinker, (in table 43 in the Toolkit the same emission factor is given for cement) is applied to wet kilns with dust collectors over 300°C. An average emission factor of 0.6 µg TEQ/t of product is applied to wet kilns where the dust collector is between 200 and 300°C. An emission factor of 0.05 µg TEQ/t of product is applied to all dry kilns and wet kilns where dust collector temperatures is held below 200°C.

The Toolkit also says that cement kilns, where materials have unusually high concentrations of organic matter and dust collector temperatures are high, should be noted for further consideration. Further, the Toolkit recommends that the use of wastes should be recorded nothing the wastes used, the means used to introduce them to the kiln and any controls on operation (e.g. prevention of feeding during combustion upsets, etc.).

The Toolkit claims that releases of PCDD/F to water is not expected and that the releases in the cement product are expected to be small since the product has been exposed to very high temperatures.

With regards to potential releases to land and through residues, the Toolkit points out the necessity to note management of cement kiln dust (CKD). Typically, the dusts from APCD are reintroduced into the kiln but in some instances the CKD is disposed of or recycled. A range of concentrations of PCDD/F has been reported in the CKD, but insufficient data are available to accurately estimate levels of PCDD/F from all kilns. Therefore, the Toolkit proposes an initial estimate of releases in CKD, differentiated in the same way as the air emissions factors, i.e. in three classes based on kiln type and APCD temperatures (UNEP, 2003).

6.4 Releases through clinker and dust

Samples of clinker, ESP dust and bypass dust are currently analysed for PCDD/F and PCB in different laboratories.

One problem encountered, is the lack of standardised methodology for sampling, sample preparation, extraction and clean-up. This is a particular problem for clinker, which is very hard to crush and difficult to extract, and the risk for contamination is great.

However, due to the high material temperature (1450^{o}C) a release of POP’s via the clinker is expected to be insignificant.

6.5 Summary of POP’s releases and discussion

A summary of all the PCDD/F measurements covered in this report is presented as average values or ranges for countries or cement companies in the table below.

The data represents more than 1,700 PCDD/F measurements and covers the period from early nineties until very recently. The data represents PCDD/F levels from both wet and dry kilns, performed under normal and worst case operating conditions, and with the co-processing of a wide range of hazardous wastes fed to both the main burner and to the kiln inlet (preheater/precalciner). The data also covers developing countries in Africa, Asia and South America.

Most of the US data are collected from trial burns done in the nineties, mostly in wet kilns with hazardous waste feeding performed under worst scenario conditions, i.e. high waste feeding rates, low temperature and oxygen in the kiln, high temperatures in the APCD etc. These higher values are considered to represent the past since the emission levels has decreased significantly the last years.

Table 26 Summary of PCDD/F measurements data

Country	**Use of AFR?**	**Concentration of [a] PCDD/F in ng TEQ/m^3**	**N**	**Emission factor µg TEQ/ton cement [a]**
Australia	Yes	0.001 – 0.07	55	0.0032 – 0.216
Belgium	Yes	<0.1	23	
Canada	Yes	0.0054 - 0.057	30	
Chile	Yes	0.0030 – 0.0194	5	
Colombia	Yes	0.00023 - 0.0031	3	
Denmark	Yes	<0.0006 – 0.0027	?	
Egypt	Yes	<0.001	3	
Europe	Yes	<0.001 – 0.163	230	<0.001-5
Germany 1989-1996	Yes	0.02	>150	
Germany 2001	Yes	<0.065	106	
Holcim 2001	Yes	0.0001 – 0.2395	71	0.104 (clinker)
Holcim 2002	Yes	0.0001 – 0.292	82	0.073 (clinker)
Holcim 2003	Yes	0.0003 – 0.169	91	0.058 (clinker)
Heidelberg	Yes	0.0003 – 0.44	>170	
Japan	Yes	0 - 0.126	164	
Lafarge	Yes	0.003 – 0.231	64	
Mexico	Yes	0.0005 – 0.024	3	
Norway	Yes	0.02 – 0.13	>20	0.04-0.40
Philippines	Yes	0.0059 – 0.013	5	
Poland	Yes	0.009 – 0.0819	7	
Portugal		0.0006 – 0.0009	4	
RMC	Yes	0.0014 – 0.0688	13	
Siam	Yes	0.0006 – 0.022	4	
South Africa	(Yes)	0.00053 – 0.001	2	
Spain	Yes	0.00695	20	0.014464
Spain Cemex	Yes	0.0013 – 0.016	5	
Spain Cimpor	Yes	0.00039 – 0.039	8	
Taiheiyo	Yes	0.011	67	
Thailand	Yes	0.0001 – 0.018	12	0.00024-0.0045
UK	Yes	0.012 - 0.423	14	<0.025-1.2
Uniland		0.002 – 0.006	2	0.005-0.011
USA[b]	Yes	0.004 - 25.8	~265	<0.216-16.7
Venezuela	Yes	0.0001 – 0.007	5	
Vietnam		0.0095 – 0.014	3	

[a] The numbers are either given as the range or the mean value

[b] The high numbers from the USA is from measurements done in the 1990's; the number of measurements are approximate.

