Formation and Release of POPs in the Cement Industry

Second edition

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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
CEMBUREAU	European Cement Association
CEMS	Continuous emissions monitoring system
CEN	European Standardisation Organisation
CFR	Code of Federal Regulations
CKD	Cement kiln dust
Cl_2	Molecular chlorine
CSI	Cement Sustainability Initiative
DL	Detection limit
CO	Carbon monoxide
CO_2	Carbon dioxide
DE	Destruction efficiency
Dioxins	A term/abbreviation for polychlorinated dibenzodioxins and polychlorinated dibenzofurans (see also PCDD/Fs)
DRE	Destruction and removal efficiency
Dscm	Dry standard cubic meter
EC	European Commission
EF	Emission factor
e.g.	For example
EPA	Environmental Protection Agency
EPER	European Pollutant Emission Register

ESP	Electro static precipitator
EU	European Union
FF	Fabric filter
g	Gram
GC-ECD	Gas chromatography with electron capture detector
GC-MS	Gas chromatography with mass spectrometry
HAPs	Hazardous air pollutants
HCB	Hexachlorobenzene
HCI	Hydrogen chloride
HF	Hydrofluoric acid
i.e.	That is
IPPC	Integrated Pollution Prevention and Control
I-TEF	International Toxicity Equivalency Factor
I-TEQ	International Toxic Equivalent
IUPAC	International Union of Pure and Applied Chemistry
J	Joules
K	(Degree) Kelvin
kcal	Kilocalorie (1 kcal = 4.19 kJ)
kg	Kilogramme (1 kg = 1000 g)
kJ	Kilojoules (1 kJ = 0.24 kcal)
kPa	Kilo Pascal (= one thousand Pascal)
L	Litre
lb	Pound
LCA	Life cycle analysis
LOD	Limit of detection
LOl	Loss of ignition
LOQ	Limits of quantification
m^3	Cubic meter (typically under operating conditions without normalization to, e.g., temperature, pressure, humidity)
MACT	Maximum Achievable Control Technology
MJ	Mega joule (l MJ= 1000 kJ)
mg/kg	Milligrams per kilogram
MS	Mass spectrometry
mol	Mole (Unit of Substance)

Na	Sodium
NA	Not applicable
NAAQS	National Ambient Air Quality Standards
NATO	North Atlantic Treaty Organisation
ND	Not determined/no data (in other words: so far, no measurements available)
NESHAP	National Emission Standards for Hazardous Air Pollutants
ng	Nanogram (1 ng = 10^{-9} gram)
Nm_3	Normal cubic metre (101.3 kPa, 273 K)
NH_3	Ammonia
NO_x	Nitrogen oxides ($NO+NO_2$)
NR	Not reported
N-TEQ	Toxic equivalent using the Nordic scheme (commonly used in the Scandinavian countries)
OECD	Organisation for Economic Co-operation and Development
O_2	Oxygen
PAH	Polycyclic aromatic hydrocarbons
PCA	Portland Cement Association (USA)
PCB	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PCDD/Fs	Informal term used in this document for PCDDs and PCDFs
PIC	Product of incomplete combustion
pg	Picogram (1 pg = 10^{-12} gram)
PM	Particulate matter
POHC	Principal organic hazardous constituent
POM	Polycyclic organic matter
POP	Persistent organic pollutants
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
QA/QC	Quality assurance/quality control
QL	Quantification limit
RACT	Reasonably Available Control Technology
RCRA	Resource Conservation and Recovery Act
RDF	Refuse derived fuel
RT	Residence time
sec	Second
SINTEF	Foundation for Industrial and Scientific Research of Norway
SNCR	Selective non catalytic reduction
SiO_2	Silicon dioxide
SCR	Selective catalytic reduction
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SOx	Sulfur oxides
SQL	Sample quantification limit
SRE	System removal efficiency
t	Tonne (metric)
TCDD	Abbreviation for 2,3,7,8-tetrachlorobidenzo-p-dioxin
TCDF	Abbreviation for 2,3,7,8-tetrachlorobidenzofuran
TEF	Toxicity Equivalency Factor
TEQ	Toxic Equivalent (I-TEQ, N-TEQ or WHO-TEQ)
TEQ/yr	Toxic Equivalents per year
THC	Total hydrocarbons
TOC	Total organic carbon
tpa	Tonnes per annum (year)
TRI	Toxics Release Inventory
TSCA	Toxics Substances Control Act
UNDP	United Nation Development Programme
UK	United Kingdom
UNEP	United Nation Environment Programme
UNIDO	United Nation Industry Development Organisation
US	United States of America
US EPA	United States Environmental Protection Agency

VDZ	Verein Deutsche Zementwerke
VOC	Volatile organic compounds
VSK	Vertical shaft kilns
WBCSD	World Business Council for Sustainable Development
WHO	World Health Organization
y	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.
Dioxins	Together with PCDD/Fs used as term/abbreviation for Polychlorinated dibenzodioxins and Polychlorinated dibenzofurans in this document
DRE/DE	Destruction and Removal Efficiency/Destruction Efficiency. The efficiency of organic compounds destruction under combustion in the kiln.
Kiln inlet/outlet	Were the raw meal enters the kiln system and the clinker leaves 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 Stockholm Convention requires Parties to take measures to reduce or eliminate releases of persistent organic pollutants (POPs) from intentional production and use, from unintentional production and from stockpiles and wastes. The chemicals intentionally produced and currently assigned for elimination under the Stockholm Convention are the pesticides aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex and toxaphene, as well as the industrial chemical Polychlorinated Biphenyls (PCBs).

The Convention also seeks the continuing minimisation and, where feasible, elimination of the releases of unintentionally produced POPs such as the by-products from wet chemical and thermal processes, polychlorinated dibenzo-p-dioxins/-furans (PCDD/Fs) as well as HCB and PCBs. Concepts of Best Available Techniques and Best Environmental Practices to achieve such minimisation and reduction from all potential source categories will be further developed by the Conference of the Parties. Cement kilns co-processing hazardous waste are explicitly mentioned in the Stockholm Convention as an "*industrial source having the potential for comparatively high formation and release of these chemicals to the environment*".

The cement industry takes any potential emission of POPs 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 the status of POPs emissions from the cement industry, to share state of the art knowledge about PCDD/F formation mechanisms in cement production processes and to show how it's possible to control and minimise PCDD/F emissions from cement kilns utilising integrated process optimisation, so called primary measures. This report provides the most comprehensive data set available on POPs emission from the cement industry,

collected from public literature, scientific databases and individual company measurements.

This report evaluates around 2200 PCDD/F measurements, many PCB measurements and a few HCB measurements made from the 1970s until recently. The data represents emission levels from large capacity processing technologies, including wet and dry process cement kilns, performed under normal and worst case operating conditions, with and without the co-processing of a wide range of alternative fuel and raw materials and with wastes and hazardous wastes fed to the main burner, to the rotary kiln inlet and to the preheater/precalciner. Vertical shaft kilns, regarded to be an obsolete technology but still common in many countries, have not been dealt with in this report due to lack of emission data. The PCDD/F data presented in this report shows that:

- Most cement kilns can meet an emission level of 0.1 ng TEQ/Nm^3 if primary measures are applied;

- Co-processing of alternative fuels and raw materials, fed to the main burner, kiln inlet or the precalciner does not seem to influence or change the emissions of POPs;

- Data from dry preheater and precalciner cement kilns in developing countries presented in this report show very low emission levels, much lower than 0.1 ng TEQ/Nm^3.

The emissions from modern dry preheater/precalciner kilns seem generally to be slightly lower than emissions from wet kilns. A common practise in many countries today is to co-process energy containing wastes and alternative raw materials in dry preheater/precalciner kilns, thereby saving fossil fuel and virgin raw materials. One example illustrates this: a UNEP project measured emissions between 0.0001-0.018 ng TEQ/m^3 from a dry preheater kiln in Thailand replacing parts of the fossil fuel with tyres and hazardous waste; the lowest concentration was found when the kiln was co-processing hazardous waste, 0.0002 ng TEQ/m^3.

Emission data from US cement kilns in the 1980s and first part of the 1990s stands in contrast with newer findings. They often indicated that cement kilns co-processing hazardous waste as a co-fuel had much higher PCDD/F emissions than kilns co-processing non-hazardous wastes or using conventional fuel only. In recent documents however, the US EPA has explained the most probable cause for these findings, namely that cement kilns burning hazardous waste were normally tested under "worst" scenario trial burn conditions, i.e. typically high waste feeding rates and high temperatures in the air pollution control device, conditions today known to stimulate PCDD/F formation. Cement kilns burning non-hazardous waste or conventional fossil fuel only were however tested under normal conditions, no "worst" scenario conditions, making a comparison between hazardous waste burning and non-hazardous waste burning kilns dubious.

Reducing the temperature at the inlet of the air pollution control device is one factor which has shown to limit dioxin formation and emissions at all types of cement kilns, independent of waste feeding, as lower temperatures are believed to prevent the post-combustion catalytic formation of PCDD/Fs. The US EPA concluded in 1999 in the new Maximum Achievable Control Technology regulation that hazardous waste burning in cement kilns does not have an impact on PCDD/F formation because they are formed post-combustion, i.e. in the air pollution control device.

This report also provides a large number of measurements of PCDD/F in products and residues from the cement industry. The levels are normally low and in the same magnitude as found in foods like fish, butter and breast milk as well as soil, sediments and sewage sludge.

For new cement plants and major upgrades the best available techniques 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 for the energy use.

The most important primary measures to achieve compliance with an emission level of 0.1 ng TEQ/Nm^3 is quick cooling of the kiln exhaust gases to lower than

200°C in long wet and long dry kilns without preheating. Modern preheater and precalciner kilns have this feature already inherent in the process design. Feeding of alternative raw materials as part of raw-material-mix should be avoided if it includes organic material and no alternative fuels should be fed during start-up and shut down.

The UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases assign emission factors to all source categories and processes that are listed in Annex C, Parts II and III of the Stockholm Convention. The emission factors for cement kilns co-processing hazardous wastes are among the lowest of all source categories.

Since PCDD/F is the only group of POPs commonly being regulated up to now, there are fewer measurements available for HCB and PCBs. 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 concentrations below the detection limit.

1. Introduction

The Stockholm Convention requires Parties to take measures to reduce or eliminate releases of persistent organic pollutants (POPs) from intentional production and use (Article 3), unintentional production (Article 5) and stockpiles and wastes (Article 6) (Stockholm Convention, 2001). The chemicals currently assigned for elimination under the Stockholm Convention are the pesticides aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex and toxaphene, as well as the industrial chemical polychlorinated biphenyls (PCBs).

The Convention also seeks the continuing minimisation and, where feasible, elimination of the releases of unintentionally produced POPs such as the industrial by-products polychlorinated dibenzo-p-dioxins/-furans (PCDD/Fs) as well as HCB and PCBs. Concepts of Best Available Techniques (BAT) and Best Environmental Practices (BEP) to achieve such minimisation and reduction from all potential source categories are to be further elaborated by the Conference of the Parties (Richter and Steinhauser, 2003).