The rest of the data is dominantly from dry preheater/precalciner kilns, which generally seems to emit slightly lower levels of PCDD/F than wet kilns. In most instances, the reported data from the dry kilns stems from co-processing of waste and alternative raw materials, which today is regarded to be the normal situation. A few examples in the table highlights this practice; the dry kiln in Colombia emits between 0.0002-0.003 nanogram TEQ/m^3 when feeding pesticide contaminated soil to the kiln inlet (preheater) and the UNEP managed project reveal emissions between 0.0001-0.018 nanogram TEQ/m^3 from a dry kiln in Thailand replacing fossil fuel with tyres and hazardous waste, the lowest levels when co-processing hazardous waste, 0.0002 nanogram TEQ/m^3.

The 47 emission measurements gathered from various developing countries show an average concentration of 0.0056 ng TEQ/m^3, with a maximum of 0.024 ng TEQ/m3 and a minimum of 0.0001 ng TEQ/m^3 (see figure below). Many of these measurements are performed when feeding alternative fuel and raw materials.

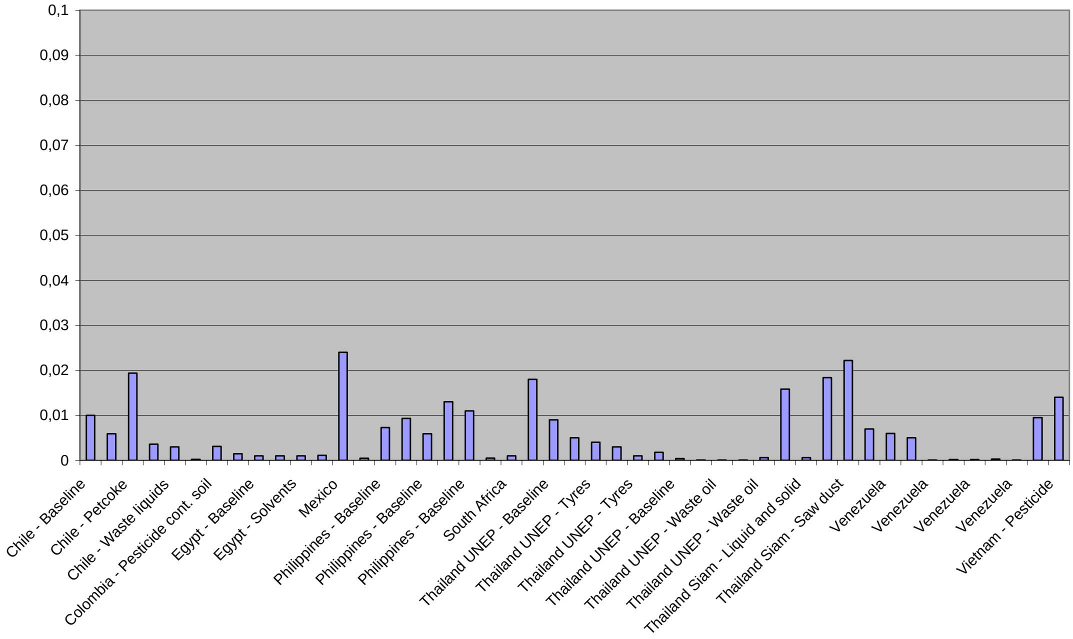


Figure 27 47 PCDD/F measurements from various developing countries.

The 1,700 PCDD/F measurements from around the world, representing all kinds of production technologies and process conditions, should allow classifying the emissions from the cement industry as low; see minimum and maximum values graphically presented in the two figures below.

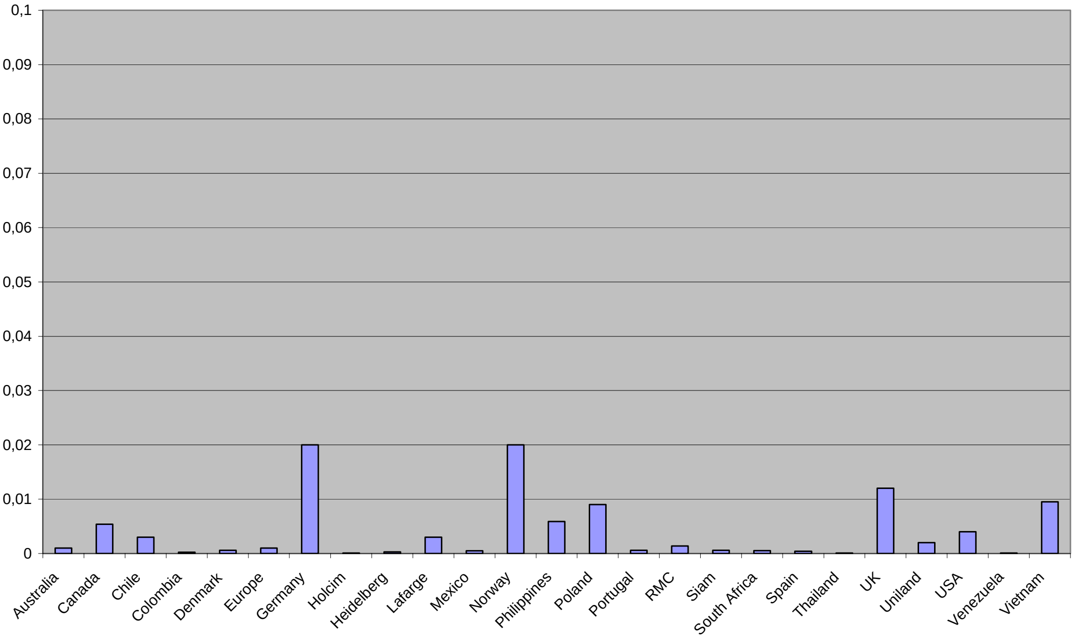


Figure 28 Minimum PCDD/F values in selected countries and companies.

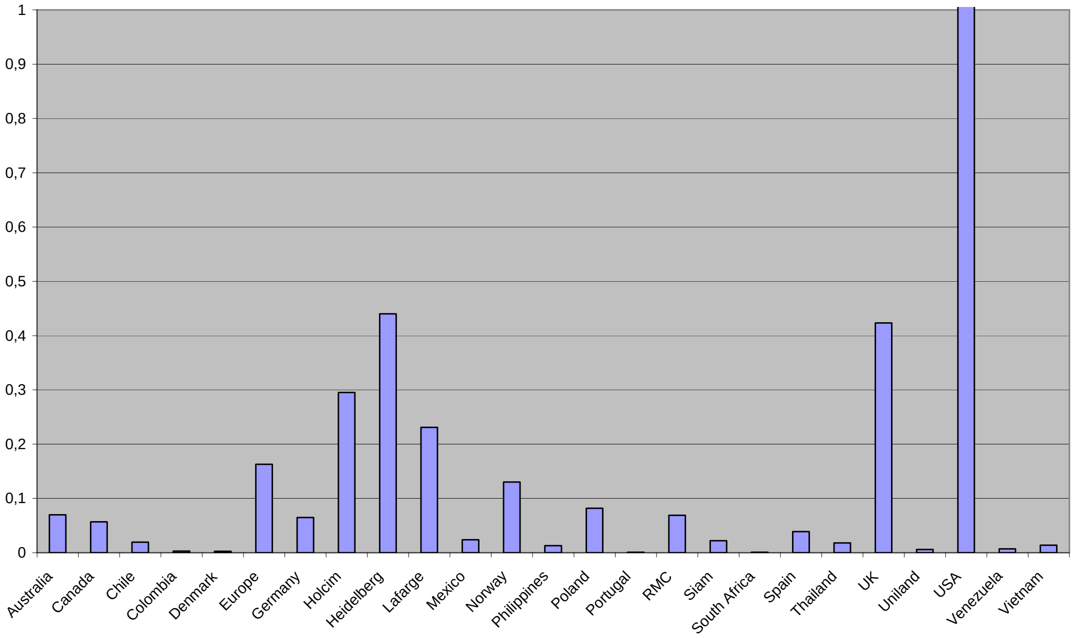


Figure 29 Maximum PCDD/F values in selected countries and companies.