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*".

1.1 The Cement Sustainability Initiative

The Cement Sustainability Initiative (CSI) was launched in 1999 under the auspices of the World Business Council for Sustainable Development (WBCSD). The multimillion dollar initiative is undertaken by 16 of the leading companies in the cement industry who collectively manufacture nearly 50% of the cement worldwide, outside of China, and representing more than 100 countries. Their goal is 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.
- Managing local impacts on land and communities.
- Progress and communications.

The objectives of the study in this report, to compile data on POPs emissions from the cement industry, contribute significantly to many of the key issues listed above. Detailed information of the CSI (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 POPs emissions from the industry and describe possibilities for control measures where needed. Information presented here has been collected both from public literature, scientific databases, and individual company measurements. The report will be further updated as more data becomes available; that's why the report is called a draft report.

In most scientific literature and databases between 50 and 200 “hits” can be found on POPs emissions from cement kilns. However, many of the hits are repetitions and the dominating subject is on dioxins and furans (PCDD/Fs). There is very little public information about PCBs release and almost nothing on HCB emissions; the data in this report comes almost exclusively from the individual cement companies collected for the purpose of this study. More data on PCB and HCB will be collected and presented in the next version of this report.

One of the main routes towards sustainability in the cement industry is to save as much as possible of non-renewable fossil fuel and virgin raw materials and

substitute by waste and secondary materials. This report gives a brief overview of production technologies for cement as well as the principles of co-processing alternative fuels and raw materials (AFR) and describes how to verify the performance of such practice making sure that co-processing is done in an acceptable manner. The main regulatory and legislative framework for the cement industry on environmental performance in the European Union (EU) and the United States of America (US) is presented. Also the possibilities to control and minimise the PCDD/Fs emissions from cement production by utilising integrated process optimisation, i.e. primary measures, is discussed in the report.

In terms of their contribution to the national environmental burden of PCDD/Fs and relative to other potential sources of emissions, cement kilns have not generally been regarded as significant emitters. For example, in the US and the UK source inventories (Schaub 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 are PCDD/Fs?

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (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). PCDD/Fs are always found in samples as a mixture of the various congeners.

Within the family of PCDD/Fs, 17 congeners are of particular concern, with the arrangement of chlorine atoms around the double-benzene molecular framework conferring to a heightened toxicological response. The most toxic is 2,3,7,8-tetra-chloro-dibenzo-p-dioxin (TCDD). Only congeners with chlorine atoms in the 2,3,7,8-positions are considered to have toxic properties and the toxicity of the other 17 congeners is estimated relative to 2,3,7,8-TCDD, which is assigned 1, and given toxic

equivalency factors (TEFs) which differs slightly depending on the system used. The total weighted toxicological response of these congeners is conventionally expressed in units of Toxic Equivalents, abbreviated to TEQs.

Significant developments are underway in assessing and responding to pollution by ‘‘dioxin-like’’ compounds, often defined to be PCDD/Fs and those PCBs which exhibit dioxin-like toxicity (Dyke and Stratford, 2002). The use of TEFs to provide a simple, single number that is indicative of overall toxicity of a sample containing a mixture of PCDD/Fs is well established. Many values set for regulation and assessment of PCDD/Fs is based on toxic equivalent concentrations including emission limits for industrial plants, tolerable daily intake (TDIs) and environmental quality standards.

There have been a number of efforts over recent years to extend the concept and methodology of TEF schemes to include other classes of compounds. The most commonly included compounds are now those congeners of the PCBs that exhibit ‘‘dioxin-like’’ activity. Various schemes have been proposed for TEF values applicable to selected PCB congeners (Dyke and Stratford, 2002). The implications of altering the TEF values for given congeners of PCDD/Fs and extending the scope to include other chemicals might have significant legal, administrative and technical implications for regulation and assessment.

Over the years a number of toxicity equivalency factor systems have been developed. The dominating system during the nineties was the international system developed by NATO. 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 by WHO 1998. This system gives in contrast to previous systems separate toxicity equivalency factors for humans/mammals, fish and birds.

The Nordic and the International systems are almost identical, whereas the German system also assigned toxicity to non-2,3,7,8-congeners. The new WHO-system differs strongly in the assessment of penta-chloro- and octa-chloro-dioxins. 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).

There is widespread acceptance that a system of TEFs, and the TEQ values derived from them, can be an effective tool for assessing and regulating complex mixtures of PCDD/Fs although there is still some uncertainty about the limitations of such an approach in some cases. Until recently, the scheme of TEF values agreed by NATO (1988) had become widely accepted as the standard system although other schemes have been used in the past. This scheme is often known as the International TEF scheme and sometimes denoted I-TEF or I-TEQ. A comparison of the alternative schemes that have been used can be found in Dyke and Stratford (2002).

In the UK and in many other places over the past decade the I-TEF scheme has been widely used and therefore the important comparison is between the NATO system and the new WHO scheme, as applied to mammals and humans (Van den Berg et al., 1998). The changes are an increase in the TEF for 1,2,3,7,8 PeCDD from 0.5 to 1 and decreases from 0.001 to 0.0001 for OCDF and OCDD.

1.2.1 Properties of dioxins

The properties of dioxins may be briefly described as follows (Jones and Sewart, 1997): 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 K_{ow}) 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 up to 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 and Sewart, 1997). The fact that dioxins have been detected in natural clay indicates that dioxins are produced through natural processes and that they have the ability under appropriate conditions to persist for thousands and maybe even millions of years.

1.3 Basic assumptions for this investigation

The formation of PCDD/F will be process specific, which means that local conditions of the individual cement plants with respect to raw materials and process conditions, flue gas cleaning and in particular temperature patterns in the flue gas cleaning system and chimneys can affect the formation. 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. The first sample collected from a cement kiln stack measured 4.2 ng I-TEQ

m^3 and the second, collected 5 hours later, 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 suggests variability within the process conditions or a change in process operation mode and demonstrates the need for caution when extrapolating emissions from a single sample to providing emissions factors for a whole industrial sector. As a consequence, high confidence is generally placed with measurements from actual plants in this study, no matter whether they are few. Still they represent actual conditions with respect to raw materials and process conditions. Less confidence is given 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. 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.

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 TEF system 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. It's still not possible to determine the accuracy of the stack gas 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's 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.

All these uncertainties are difficult or sometimes impossible to eliminate and must be taken into consideration when reading this document. More about sampling and analysis can be found in chapter 4.

2. Cement production process

The description of the cement production process is an excerpt from CEMBUREAUs BAT document (1999), the UK Environment Agency "Integrated pollution prevention and control – Guidance for the Cement and Lime sector" (Environment Agency, 2001) and the European Integrated Pollution Prevention and Control document "Reference document on Best Available Techniques in the Cement and Lime Manufacturing Industries" (IPPC, 2001), from Duda (1985) and Roy (1985).

2.1 Main processes

There are four main process routes in the manufacturing of cement – the dry, semi-dry, semi-wet and wet process. The main features of these processes are described in more detail in the following chapters. Common to all these processes are the following sub-processes:

- Quarrying;
- Raw materials preparation;
- Fuels preparation;
- Clinker burning;
- Mineral additions preparation;
- Cement grinding;
- Cement dispatch.

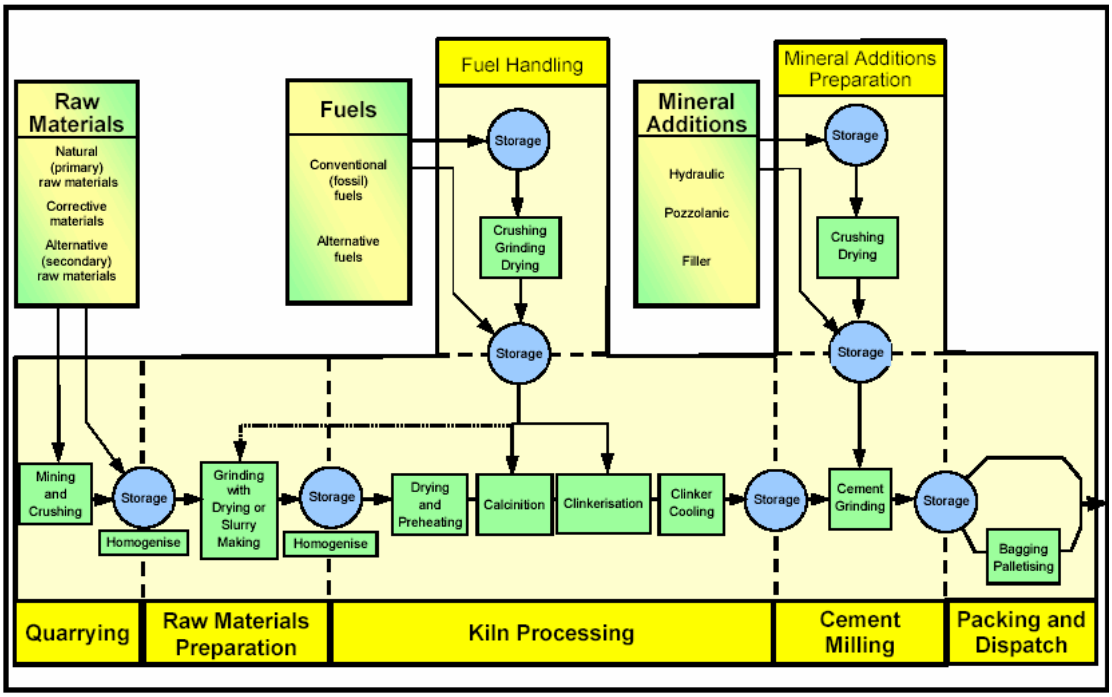

Figure 1 Processes identification and system boundaries of cement production (Environment Agency, 2001)

2.1.1 Quarrying

Natural ("primary") raw materials such as limestone/chalk, marl, and clay/shale are extracted from quarries which, in most cases, are located close to the cement plant. After extraction, these raw materials are crushed at the quarry site and transported to the cement plant for intermediate storage, homogenization and further preparation.

"Corrective" materials such as bauxite, iron ore or sand may be required to adapt the chemical composition of the raw mix to the requirements of the process and product specifications. The quantities of these corrective materials are usually low compared to the huge mass flow of the main raw materials.

To a limited extent, “secondary” (or “alternative”) raw materials originating from industrial sources are used to substitute for natural raw materials and correctives. In the same way as traditional raw materials, they may be fed to the quarry crusher or – more commonly – directly to the cement plant’s raw material preparation system. Today, modern computerised methods are available to evaluate the raw material deposits and to optimise the long-term and short-term production schedule.

2.1.2 Raw materials preparation

After intermediate storage and pre-homogenisation, the raw materials are dried and ground together in defined and well-controlled proportions in a raw mill to produce a raw meal for the dry (and semi-dry) process. In the wet (and semi-wet) process, the raw materials are slurried and ground with addition of sufficient water to produce raw slurry. Depending on the technological process applied, additional steps may be required such as preparing raw meal “pellets” from dry meal (semi-dry process) or “filter cake” by dewatering of the slurry in filter presses (semi-wet process).

The resulting intermediate product – i.e. raw meal or raw slurry (or their derivatives) – is stored and further homogenised in raw meal silos, storage bins or slurry basins to achieve and maintain the required uniform chemical composition before entering the kiln system. As a rule of thumb, approximately 1.5 – 1.6 tons of (dry) raw materials are required to produce one ton of the burnt product clinker.

2.1.3 Fuels preparation

Conventional (fossil) fuels used in the European cement industry are mainly coal (lignite and hard coal), petcoke (a product from crude oil refining), and heavy oil (“bunker C”). Natural gas is rarely used due to its higher cost. “Alternative” fuels –

i.e. non-fossil fuels derived from industrial ("waste") sources – are widely used today to substitute in part for the traditional fossil fuels.

Fuels preparation – i.e. crushing, drying, grinding, and homogenising – usually takes place on site. Specific installations are required such as coal mills, silos and storage halls for solid fuels, tanks for liquid fuels, and the corresponding transport and feeding systems to the kilns. The thermal fuel consumption is largely dependent on the basic process design applied in the burning of clinker.

2.1.4 Clinker burning

The prepared raw material ("kiln feed") is fed to the kiln system where it is subjected to a thermal treatment process consisting of the consecutive steps of drying/preheating, calcination (e.g. release of CO_2 from limestone), and sintering (or "clinkerisation", e.g. formation of clinker minerals at temperatures up to 1450 °C). The burnt product "clinker" is cooled down with air to 100-200 °C and is transported to intermediate storage.

The kiln systems commonly applied are rotary kilns with or without so-called "suspension preheaters" (and, in more advanced systems, "precalciners") depending on the main process design selected. The rotary kiln itself is an inclined steel tube with a length to diameter ratio between 10 and 40. The slight inclination (2.5 to 4.5 %) together with the slow rotation (0.5–4.5 revolutions per minute) allow for a material transport sufficiently long to achieve the thermal conversion processes required.

Exhaust heat from the kiln system is utilised to dry raw materials, solid fuels or mineral additions in the mills. Exhaust gases are dedusted using either electrostatic precipitators or bag filter systems before being released to the atmosphere.

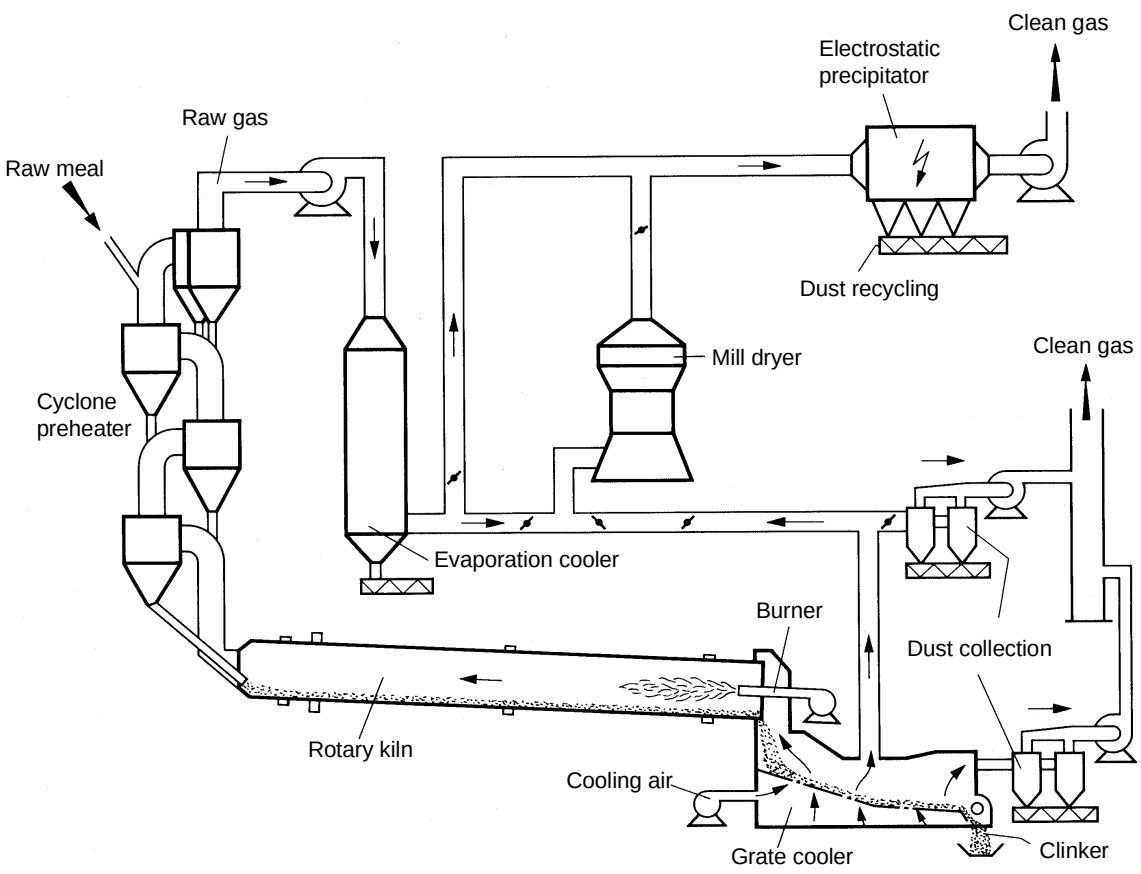

Figure 2: Rotary kiln with cyclone preheater and gas dust collection

2.1.5 Cement grinding

Portland cement is produced by intergrinding cement clinker with a few percent of natural or industrial gypsum (or anhydrite) in a cement mill. Blended cements (or "composite" cements) contain other constituents in addition such as granulated blast-furnace slag, natural or industrial pozzolana (for example, volcanic tuffs or fly ash from thermal power plants), or inert fillers such as limestone.

Mineral additions in blended cements may either be interground with clinker or ground separately and mixed with Portland cement. Grinding plants may be

located remotely from the clinker production facility. The different cement types have to be stored separately in cement silos prior to bagging and dispatch.

2.1.6 Mineral additions preparation

Mineral additions from natural or industrial sources intended to be used in blended cements may need to be dried, crushed or ground in separate installations on site. Separate "grinding plants" where mineral additions and blended cements only are produced may also be located remote from the clinker production facility.

2.1.7 Cement dispatch

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Cement may be shipped as bulk cement or – usually to a lesser extent – packed into bags and palletised for dispatch. Transport methods used (i.e. road, railway, waterways) depend on local conditions and requirements.

2.2 Material technological characteristics in cement production

Portland cement clinker is produced from a mixture of raw materials containing calcium, silicon, aluminium, and iron as the main elements. When mixed in the correct proportions, new minerals with hydraulic properties – the so-called clinker phases – are formed upon heating up to the sintering (or clinkerisation) temperature as high as 1450 °C.

2.2.1 Main Clinker Phases

The main mineral components in clinker are silicates, aluminates and ferrites of the element calcium.

▪ Tri-calcium silicate	3 CaO x SiO_2	C3S	Alite
▪ Di-calcium silicate	2 CaO x SiO_2	C2S	Belite
▪ Calcium aluminate	3 CaO x Al_2O_3	C3A	Aluminate
▪ Calcium ferrite	4 CaO x Al_2O_3 x Fe_2O_3	C4AF	Ferrite

The clinker formation process can be divided into 4 steps:

- Drying and preheating (20–900 °C): release of free and chemically bound water;
- Calcination (600–900 °C): release of CO_2: initial reactions with formation of clinker minerals and intermediate phases;
- Sintering or clinkerisation (1250–1450 °C): formation of calcium silicates and liquid phase;
- Kiln internal cooling (1350–1200 °C): crystallisation of calcium aluminate and calcium ferrite.

Minor mineral constituents in cement clinker include uncombined calcium oxide ("free lime") and magnesium oxide, as well as alkali sulphates. Additional chemical elements present in the raw materials such as manganese, phosphorus, titanium or heavy metals are mainly incorporated in the mineral structure of the major clinker phases.

The properties of clinker (and thus, of the cement produced from it) are mainly determined by its mineral composition and its structure. Some elements in the raw materials such as the alkalis, sulfur and chlorides are volatilised at the high temperatures in the kiln system resulting in a permanent internal cycle of vaporisation and condensation ("circulating elements"). A large part of these elements will remain in the kiln system and will finally leave the kiln with the clinker. A small part will be

carried with the kiln exhaust gases and will be mainly precipitated with the particulates in the dedusting system.

At a high surplus of volatile elements, the installation of a preheater "bypass" may become necessary where part of the dust laden exhaust gases of the rotary kiln is extracted from the system. Both filter and bypass dust can totally or partially be recycled to the cement manufacturing process.

2.2.2 Raw mix components

A well designed raw mix in clinker manufacturing typically consists of calcareous components rich in calcium, e.g. > 75 % of carbonates (limestone, chalk, marble, calcareous marl), argillaceous components rich in aluminium, silicon and iron (marl, marly clay, shale, clay) and corrective components specifically enriched in one of the four main elements (bauxite, iron ore, sand, high-grade limestone, etc.). Correctives are used in small quantities only to adjust the chemical composition of the raw mix to the required quality targets.

Depending on availability and chemical composition, both main and corrective raw mix components may also originate from industrial ("non-fossil") sources ("alternative" raw materials). Examples are coal fly ash from power stations, steel slag, foundry sand, sewage sludge, lime sludge, FCC catalysts from oil refineries, and many more.

A proper raw mix design is based on the given raw materials situation, on the process design and process requirements, on the product specifications, and on environmental considerations. A well designed raw mix, adequate fineness of the raw meal and constant chemical composition are essential both for a good product quality and for a smooth kiln operation. Homogeneity and uniformity of the raw mix composition has to be carefully controlled on a permanent basis by adequate sampling and chemical analysis.

2.2.3 Fuels

Main fossil fuels ("primary" fuels) in the cement industry are coal, petcoke, heavy oil, and – to a lesser extent – natural gas. Non-fossil "alternative" fuels derived from industrial sources such as tyres, waste oil, plastics, solvents and many more are commonly used as substitute fuels today. The chemical components of the ash of solid fuels combine with the raw materials and will be fully incorporated in the clinker produced. Thus, the chemical composition of the ash has to be considered in the raw mix design.

In the same way as the major elements, metals which may be introduced with liquid or solid fuels will also be incorporated into the clinker structure to a large extent. Exceptions are metals which are partly or completely volatilised in the kiln system such as mercury, thallium or cadmium. These elements will be captured in the kiln (filter) dust or may to some extent escape with the stack emissions (mercury) if not managed appropriately.