Not many studies report emissions factors. The ranges found in recent studies are between 0.0032-0.4 µg I-TEQ/ton cement. Most of the inventory data presented in chapter 6.3 used the emission factors published by the US EPA in 1996, i.e. 16.7 and 0.216 µg I-TEQ/ton cement for cement kilns co-processing and not co-processing hazardous waste, respectively. CEMBUREAU argues that this emission factor is too high (van Loo, 2003) and consider 0.037 µg TEQ/ t cement to be a reasonable emission factor. The US emission factors, frequently used in inventories, are definitely too high. It should also be made clear if the emission factor used represents clinker or cement.

Since PCDD/F is the only group of compounds currently being regulated, there are fewer data measurements available for PCB and HCB. However, the more than 50 PCB measurements referred to in this report show that all values are below 0.4 µg PCB TEQ/m^3, many at a few nanogram level or below the detection limit. Approximately 10 HCB measurements are referred to in this report and show a concentration of a few nanograms per cubic meter or below the detection limit.

Some of the estimates made in national inventories presented, for example the Italian inventory in chapter 6.2.2, overestimate the cement industry PCDD/F contribution considerably. Experience from inventories based on measurements, like the Australian, show that the cement industry contribution is lowest compared to other industry sources and insignificant compared to natural sources (Environment Australia, 2003).

7. Measures for minimisation and control of PCDD/F emissions

The options for controlling PCDD/F emissions from cement kilns broadly fall into two categories:

(1) controlling quality of the feed material;

(2) controlling post-kiln operating conditions in wet kilns;

7.1 Process selection

The cement production process has an impact on the energy use and air emissions and for new plants and major upgrades the best available technique for the production of cement clinker is a dry process kiln with multi-stage preheating and precalcination.

7.2 Primary measures to control/minimise PCDD/F emissions

The best available techniques for the manufacturing of cement include the following general primary measures:

- A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. This can be obtained by applying:

  - Process control optimisation, including computer-based automatic control systems.

  - The use of modern, gravimetric fuel feed systems.

- Minimising fuel energy use by means of:

  - Preheating and precalcination to the extent possible, considering the existing kiln system configuration.

- Careful selection and control of substances entering the kiln can reduce emissions and when practicable, homogenous raw materials and fuels with low contents of sulphur, nitrogen, chlorine, metals and volatile organic compounds should be selected.

In most cases, primary measures (integrated process optimisation) have shown to be sufficient to comply with an emission level of 0.1 ng I-TEQ/Nm^3 in existing installations.

The following primary measures are considered to be most critical:

- Quick cooling of kiln exhaust gases to lower than 200°C in wet kilns (already inherent in preheater/precalciner kilns).

- Limit alternative raw material feed as part of raw-mix if it includes organics.

- No alternative fuel feed during start-up and shut down.

- Monitoring and stabilisation of process parameters:

  - Homogenous raw mix and fuel feed;
  - Regular dosage;
  - Excess oxygen.

7.3 BAT and BEP for emission control

Expert judgement by the European IPPC Bureau has played a key role in identification of BEP and BAT for the cement industry (IPPC, 2000).

In the BREF document (IPPC, 2000), techniques and possible emission levels associated with the use of BAT, are presented that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector.

Where emission levels "*associated with best available techniques*" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are not emission limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole.

The concept of "*levels associated with BAT*" is to be distinguished from the term "*achievable level*". Where a level is described as "*achievable*" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully.

It is intended that the general BAT could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate "BAT-based" conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general "BAT" levels. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or do better.

While the BAT and BEP levels do not set legally binding standards, they are meant to give information for the guidance of industry, States and the public on achievable emission levels when using specified techniques.

8. Conclusion

The objective of this study is to compile data on POP's emissions from the cement industry, to share state of the art knowledge about PCDD/F formation mechanisms in cement production possesses and how it is possible to control PCDD/F emissions from cement kilns by utilising primary measures, i.e. integrated process optimisation. This report is providing the most comprehensive data set available, collected from public literature, scientific databases and individual company measurements.

The report covers more than 1,700 PCDD/F measurements and many PCB measurements from the early 1990's until recently. The data represents PCDD/F levels from both wet and dry kilns, performed under normal and worst case operating conditions, with and without the co-processing of a wide range alternative fuel and raw materials and with wastes and hazardous wastes fed to both the main burner and to the kiln inlet.

Since PCDD/F is the only group of compounds currently being regulated, there are fewer data measurements available for PCB and HCB. However, the more than 50 PCB measurements referred to in this report show that all values are below 0.4 µg PCB TEQ/m^3, many at a few nanogram level or below the detection limit. 10 HCB measurements show a concentration of a few nanograms per cubic meter or below the detection limit.