2.2.4 Cement constituents

Portland cement is produced by intergrinding clinker with a few percent of natural or industrial gypsum or anhydrite (calcium sulphate) acting as a set regulator. In many European countries, the addition of up to 5 % of "minor constituents" such as raw meal, limestone or filter dust is allowed.

In blended (or "composite") cements, part of the cement consists of mineral additions originating from natural or industrial sources. These mineral additions may have hydraulic (granulated blast furnace slag), pozzolanic (volcanic rocks, coal fly ash, micro silica, calcined clay) or filler properties (limestone). The composition of blended cements is specified in the national cement standards. The standards usually also includes quality specifications for the individual mineral additions used.

2.3 The four main process routes

Historically, the development of the clinker manufacturing process was characterised by the change from “wet” to “dry” systems with the intermediate steps of the “semi-wet” and “semi-dry” process routes. The first rotary kilns – introduced around 1895 – were long wet kilns.

“Wet” kilns allowed for an easier handling and homogenisation of the raw materials, especially in cases when the raw materials are wet and sticky or exhibit large fluctuations in the chemical composition of the individual raw mix components. With more advanced modern technology however, it is possible to prepare a homogeneous raw meal using the “dry” process, i.e. without addition of water to prepare raw slurry. The main advantage of a modern dry process over a traditional wet system is the far lower fuel consumption and thus, lower fuel cost. Today, the selection of the wet process is only feasible under very specific raw material and process conditions.

The four different basic processes can be briefly characterised as follows:

- Dry process: Dry raw meal is fed to a cyclone preheater or precalciner kiln or, in some cases, to a long dry kiln with internal chain preheater.

- Semi-dry process: Dry raw meal is pelletised with water and fed to a travelling grate preheater prior to the rotary kiln or in some cases, to a long kiln equipped with internal cross preheaters.

- Semi-wet process: Raw slurry is first dewatered in filter presses. The resulting filter cake is either extruded into pellets and fed to a travelling grate preheater or fed directly to a filter cake drier for (dry) raw meal production prior to a preheater/precalciner kiln.

- Wet process: The raw slurry is fed either directly to a long rotary kiln equipped with an internal drying/preheating system (conventional wet process) or to slurry drier prior to a preheater/precalciner kiln (modern wet process).

2.4 Process technological characteristics of clinker production

All processes have in common that the kiln feed is first dried, then calcined by dissociation of carbon dioxide (CO_2) from the $CaCO_3$ in the feed material, and finally sintered to clinker at temperatures between 1400 and 1450 ºC. During this process the feed loses approximately one third of its original dry mass. The hot clinker is cooled by air to 100-200 ºC in a clinker cooler. The heated air is used as secondary combustion air in the kiln.

2.4.1 The dry process

For dry and semi-dry kiln systems, raw meal is prepared by drying and grinding of the raw material components in tube mills or vertical roller mills, making use of the hot kiln exhaust gases or cooler exhaust air for drying. Prior to being fed to the kiln, the raw meal is homogenised and/or blended either in batch type or in continuously operating homogenising silo systems.

In suspension preheater kilns, the raw meal is fed to the top of a series of cyclones passing down in stepwise counter-current flow with hot exhaust gases from the rotary kiln thus providing intimate contact and efficient heat exchange between solid particles and hot gas. The cyclones thereby serve as separators between solids and gas.

Prior to entering the rotary kiln, the raw meal is heated up to a temperature of approximately 810-830 °C where the calcination (i.e. the release of CO_2 from the carbonates) is already about 30 % complete. The exhaust gases leave the preheater at

a temperature of 300-360 °C and are further utilised for raw material drying in the raw mill. 4-stage preheater kilns are susceptible to blockages and build-ups caused by excessive input of elements such as sulfur, chlorides or alkalis which are easily volatilised in the kiln system. This input has to be carefully controlled. Excessive input may require the installation of a system which allows part of the rotary kiln gases to bypass the preheater. Thereby part of the volatile compounds are extracted together with the gas.

A bypass system extracts a portion (typically 5-15 %) of the kiln gases from the riser pipe between the kiln and preheater. This gas has a high dust burden. It is cooled with air, volatile compounds are condensed onto the particulates and the gas then passes through a dust filter.

Modern suspension preheater kilns usually have 4 cyclone stages with a maximum capacity limited to approximately 4000 ton pr day (t/d). In some cases, 2-stage cyclone preheaters or 1-stage preheaters supported by internal chain heat exchangers are still in operation.

A considerable capacity increase can be obtained with precalciner kilns with a second combustion device between the rotary kiln and the preheater section. In the precalciner, up to 60 % of the total fuel of the kiln system can be burnt. At an exit temperature of about 880 °C, the hot meal is calcined to a degree of around 90 % when entering the rotary kiln.

Kiln systems with 5 to 6 stage cyclone preheater and precalciner are considered standard technology for new plants today, as the extra cyclone stages improve thermal efficiency.

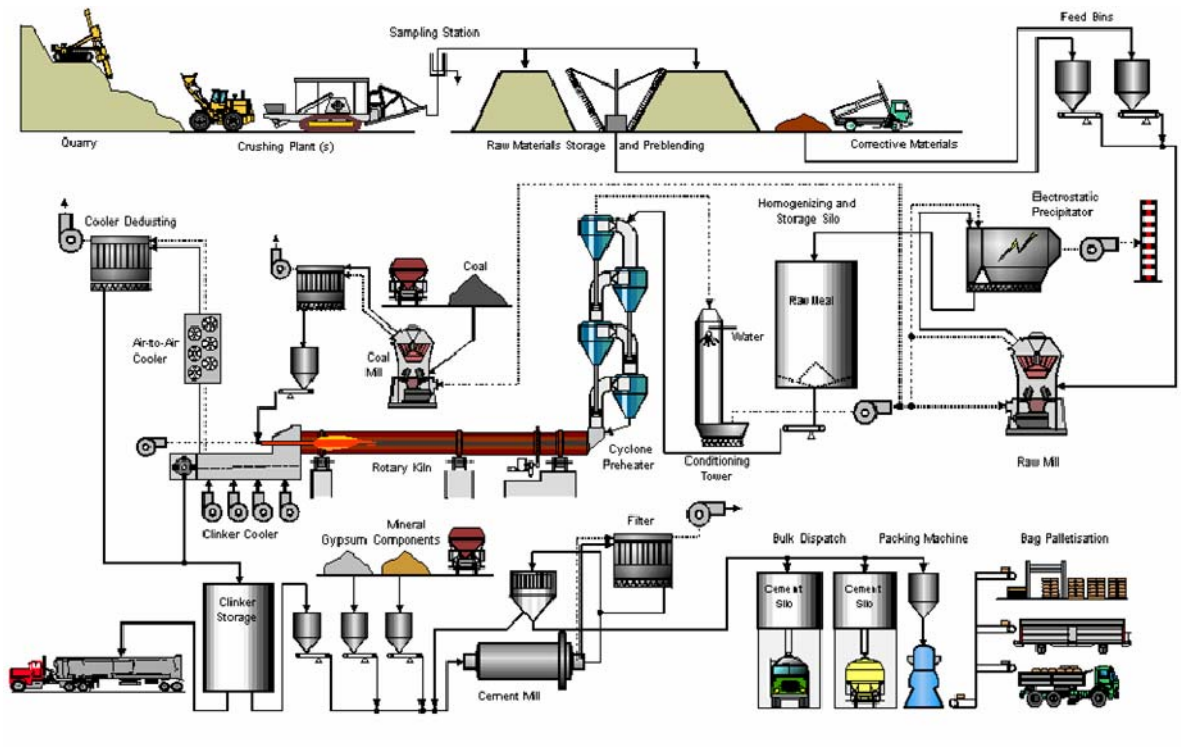

Figure 3. Production of cement by the dry process (CEMBUREAU, 1999)

In some cases, the raw meal is fed directly to a long dry kiln without external preheater. A system of chains in the inlet part of the rotary kiln provides the heat exchange between the hot combustion gases from the hot zone of the kiln and the kiln feed. Long dry kilns have high heat consumption and high dust cycles requiring separate dedusting cyclones.

2.4.2 The semi-dry process

In the semi-dry process, dry raw meal is pelletised with 10-12 % of water on an inclined rotating table ("granulating disc") and fed to a horizontal travelling grate preheater in front of the rotary kiln ("Lepol" system). The pelletised material is dried, pre-heated and partly calcined on the two-chamber travelling grate making use

of the hot exhaust gases from the kiln. A higher degree of calcination can be achieved by burning part of the fuel in the hot chamber of the grate preheater.

The hot exhaust gases from the kiln first pass through a layer of preheated pellets in the hot chamber. After intermediate dedusting in cyclones, the gases are drawn once again through a layer of moist pellets in the drying chamber of the grate. As much of the residual dust is precipitated on the moist pellet bed, the total dust load of the exhaust gases at the preheater outlet is low.

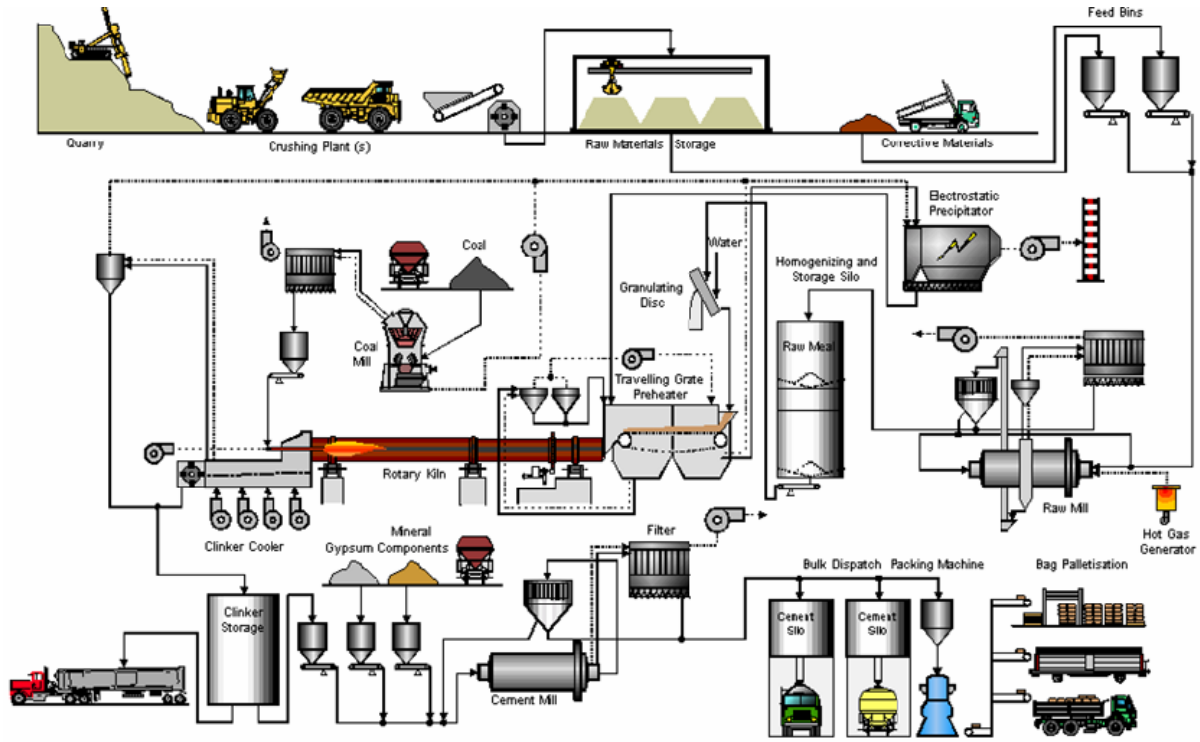

Figure 4. Production of cement by the semi-dry process (CEMBUREAU, 1999)

As a drawback of the semi-dry process, kiln exhaust gases cannot be utilised in the raw meal drying and grinding system due to the low temperature level. The maintenance costs of grate preheaters are high. Modern installations rarely use the semi-dry process.