The PCDD/F data presented and discussed in this report shows that:

- Most cement kilns can meet an emission limit of 0.1 ng TEQ/Nm^3;
- Co-processing of alternative fuels and raw materials, fed to the main burner or the preheater/precalciner does not influence or change the emissions of POP's;
- Cement kilns in developing countries presented here meet an emission level of 0.1 ng TEQ/Nm^3.

The emissions from dry preheater/precalciner kilns seem to slightly lower than emissions from wet kilns. In most instances, the reported data from the dry kilns stems from co-processing of waste and alternative raw materials, which today is regarded to be normal practise. Two recent examples; a dry kiln in Colombia emits between 0.00023-0.0031 nanogram TEQ/m^3 when feeding pesticide contaminated soil to the kiln inlet (preheater). A UNEP managed project measured emissions between 0.0001-0.018 ng TEQ/m^3 from a dry kiln in Thailand replacing parts of the fossil fuel with tyres and hazardous waste; the lowest concentration was found when co-processing hazardous waste, 0.0002 ng TEQ/m^3. This conclusion is also drawn by the US EPA, which after many years of research and testing in 1999 stated "*that hazardous waste burning does not have an impact on PCDD/F formation; PCDD/F is formed post-combustion*".

Estimates made in some recent national inventories overestimate the cement industry PCDD/F contribution considerably. Experiences from inventories where emission factors are established by actual measurements, like Australia, shows that the cement industry contribution is insignificant compared to, for example, natural sources and is also lowest among industry sources.

For new cement plants and major upgrades the best available technique for the production of cement clinker is a dry process kiln with multi-stage preheating and precalcination. A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. Quick cooling of kiln exhaust gases to a temperature lower than 200°C is considered to be the most important measure to avoid PCDD/F emissions in wet kilns (already inherent in suspension preheater and precalciner kilns). Primary measures have shown to be sufficient to comply with an emission level of 0.1 ng TEQ/Nm^3 in existing suspension preheater and precalciner kilns.

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Annex 1 The Stockholm Convention and destruction of POP’s

The Stockholm Convention has identified some important issues which needs to be taken into consideration regarding destruction technologies for POP’s:

- Technologies needs to destroy or irreversibly transform POP wastes in an environmentally sound manner;

- Criteria for levels of destruction needs to be developed.

The following are the technologies are currently used for POP’s wastes destruction: They can be classified into three distinct categories – physical, chemical and biological.

Physical:	Engineered Landfills Long Term Storage Deep well Injection
Chemical:	Incineration Gas Phase Chemical Reduction Electrochemical Oxidation Molten Metal Oxidation Solvated Electron Process (SET Process) Plasma Arc Process Thermal Desorption – BCD / APEG Lasagna^{TM} Process Immobilisation
Biological:	Bioremediation Phytoremediation

The requirements of destruction under the Stockholm Convention, could be summarised as follows:

- The necessary levels of destruction and irreversible transformation should be in the order of 99.9999% as most technologies commercially available or being tested have the capability of achieving this level of destruction;

- The technologies range from very simple to extremely complicated and expensive, and the amount of operator training also varies from simple to extensive;

- The environmentally sound disposal of POP's wastes is a complex issue – encompassing in it the concept of both sustainability and environmentally friendly nature of the disposal methodologies. At the heart of this concept is to ensure that the disposal is acceptable technically and socially (short and long-term health and economic impacts);

- The economics of the disposal process itself can be a limitation for many countries.

Stockholm Convention

The objective of the Convention is to protect human health and the environment from POP's. It takes a precautionary approach to identifying and acting against chemicals with POP characteristics.

Article 6.1 (d) requires that Parties take appropriate measures such that POP wastes are handled, collected, transported and stored in an environmentally sound manner. It further stipulates that POP wastes be disposed in such a way that the persistent organic pollutant content is destroyed, or irreversibly transformed, so that they do not exhibit the characteristics of persistent organic pollutants or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option or the persistent organic pollutant content is low, taking into account international rules, standards, guidelines and relevant global and regional regimes governing the management of hazardous wastes.

Article 6.2 states that the Conference of Parties shall cooperate closely with the appropriate bodies of the Basel Convention to: (a) establish levels of destruction and irreversible transformation necessary to ensure that the characteristics of persistent organic pollutants are not exhibited; (b) determine what they consider to be the methods that constitute environmentally sound disposal; and (c) work to establish the concentration levels of the chemicals listed in Annexes A, B and C in order to define low persistent organic pollutant content.

Basel Convention

The main objectives of the Basel Convention are to:

- Ensure that the generation of hazardous waste is reduced to a minimum;
- As much as possible, dispose of hazardous wastes within the country of their generation;
- Establish enhanced controls (e.g. prior informed consent, notification and manifesting) on exports and imports of hazardous waste;
- Prohibit shipments of hazardous wastes to countries lacking the legal, administrative and technical capacity to manage and dispose of them in an environmentally sound manner;
- Co-operate on the exchange of information, technology transfer, and the harmonisation of standards, codes and guidelines among signatory countries.

A nation ratifies the Basel Convention by putting in place the necessary legislation and measures that will enable it to implement the Convention.

Some of the key interrelationships between the Basel and the Stockholm convention are:

- All of the POP's currently listed in the Stockholm Convention are also classified as hazardous wastes under the Basel Convention;
- Both conventions require POP's wastes to be managed in accordance with Environmentally Sound Management (ESM) practices;
- The Conference of the Parties to the Basel Convention has adopted several sets of technical guidelines prepared by its Technical Working Group that concern, or are related to, POP's as wastes including technical guidelines on disposal operations and technical guidelines on waste streams; and
- Article 6.2 of the Stockholm Convention states that the Conference of Parties shall cooperate closely with the appropriate bodies of the Basel Convention to establish levels of destruction and irreversible transformation, determine methods that constitute environmentally sound disposal, and establish concentration levels of chemicals to define low persistent organic pollutant content.

Based on the above, it can be seen that many developing countries have yet to adopt and ratify Stockholm Convention as the demands under the convention are quite stringent and may turnout onerous and expensive for developing countries to meet.

Environmentally sound management

Environmentally Sound Management Principles (ESM) is defined as: "*a concept for ensuring that wastes are managed in a manner which will save natural resources and protect human health and the environment against adverse effects which may result from the management of such wastes and materials*" (OECD 2001)

The core performance elements of ESM are those that are applicable to all evaluation, dismantling, refurbishment, pre-treatment, treatment and disposal of wastes. They require that each facility should:

- Have adequate regulatory infrastructure and enforcement to ensure compliance with applicable regulations;
- Be appropriately authorized;
- Have waste minimisation/ recovery/ recycling procedures;
- Be appropriately certified under an applicable Environmental Management System;
- Have an appropriate operational monitoring and reporting programme;
- Have an operational inspection and recording programme for all input and output materials;
- Have appropriate in-house record keeping;
- Have an appropriate and verified emergency plan;
- Have an appropriate and operational training programme for its personnel;
- Have an adequate financial guarantee for emergency situations and closure.

Handling, Storage and Transportation

The storage of POP's wastes, and its proper execution, involves a number of considerations and factors. In fact, the method of on-site POP's wastes storage or handling is important for the success or failure of the POP's wastes management program. Proper planning from the initial stages of the program is necessary to ensure success, reduced liability, and regulatory compliance.

Some key practices for storage of POP's wastes in warehouses/ stores include:

- The site for a new shed or warehouse should not be close to communities, hospitals, schools, shops, food markets and public areas; it should be well removed from water courses/ wells;

- The storage site should have easy access for loading/ unloading and for emergency vehicles from at least three sides of the building;

- The design capacity of the building should be generous and should avoid unnecessary stacking of the material;

- The storage site should be always secure and access should be restricted to authorized personnel to reduce exposure. Adequate notices should be posted to keep people informed of the contents and its potential danger;

- The containers should be stocked away from direct sunlight;

- The facility should be well ventilated and well laid for easy access;

- The storage facility should have at least 15 % to 20% free space for movement of fork lifts and other vehicles for stocking and dispensing;

- Compatibility of materials kept in the areas is a key issue and other materials like waste acids/ bases etc. should be not stored along with pesticides and PCBs; liquids (PCBs) and solids (pesticides) should not be kept next to each other to prevent chemical reaction and contamination;

- Stacked containers should be on pallets; corrosion resulting from rising damp or leaking chemicals should be promptly observed and dealt with appropriately;

- Dust, granule and wet table powder formulations should be kept in cartons during storage to avoid caking;

- Liquids should always be kept in bunded areas with floor drain collection system;

- Stacks should be arranged to minimize handling and to avoid damage during handling.

Floor spaces should be uncluttered, well marked and containers and cartons should be stacked at safe heights ensuring that they are stable.

Storage of POP contaminated soils:

Contaminated soils containing POP's are likely to be received in bulk and would need storing until disposal options have been finalized. Key issues for soil storage include:

- Keep the material secure (restricted access area);

- Store under a roof to avoid direct sunlight and ensure that in case of rains/ washes, the water is collected and sent for treatment and does not contaminate watercourses;

- Keep soils dry and well-ventilated;

- Post a notice in the area to ensure that people are aware of the contents.