2.4.3 The semi-wet process

In the semi-wet process the raw slurry is dewatered in filter presses. Typically, modern chamber filtration systems produce filter cakes with a residual moisture content of 16-21 %. In the past, filter cakes were further processed in extruders to form pellets which were then fed to grate preheater kilns with three chambers.

With modern cement plants, slurry filtration is applied only where raw materials have a very high natural moisture content, i.e. chalk. Filter cake coming from the filter presses is kept in intermediate storage bins before it is fed to heated crushers or dryers where a dry raw meal is produced which is fed to a modern preheater or precalciner kiln. With the dryers/crushers operating full time in parallel with the kiln (compound operation), these systems have a very good energy recovery by making full use of the kiln exhaust gases and the cooler exhaust air.

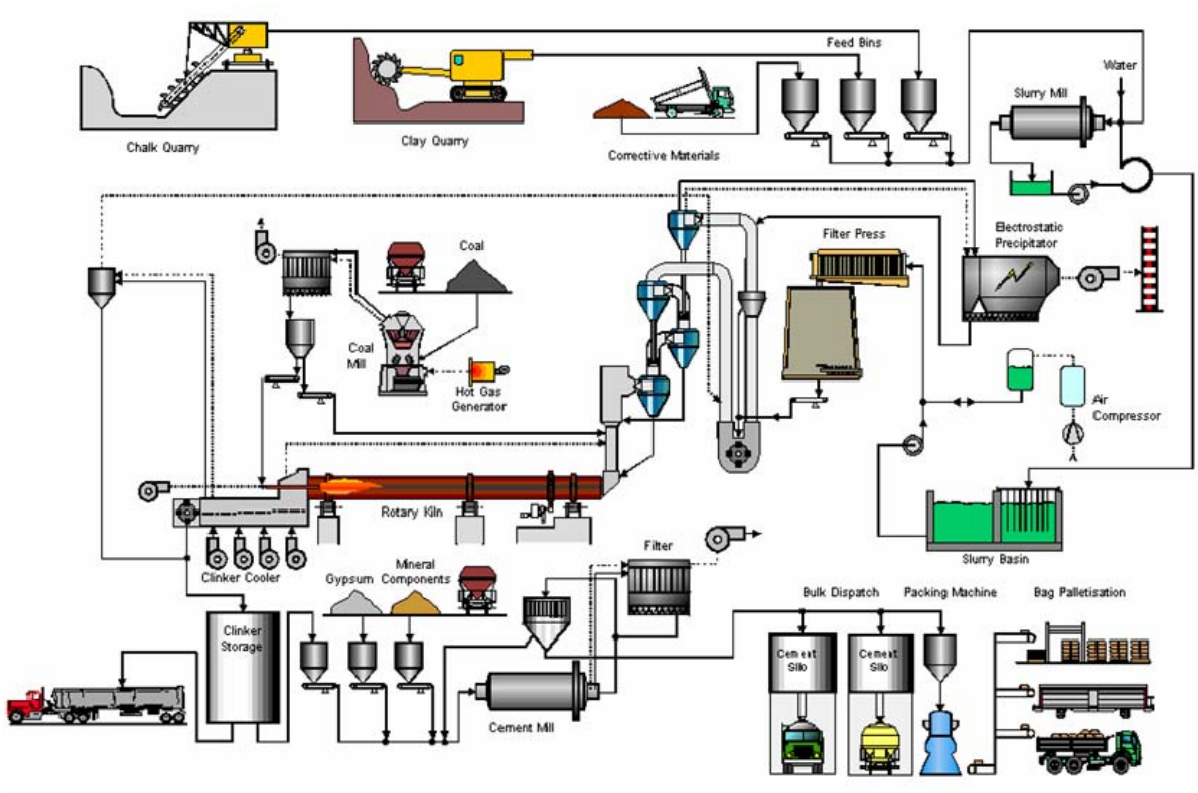

Figure 5. Production of cement by the semi-wet process (CEMBUREAU, 1999)

2.4.4 The wet process

Conventional wet process kilns are the oldest type of rotary kilns to produce clinker. Wet kiln feed (raw slurry) typically contains 28 to 43 % of water which is added to the raw mill (slurry drums, wash mills and/or tube mills). Batch blending and homogenisation is achieved in special slurry silos or slurry basins where compressed air is introduced and the slurry is continuously stirred.

The slurry is pumped into the rotary kiln where the water has to be evaporated in the drying zone at the kiln inlet. The drying zone is designed with chains and crosses to facilitate the heat exchange between the kiln feed and the combustion gases. After having passed the drying zone, the raw material moves down the kiln to be calcined and burnt to clinker in the sintering zone.

Conventional wet kiln technology has high heat consumption and produces large volumes of combustion gases and water vapour. Wet rotary kilns may reach a total length of up to 240 m compared to short dry kilns of 55 to 65 meter length (without the preheater section).

In modern wet kiln systems, the raw slurry is fed to slurry drier where the water is evaporated prior to the dried raw meal entering a cyclone preheater/precalciner kiln. Modern wet kiln systems have a far lower specific heat consumption compared to conventional wet kilns.

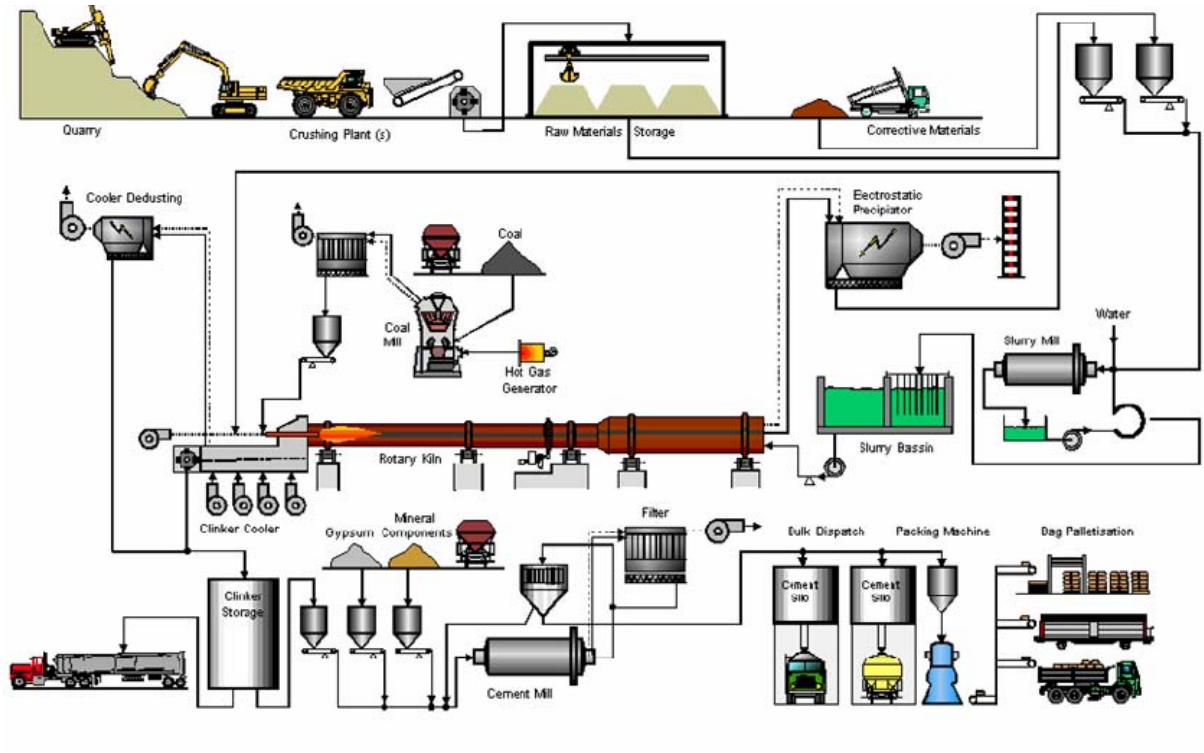

Figure 6. Production of cement by the wet process (CEMBUREAU, 1999)

2.4.5 Vertical shaft kilns

Shaft kilns consist of a refractory-lined, vertical cylinder 2-3 meter in diameter and 8-10 meter 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.

2.4.6 Operating characteristics - a summary

A summary of the operating characteristics of the four main process routes is given in the figure below.

Process Type	Dry			Semi - dry		Semi - wet		Wet	
Kiln Type Lepol = Travelling grate pre-heater kiln SP = Cyclone preheater kiln PC = Cyclone preheater / precalciner kiln	Long 1 stage SP 2 stage SP	4 stage SP	4 to 5 stage PC	Long	Lepol	Lepol (3 chambers)	3 and 4 stage SP and PC with dryer	Long	2 stage PC with dryer
Kiln characteristics: Feedstock	Dry raw meal			Pelletised raw meal		Filter cake		Slurry	
Kiln characteristics: Moisture content [%]	0.5 – 1.0			10 – 12		16 – 21		28 – 43	
Kiln characteristics: Heat exchange devices	Chains and cyclone preheater	Cyclone preheater	Cyclone preheater	Grooves	Travelling grate preheater	Travelling grate preheater	Cyclone preheater	Chain and cyclone	Cyclone preheater
Kiln characteristics: Kiln capacity [t/d]	300 – 3000	300 – 4000	2000 – 10000	300 – 1500	300 – 3000	300 – 3000	2000 – 9000	300 – 3000	2000 – 4000
Kiln characteristics: Spec. heat consumption [GJ/t]	3.6 – 4.5	3.1 – 3.5	3.0 – 3.2	3.5 – 3.9	3.2 – 3.6	3.6 – 4.5	3.4 – 3.6	5.0 – 7.5	4.5 – 5.0
Process characteristics: Spec. exh. gas quantity at system stack [Nm³/kg cl]	1.7 – 2.0	1.8 – 2.0 / 2.2 – 2.4 *	1.9 – 1.97 / 2.1 – 2.2 *	1.7 – 1.8	1.9 – 2.1	3.4 – 4.0	2.1 – 2.5	2.2 – 3.2	2.1 – 2.3
Process characteristics: O_2 content at system stack [% vol]	4 – 5	3 – 6 / 6 – 11 *	3 – 6 / 6 – 11 *	4 – 5	6 – 10	12 – 14	6 – 10	4 – 6	5 – 6
Process characteristics: Temperature at filter inlet (with FP dedusting) [°C]	100	150/100 *	150/100 *	200	100	100	120 – 150	100 – 220	130 – 150
Process characteristics: Dampen. [°C]	45 – 65			50 – 60		55 – 65		10 – 20	

*Direct operation / compound operation

Figure 7. Operating characteristics of kiln processes (CEMBUREAU, 1999)

2.5 Kiln exhaust gases

In all kiln systems, the exhaust gases are finally passed through an air pollution control device for separation of the dust before being released to the atmosphere via stacks. Today, two types of dust separators are commonly used in the cement industry, i.e. electrostatic precipitators and bag filters.

Bag filters have been used in the cement industry since well before the development of electrostatic precipitators. Bag filters make use of a fabric filter

system, the “bags” which separate the dust particles from the exhaust gas. The dust particles are captured on the bag surface while the gas passes through the bag tissue. Two main types of bag filters are used, i.e. the “reverse gas” filter and the “pulse jet” filter with the main difference being in the cleaning procedure. Bag filter performance is not susceptible to process disturbances or “CO peaks”.

Electrostatic precipitators use electrostatic forces to separate the dust from the exhaust gas. By means of discharge electrodes, the dust particles are negatively charged and can be separated on corresponding collecting electrodes. The particles are then discharged from the collecting electrodes to dust hoppers by electrode rapping. In contrast to bag filters, the design of electrostatic precipitators allows the separate collection of coarse and fine particles. ESP's are susceptible to process changes such as CO peaks. The dedusting efficiency can be increased by making use of more than one electric “field” operating in series.

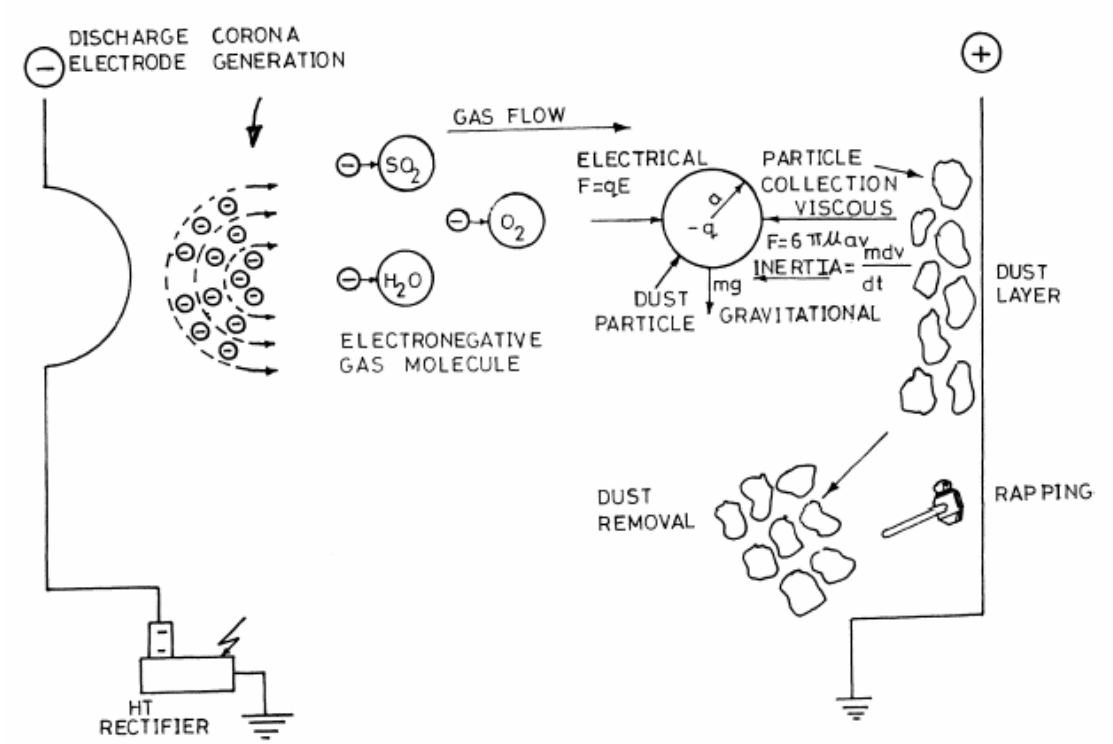

Figure 8 Principle of electrostatic precipitators

With a dedusting efficiency of up to 99.99 % in modern control devices, it is possible to achieve a dust emission level from the stack below 20 mg per cubic meter of gas.

In the dry process, the kiln exhaust gases have relatively high temperature and low humidity. Therefore, they can be utilised for drying of the raw materials in the raw mill during "compound operation", i.e. when the raw mill is in operation. During "direct operation" (with the raw mill off), the hot exhaust gases have to be cooled down by means of water injection in a conditioning tower to a temperature suitable to the dust collector. With this procedure the gas volume is reduced, too, and the precipitation characteristics of the dust in the filter system are improved.

The dust collected in the filter devices can be fed back to the process, either by reintroducing it to the raw materials preparation system (dry process), by insufflations into the sintering zone (wet kilns), or by feeding the dust to the cement mill (if allowed in the cement standards).

In certain cases where the level of alkali elements is limited in cement clinker ("low alkali" clinker), not all the kiln dust can be returned to the system. Whereas an electrostatic precipitator allows the high alkali part of the dust to be separated and rejected, such a separation cannot be achieved with a bag filter and all the dust would have to be rejected.

The other main sources of dust in the cement manufacturing process which require dedusting are the clinker cooler, the raw mill and the cement mills. Due to its low temperature, exhaust air from cement mills does not require cooling.

Depending on the process stage where it is extracted, the chemical and mineralogical composition of the dust corresponds respectively to that of the raw meal, the clinker or the cement, or their intermediate products.

2.6 Clinker coolers

Clinker leaving the rotary kiln at a temperature around 1200-1250 °C has to be cooled down rapidly to allow further transport and handling. This process also recovers heat from the clinker back to the kiln by preheating the air used for combustion in the main burner and in any secondary firing. In addition, rapid cooling prevents undesired chemical reactions in the clinker which may negatively affect the quality and the grindability of the clinker. Three main types of clinker coolers are used:

- Rotary (tube) coolers
- Planetary (satellite) coolers, and
- Grate coolers

Tube coolers placed underneath the kiln outlet make use of the same principle as the rotary kiln for clinker burning, but for reverse heat exchange with cooling air drawn through the tube in counter-current flow to the hot clinker. This cooler type is rarely used in the cement industry nowadays.

In a planetary (or satellite) cooler, 9 to 11 tubes are arranged peripherally at the discharge end of the rotary kiln. Hot clinker enters the tubes through inlet ports and passes through the tubes in cross counter-current to the cooling air. Due to their design, planetary coolers are susceptible to comparatively high wear and to thermal shock effects, and – similarly to tube coolers – clinker exit temperatures may still be high without additional cooling by water injection. Planetary coolers are not suited for precalciner kilns as exhaust air cannot be extracted for combustion in the secondary firing.

Grate coolers are preferably used in modern installations. Cooling is achieved by cross-flow air blown through a clinker layer travelling slowly on a reciprocating grate which consists of perforated plates. The whole cooling zone includes a

"recuperation zone" and an "aftercooling zone". From the recuperation zone, preheated air is recovered for combustion of the main burner fuel ("secondary air") and of the precalciner fuel ("tertiary air"). The hot air from the aftercooling zone can be used for drying of raw materials or coal. Grate coolers thus provide the most efficient and most flexible heat recovery system for modern dry process kilns.

2.7 Fuels preparation

The physical nature of the fuels used in a cement plant – solid, liquid or gaseous – determines the design of the storage, preparation and firing systems – both for conventional fossil fuels and for alternative fuels from industrial sources. The main fuel input has to be delivered in a form that allows uniform and reliable metering as well as easy and complete combustion. This is usually the case with all pulverised, liquid and gaseous fuels. A limited input (up to 35 %) may also be delivered by the addition of coarse materials at specific feed points.

Coal and petcoke are ground to fineness similar to raw meal in coal mills (tube mills, vertical roller mills or impact mills). For safety reasons, the whole coal preparation system is designed for protection from fire or explosion. The pulverised fuel may be fed directly to the burner (without intermediate storage and metering system) or – which is common practice today – may be stored in fine coal silos with adequate metering and feeding systems.

Fuel oil is stored in large tanks on site. Handling is facilitated by heating up the oil to a temperature of about 80 °C. Metering and combustion are facilitated by additional heating of the oil up to a temperature of 120-140 °C, resulting in a reduction of the viscosity.

Natural gas is delivered by national or international distribution systems without on- site storage. Prior to combustion in the kiln, the pressure of the gas has to be reduced to the plant's network pressure in gas transfer stations where also the fuel metering takes place.

Alternative fuels originating from industrial sources may require specific treatment. Gaseous, liquid and pulverised or fine crushed solid fuels can be fed to the kiln system similarly to the fossil fuels mentioned above. Coarsely shredded or even bulky materials can be fed to the preheater/precalciner section or, rarely, to the mid kiln section only. For process reasons, the contribution of bulky fuels to the total heat consumption should be limited to about 15 to 30 % depending on the kiln system.

Alternative fuels are frequently prepared and blended outside the cement plant by specialised companies in facilities specifically designed for this purpose. The cement plant has to provide the storage and feeding systems only on site. Alternative fuel plants are often designed as “multi-purpose plants” in order to handle a variety of different wastes.

2.8 Mineral additions preparation

Mineral additions used in the manufacture of blended cements require separate installations for storage, preblending, crushing, drying and feeding. Commonly used mineral additions include natural materials such as volcanic rocks, limestone or calcined clay, and materials originating from industrial sources such as granulated blast-furnace slag, pulverised fly ash from power stations, or micro silica.

Pre-drying may be required for materials with a high moisture content, for example, granulated blast-furnace slag. Rotary tube driers or flash driers make use of the kiln exhaust gases or cooler exhaust air or are operated with a separate hot gas source. Mineral additions may be interground with cement clinker and gypsum in a cement mill or may be ground separately and blended with Portland cement subsequently. Separate grinding and blending is mainly applied in the production of slag cements. For separate grinding of mineral additions, the same installations are used as in cement grinding.

2.9 Environmental significance of cement production

The main environmental impacts in the manufacture of cement are related to the following categories:

- Dust from stack emissions and fugitive sources;
- Gaseous atmospheric emissions of NO_x, SO_2, CO_2, VOC and others;
- Other emissions like noise and vibrations, odour, process water, production waste, etc.;
- Resources consumption of energy and raw materials.