Handling and transportation

Recommended procedures for POP wastes handling and transportation include:

- Waste should be transported in dedicated trucks only;
- Open and leaking containers of waste pesticides, PCBs, etc. should not be transported. Contents should be transferred into another container before being transported;
- All loads should be securely fastened on the truck and all labels must be clearly readable;
- The truck should have in place appropriate placards and markings to indicate it is a hazardous cargo based on the regulatory requirements of the jurisdiction;
- The truck driver should be adequately trained to transport hazardous waste cargo and must have certification to prove this (as required by the jurisdictions);
- If there is an accident, the driver must be able to produce the manifest and emergency management procedures for the cargo to assist police/ fire personnel in dealing with the incident;
- The trucking company must be adequately insured (based on jurisdictional requirements) to handle any third party and environmental impairment liability claims in case of an accident;
- The loads should be periodically checked by a central authority (e.g. during rest stops), to assure that the cargo is intact and there is not leakage;
- Proper paper work must accompany the truck and the material should be handed over appropriately at the receivers end;

- The waste consignment must be carefully unloaded/ loaded from the truck.

Disposal of Pesticide Containers

Recommended procedures for handling and disposal of pesticide containers include

- Empty containers should always be cleaned;
- Containers that have contained wet table powder formulations should be rinsed with water several times and the rinsings to be added to the spray tank before it is topped up to the required volume. Then the containers can be washed out with a mixture of water, detergent and caustic soda;
- Containers of liquid formulations may be cleaned with kerosene (paraffin) or diesel fuel;
- The washings (small quantities of about 5 litres) should be collected for disposal in a safe environmentally sound manner at a central location authorized by the national authority;
- Highly contaminated cardboard, paper and jute materials should be collected and sent to the central disposal centres along with other toxic waste;
- Glass containers should be smashed and steel drums and metal and plastic containers punctured and crushed (do not puncture aerosol containers) before being sent to a central location for disposal by the national authority.

Destruction/irreversible transformation technologies

Destruction/irreversible transformation of POP’s wastes present many concerns. Some of these are briefly described below.

Regulatory Requirements in Place - The management of POP's waste require an effective regulatory regime covering all aspects of the waste cycle from generation to ultimate destruction. Many developed countries have enacted legislation for the management of POP's wastes, encompassing collection, containment, storage and disposal, and have implemented procedures for monitoring and enforcement. On the other hand, many developing and underdeveloped countries lack the necessary regulations and/or, financial and technical resources to ensure compliance, in cases where regulations exist.

Inadequate Inventories - The design and conduct of POP's wastes inventories are both complex and expensive. Many countries lack the necessary regulations to require inventories as well as the resources to undertake them. As a result, the full extent of the waste problem within most countries is probably unknown.

Size of the Stockpiles - Larger stockpiles are generally more difficult to manage and more expensive to dispose of. The situation is further complicated if large stockpiles of different types of POP's are involved, thus requiring a variety of destruction technologies.

Method of Storage and Containment - In countries where POP's wastes are strictly regulated and storage and containment requirements are monitored and enforced, the risks associated with deliberate and accidental release to the environment is significantly reduced. On the other hand, leaking and corroding metal drums filled with obsolete pesticides and other POP's waste, such as PCBs, are commonly observed in urban and rural areas in developing countries.

Potential for Environmental Contamination at the Storage Location - A failure to implement proper storage procedures could result in contamination of soil, water, building structures, etc. at storage sites, thus increasing the quantity of wastes and potential for human and environmental harm.

Physical Form and Occurrence of the Wastes - The method of collection, storage, and disposal of POP's wastes depends on the nature of the wastes, be they liquid, contaminated soil, metal components (e.g. PCB transformers and capacitors), sludge, ash, etc. Failure to implement appropriate management procedures can potentially lead to losses from existing stockpiles and the creation of new wastes due to cross-contamination or formation of by-products from inadequate disposal/destruction.

Health, Safety and Environmental concerns associated with the Transport of the Wastes - There are inherent risks with waste transport. In particular, accidents resulting in spills or atmospheric releases, sabotage, theft, etc., can divert wastes from their intended destination and thus, pose significant risks to humans and the environment. Workers involved in waste transport and emergency response teams are especially at risk during such occurrences and require proper training.

Ability of the Technology to ensure Complete Containment and Control of all Residues, By-products and Emissions - Destruction/irreversible transformation of POP's wastes require the implementation of technologies to destroy POP's without creating new POP's. Existing technologies, which primarily consist of incineration, chemical treatment and landfilling, are generally very expensive and require highly skilled individuals to manage and operate destruction facilities.

Many of the existing incineration technologies do not completely destroy the POP content in the targeted waste and may create new POP's such as dioxins, furans and HCB. Landfills are known for leaching toxic chemicals into waterways and drinking water systems, and releasing noxious fumes. Chemical treatment generally produces a larger volume of less hazardous chemical wastes, which then require treatment and disposal.

Incineration

Incineration is a high-temperature thermal oxidation process suited for organic contaminants in soil, sludge or sediments. Temperatures of 850-1200°C and appropriate residence time (minimum 2 seconds) are used to volatilise and combust the organics, using units comprised of main chamber and afterburner sections. Gas cleaning equipment, such as scrubbers and/or electrostatic filters are generally included. The solid residues are expected to be landfilled in a secure landfill.

Incinerators come in a variety of designs. Some are small-scale fixed types, designed for specific users, local formulation plants, or for relatively small quantities of low hazard waste etc. Others can be fairly large mobile units with rotary kilns and air pollution control devices, such as baghouses and scrubbers. These latter units can handle large amounts of liquid, solid and sludge waste, as well as contaminated soil. Incinerators can be classified into several types such as fluidised bed, liquid injection, rotary kiln and infrared.

Cement kilns (high temperature rotary kilns) have been used in many instances for the destruction of POP's and pesticide wastes. The wastes can either be mixed with the fuel or injected into the flame of the kiln, which turns slowly exposing the mix of sand, limestone and clay to temperatures of up to 2000^0C. While liquid wastes can be handled rather easily, care must be taken to introduce soils or solid material at an appropriate point in the kiln. The ratio of the waste to cement also requires consideration in view of the chemistry of the final product. Decomposition of chlorinated organics is facilitated by the alkaline conditions in the kiln. Cement kilns have also been used to destroy PCB liquids. Some changes in the treatment of off-gases may be needed depending on the type of wastes burned.

With proper design and operation, the Destruction & Removal Efficiency (DRE) of incinerators can be >99.9999%. Proper design components include considerations of (but not limited to):

- Process control;
- Maintenance;
- Residence time;
- Turbulence;

- Temperature; and
- Selection of appropriate waste.

Failure to ensure proper design can potentially result in severe health and environmental concerns due to the formation other POP's such as dioxins and furans. Incinerators have been put forward as the most efficient means of destroying POP wastes as they can achieve >99.9999% of efficiency of destruction if operated properly. However the design and operation are key issues for incineration and improper operation can be harmful. Operators for these facilities need a high degree of training. The cost per unit for destruction can also be high for incineration. Therefore, incineration is not a universal solution for POP's waste destruction.

Selection of Environmentally Sound Disposal Method

The selection of the appropriate technology for a particular type of POP's waste offers distinct challenges. Some typical forms of POP's wastes include:

- "Pure" POP's solids – obsolete pesticide stocks;
- "Pure" POP's liquid – PCB contaminated oils;
- POP's contaminated structures/ equipments – transformers/ capacitors;
- POP's contaminated containers – drums/ barrels etc.
- POP's contaminates soils/ sediments;
- POP's contaminated building materials;
- POP's contaminated residues – fly ash, bottoms slag etc.;

The selection of appropriate technology anywhere in the world would involve issues like:

- Quantity and location of the material;
- Available technology options;
- Transportation and permitting issues; and
- Economics.

Based on the evaluation of various technologies and their capability to destroy POP's as well as considering the requirements of destruction under the Stockholm Convention, the following observations are presented:

- The necessary levels of destruction and irreversible transformation should be in the order of 99.9999% as most technologies commercially available or being tested have the capability of achieving this level of destruction either on their own or in combination;
- The technologies presented range from very simple to extremely complicated and expensive, and include technologies that are currently being pilot tested. The amount of operator training also varies from simple to extensive;
- The environmentally sound disposal of POP's wastes is a complex issue – encompassing in it the concept of both sustainability and environmentally friendly nature of the disposal methodologies. At the heart of this concept is to ensure that the disposal is acceptable technically and socially (short and long-term health and economic impacts);
- The economics of the disposal process itself can be a limitation for many countries. While one process may be affordable in one region and this may

not be the case in another; therefore caution must be taken to avoid over generalization in developing disposal criterion or evaluating disposal technologies;