2.9.1 Dust

Historically, the emission of dust – particularly from kiln stacks – has been the main environmental concern in cement manufacture. "Point source" dust emissions originate mainly from the raw mills, the kiln system, the clinker cooler, and the cement mills. A general feature of these process steps is that hot exhaust gas or exhaust air is passing through pulverised material resulting in an intimately dispersed mixture of gas and particulates. Primary reduction measures are therefore hardly available. The nature of the particulates generated is linked to the source material itself, i.e. raw materials (partly calcined), clinker or cement.

Dust emissions in the cement industry have been reduced considerably in the last 20 years, and state-of-the-art abatement techniques now available (electrostatic precipitators, bag filters) result in stack emissions which are insignificant in a modern and well managed cement plant.

Dust from dispersed sources in the plant area ("fugitive dust") may originate mainly from materials storage and handling, i.e. transport systems, stockpiles, crane driving, bagging, etc., and from traffic movement on unpaved roads. Techniques for control and containment of fugitive dust include dedusting of material transfer points, closed storage installations with proper ventilation, or vacuum cleaning equipment, etc.

As the chemical and mineralogical composition of dust in a cement plant is similar to that of natural rocks, it is commonly considered as a "nuisance" and not as a toxic product in applicable health and safety regulations. Reduction and control of dust emissions in a modern cement plant requires both investments and adequate management practices but is not a technical problem.

Kiln dust collected from the gas cleaning devices is highly alkaline and may contain trace elements such as heavy metals corresponding to the contents in the source materials. Usually, kiln dust is completely returned to the process – either to the kiln system or to the cement mill. In rare cases, it is not possible to recycle kiln dust or bypass dust completely in the process. This residual dust is disposed of on site (or in controlled landfills) or is treated and sold to other industries, i.e. as binder for waste stabilisation or even as fertiliser.

Heavy metals delivered by either conventional raw materials and fuels or by alternative raw materials and fuels from industrial sources will be mainly incorporated in clinker or – to a lesser extent – in kiln dust.

Bypass dust extracted from the kiln system may be highly enriched in alkalis, sulphates and chlorides and – similarly to filter dust – in some cases cannot be completely recycled to the process. For both types of dust, conditioning and safe disposal avoiding contamination of groundwater or soil is a site-specific requirement.

2.9.2 Gaseous atmospheric emissions

Gaseous emissions from the kiln system released to the atmosphere are the primary environmental concern in cement manufacture today. Major gaseous emissions are NO_x and SO_2. Other emissions of less significance are VOCs (volatile organic compounds), CO, ammonia, and heavy metals. CO_2 as the main greenhouse gas is released in considerable quantities.

Other gaseous emissions such as hydrochloric acid or hydrofluoric acid are nearly completely captured by the inherent and efficient alkaline scrubber effect of the cement kiln system.

Natural raw materials used for clinker production may contain volatile components in small quantities. These components will be volatilised and partly emitted under the conditions prevailing in the preheater section of a dry process cement kiln or in the drying/preheating zone of a long wet or long dry kiln, i.e. before entering the burning zone of the rotary kiln.

2.9.2.1 Nitrogen oxides

NO_x formation is an inevitable consequence of the high temperature combustion process, with a smaller contribution resulting from the chemical composition of the fuels and raw materials. Nitrogen oxides are formed by oxidation of molecular nitrogen in the combustion air ("thermal" NO_x is the sum of nitrogen oxides; in cement kiln exhaust gases, NO and NO_2 are dominant (> 90 % NO, < 10 % NO_2). Thermal NO_x formation is strongly dependent on the combustion temperature with a marked increase above 1400 °C. "Hard" burning required by certain raw mixes – i.e. at a higher temperature profile – increases NO_x formation.

While thermal NO_x is the dominant contribution to total NO_x generation, a smaller part may also result from nitrogen compounds contained in the fuels which are oxidised in the flame as well ("fuel NO_x"). In the main burner flame, the contribution of fuel NO_x is much lower than that of thermal NO_x.

In the secondary firing of a preheater/precalciner kiln with a flame temperature of not more than 1200 °C, the formation of thermal NO_x is much lower compared to the main burner flame. Therefore, in precalciner kilns where up to 60 % of the total fuel can be burnt in the calciner flame, fuel NO_x may be a higher proportion of the reduced total NO_x emissions.

Natural raw materials such as clays or shale's may also contain nitrogen compounds. Part of these compounds may be released and oxidised upon heating in the kiln system and may thus in certain cases considerably contribute to the total NO_x emissions.

NO_x formation is reduced if fuel is burnt in a more "reducing" atmosphere with low oxygen content. Operation under reducing conditions is limited due to process requirements in order to maintain good clinker quality and undisturbed kiln operation. NO_x emissions in cement kilns (expressed as NO_2) typically vary between 500 and 2000 mg/m^3.

2.9.2.2 Sulfur oxides

Sulfur compounds enter the kiln system either with the fuels or with the raw materials. Sulfur compounds in raw materials are present mainly as sulphates (for example, calcium sulphate $CaSO_4$) or as sulphides (i.e. pyrite or marcasite FeS_2).

Sulphates in the raw materials are thermally stable up to temperatures of 1200 °C, and will thus enter the sintering zone of the rotary kiln where they are decomposed to produce SO_2. Part of the SO_2 combines with alkalis and is incorporated into the clinker structure. The remaining part of SO_2 is carried back to

the cooler zones of the kiln system where it reacts either with calcined calcium oxide or with calcium carbonate thus being reintroduced to the sintering zone again ("chemical SO_2 absorption").

Inorganic and organic sulfur compounds introduced with the fuels will be subject to the same internal cycle consisting of thermal decomposition, oxidation to SO_2 and reaction with alkalis or with calcium oxide. With this closed internal cycle, all the sulfur which is introduced via fuels or via raw material sulphates will leave the kiln chemically incorporated in clinker, and will not give rise to gaseous SO_2 emissions.

Sulphides (and also organic sulfur compounds) in raw materials however, are decomposed and oxidised at moderate temperatures of 400 to 600 °C to produce SO_2 when the raw materials are heated by the exhaust gases. At these temperatures, not enough calcium oxide is available to react with the SO_2. Therefore, in a dry preheater kiln about 30 % of the total sulphide input may leave the preheater section as gaseous SO_2. During direct operation – i.e. with the raw mill off – most of it is emitted to the atmosphere. During compound operation – i.e. with the raw mill on-line – typically between 30 and 90 % of that remaining SO_2 is additionally adsorbed to the freshly ground raw meal particles in the raw mill ("physico-chemical absorption").

In grate preheater kilns SO_2 absorption is also good because the gas is passing through the turbulent flow of material from grate to kiln and then passing at low velocities firstly through the bed of material which is partly calcined and then through the moist calcium carbonate in the drying chamber.

In long dry and long wet kilns, the chemical absorption capacity for SO_2 is generally less efficient due to the reduced contact between kiln exhaust gas and raw materials. In these kiln systems, all kinds of sulfur input may partially contribute to SO_2 emissions, and the general emission level may be higher than in dry preheater kilns.

Gaseous emissions such as SO_2 or VOC are to a large extent determined by the chemical characteristics of the raw materials used, and not by the fuel composition. Emissions are lowest with raw materials low in volatile components.

2.9.2.3 Carbon dioxide

Carbon dioxide emissions arise from the calcination of the raw materials and from the combustion of fossil fuels. CO_2 resulting from calcination can be influenced to a very limited extent only. Emissions of CO_2 resulting from fuel combustion have been progressively reduced due to the strong economic incentive for the cement industry to minimise fuel energy consumption.

CO_2 reduction of some 30 % in the last 25 years – arising mainly from the adoption of more fuel efficient kiln processes – leaves little scope for further improvement. Potential is mainly left to the increased utilisation of renewable alternative fuels or other waste derived fuels and to the production of blended cements with mineral additions substituting clinker.

2.9.2.4 Organic compounds

Natural raw materials such as limestone's, marls and shale's may also contain up to 0.8 % w/w of organic matter ("kerogene") – depending on the geological conditions of the deposit. A large part of this organic matter may be volatilised in the kiln system even at moderate temperatures between 400 and 600 °C.

Kiln tests with raw meals of different origin have demonstrated that approximately 85 to 95 % of the organic matter in the raw materials are converted to CO_2 in the presence of 3 % excess oxygen in the kiln exhaust gas, and 5 to 15 % are oxidised to CO. A small proportion – usually less than 1 % – of the total organic

carbon ("TOC") content may be emitted as volatile organic compounds ("VOC") such as hydrocarbons.

The emission level of VOC in the stack gas of cement kilns is usually between 10 and 100 mg/Nm^3, with a few excessive cases up to 500 mg/Nm^3. The CO concentration in the clean gas can be as high as 1000 mg/Nm^3, even exceeding 2000 mg/Nm^3 in some cases.

The carbon monoxide and hydrocarbon contents measured in the stack gas of cement kiln systems are essentially determined by the content of organic matter in the raw materials, and are therefore not an indicator of incomplete combustion of conventional or alternative fuels.

Organic matter introduced to the main burner and to the secondary firing will be completely destroyed due to the high temperatures and the long retention time of the combustion gases.

2.9.2.5 Trace elements

During the clinker burning process, all mineral input delivered by the raw materials – be it natural or alternative raw materials sources – is converted into the clinker phases at the high temperatures prevailing in the sintering zone of the rotary kiln. Combustion ashes from conventional and alternative fuels are also completely incorporated into the clinker minerals. Therefore cement kiln systems do not generate combustion ashes which require separate disposal.

Consequently, the fuel ashes substitute for part of the (natural) raw materials input. In order to maintain a good clinker quality, the ash composition of the fuels has to be taken into account in the raw mix design. Trace elements such as heavy metals are naturally present in low concentrations in the raw materials and fuels used for the manufacture of cement clinker. The behaviour of these metals in the burning process depends largely on their volatility.

- Non-volatile metals remain completely within the product and leave the kiln system fully incorporated in the mineral structure of the clinker – similarly to the main elements. Most of the common metals are non-volatile.

- Semi-volatile elements such as cadmium or lead may in part be volatilised with the high temperature conditions in the sintering zone of the kiln system. They condense on the raw materials in cooler parts of the kiln system and are reintroduced to the hot zone again. A major part of cadmium and lead will be incorporated in clinker; the remaining part will precipitate with the kiln dust and will be collected in the filter systems.

- Volatile metals such as mercury and thallium are more easily volatilised and condense on raw material particles at lower temperatures in the kiln system (thallium at approximately 300-350 °C, mercury at 120-150 °C). Whereas thallium is nearly completely precipitated onto the kiln dust particles, only part of the mercury will be collected within the filter system. Volatile metals are retained in the clinker minerals to a very small extent only.

Being the only metal which can be emitted with the clean gas in gaseous form, the input of mercury with raw materials and fuels has to be carefully controlled.

2.9.3 Normal emission levels

Average emission data (long term average values) from European cement kilns in operation are summarised in the table below.

Table 1 Long term average emission values from European cement kilns (CEMBUREAU, 1999)

Emission	mg per standard cubic meter [mg/Nm^3]
Dust	20 – 200
NO_x	500 – 2,000
SO_2	10 – 2,500
Total organic carbon (TOC)	10 – 100
CO	500 – 2,000
Fluorides	< 5
Chlorides	< 25
PCDD/F	< 0.1 [ng/Nm3]
Heavy metals:	
- class 1 (Hg, Cd, Tl)	< 0.1
- class 2 (As, Co, Ni, Se, Te)	< 0.1
- class 3 (Sb, Pb, Cr, Cu, Mn, V, Sn) incl. Zn	< 0.3

The figures given above are representative of the ranges within which kilns normally operate. Due to the age and design of the plant, the nature of the raw materials, etc., individual kilns may operate outside these ranges.

2.9.4 Other emissions

Heavy machinery and large fans used in the cement manufacture may give rise to emissions of noise and vibrations.

Odour emissions are seldom a problem with a well operated plant, but may be mainly related to emissions from handling and storage of conventional or alternative fuels. In exceptional cases, nitrogen compounds in the raw materials may lead to ammonia emissions which – even at low concentrations – may give rise to odour.

Process water in cement manufacturing will usually be completely evaporated or recycled in the process. Filtrate water from filter presses used in the semi-wet process is fairly alkaline and contains suspended solids requiring site-specific treatment and/or disposal options.

Emergencies such as fire, explosions or spillage/leakage are extremely rare in the cement industry. Potential consequences for the environment are minimised by adequate prevention and protection measures such as fire and explosion proof design of machinery and emergency response schemes.

2.9.5 Circulating elements

Volatile components such as alkalis, sulfur and chlorine introduced with raw materials and fuels may give rise to problems in kiln operation when present in high concentrations. Build-up formation in the preheater cyclones or rings in the rotary kiln inlet zone may lead to reduced kiln availability and productivity. Thus, the input of these volatile components is carefully controlled for operational and economic reasons. Input control is also required to achieve and maintain the required quality of clinker and cement.

Depending on their volatility, alkalis, sulfur and chlorides evaporate in the sintering zone of the rotary kiln and recondense at cooler parts of the system either on the raw meal particles or on the surrounding walls. With the raw meal, they are reintroduced to the sintering zone again thus establishing a permanent "internal cycle" of volatile “circulating” elements. By reaching equilibrium between input and output, a major part of the volatile components will finally leave the system incorporated in the clinker.

Part of the volatile components however, may form new compounds such as alkali chlorides or alkali sulphates and other intermediate phases such as spurrite which will then contribute to the build-up phenomena mentioned above by producing

a “sticky” raw meal adhesive to the walls of the cyclones, the ducts or the kiln tube. A small part only of the circulating elements leaves the kiln with the exhaust gas dust and is precipitated in the dedusting device of the system.

With excessive input of volatile elements, the installation of a kiln gas bypass system may become necessary in order to extract part of the circulating elements from the kiln system. This bypass dust which is usually highly enriched in alkalis, sulfur or chlorides is cooled down and then passed through a dust collector before being discharged.

2.9.6 Inherent "scrubbing" of exit gases

In all kiln systems, the finely ground raw material moves in counter-current flow to the hot combustion gases. Thus, it acts perfectly as an integrated multi-stage exhaust gas cleaning system very similar to the operating principle of a circulating fluidised bed absorber. Components resulting from the combustion of the fuels or from the transformation of the raw materials remain in the exhaust gas only until they are absorbed by the fresh raw meal flowing in counter-current.

Wet kilns and long dry kilns provide intimate contact between gas and solid particles mainly at the kiln inlet with its chain system for heat exchange. Semi-dry and semi- wet kilns provide this “scrubber effect” mainly in the grate preheater section of the kiln system, and also in heated crushers or dryers when these are used.

Suspension preheater kilns with 4 to 6 cyclone stages are especially well suited to achieve a “multi-stage” scrubber effect especially when operating together with the raw mill (compound operation). At least 5 scrubber stages operate in series at different temperature levels between 100 and 800 °C consuming roughly 1 kg of absorbent (i.e. raw meal/hot meal) per Nm^3 of exhaust gas.

The raw meal with its large specific surface and its high alkalinity provides an excellent medium to retain gas components within the kiln system. For instance,

calcined or partly calcined raw meal with its high content of reactive calcium oxide has a high absorption capacity for acid gases such as sulfur dioxide and hydrochloric or hydrofluoric acid, but also for other pollutants such as heavy metals.

2.9.7 Resources consumption

Cement manufacturing is a "high volume process" and correspondingly requires adequate quantities of resources, i.e. raw materials, thermal fuels and electrical power.

A "medium-sized" plant with a clinker production of 3000 tons per day or 1 million tons per year corresponds to a cement production of 1.23 million tons per year (based on average figures for the clinker content in cement in Europe).

Cement manufacturing is also an energy intensive process. The specific thermal energy consumption of a cement kiln varies between 3000 and 7500 MJ per ton of clinker, depending on the basic process design of the plant.

Major consumers of electrical energy in the cement manufacturing process are the mills (cement mills, raw mills, coal mills) and the large fans (predominantly in the kiln system and with the cement mills). The specific electrical energy consumption ranges typically between 90 and 130 kWh per ton of cement.

Improvements continue with regard to equipment design and process technology to further improve the overall energy efficiency. In addition, conservation of natural resources can be achieved through increased substitution of natural raw materials and fossil fuels by industrial by-products and residues in the manufacturing process.

2.10 Characteristics of the cement production process - a summary

In the burning of cement clinker it is necessary to maintain material temperatures of up to 1450 °C in order to ensure the sintering reactions required. This is achieved by applying peak combustion temperatures of about 2000 °C with the main burner flame. The combustion gases from the main burner remain at a temperature above 1200 °C for at least 5-10 seconds.

An excess of oxygen – typically 2-3 % – is also required in the combustion gases of the rotary kiln as the clinker needs to be burned under oxidising conditions. These conditions are essential for the formation of the clinker phases and the quality of the finished cement.

The retention time of the kiln charge in the rotary kiln is 20-30 and up to 60 minutes depending on the length of the kiln. The figure below illustrates the temperature profiles for the combustion gases and the material for a preheater/precalciner rotary kiln system. While the temperature profiles may be different for the various kiln types, the peak gas and material temperatures described above have to be maintained in any case.

The burning conditions in kilns with precalciner firing depend on the precalciner design. Gas temperatures from a precalciner burner are typically around 1100 °C, and the gas retention time in the precalciner is approximately 3 seconds.

Under the conditions prevailing in a cement kiln – i.e. flame temperatures of up to 2000 °C, material temperatures of up to 1450 °C and gas retention times of up to 10 seconds at temperatures between 1200 and 2000 °C – all kinds of organic compounds fed to the main burner with the fuels are reliably destroyed.

The combustion process in the main flame of the rotary kiln is therefore complete. No (hydrocarbon type) products of incomplete combustion can be identified in the combustion gases of the main burner at steady-state conditions.

The cement manufacturing process is an industrial process where large material volumes are turned into commercial products, i.e. clinker and cement. Cement kilns operate continuously all through the year – 24 hours a day – with only minor interruptions for maintenance and repair.

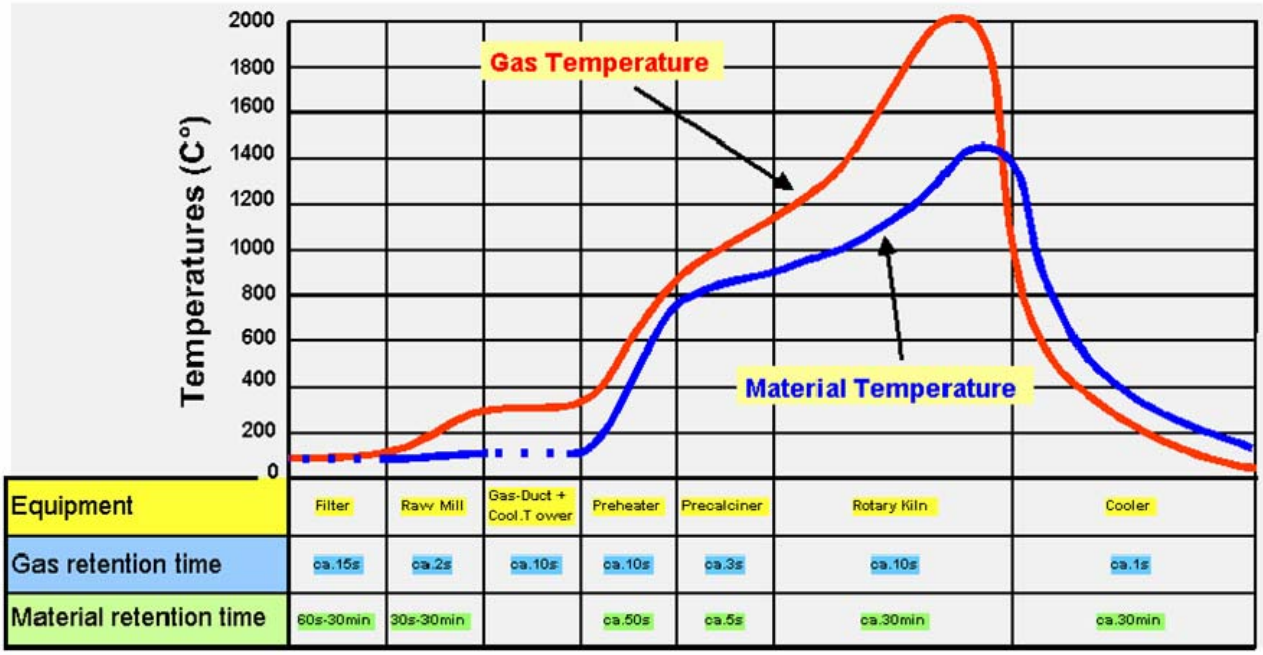

Figure 9. Gas and material profiles in cyclone preheater/precalciner system in compound operation (CEMBUREAU, 1999)

A smooth kiln operation is necessary in a cement plant in order to meet production targets and to meet the quality requirements of the products. Consequently, to achieve these goals, all relevant process parameters are permanently monitored and recorded including the analytical control of all raw materials, fuels, intermediate and finished products as well as environmental monitoring.

With these prerequisites – i.e. large material flow, continuous operation and comprehensive process and product control, the cement manufacturing process seems to be well suited for co-processing by-products and residues from industrial sources, both as raw materials and fuels substitutes and as mineral additions.

The selection of appropriate feed points is essential for environmentally sound co- processing of alternative materials, i.e.:

- Raw materials: mineral waste free of organic compounds can be added to the raw meal or raw slurry preparation system. Mineral wastes containing significantly quantities of organic components are introduced via the solid fuels handling system, i.e. directly to the main burner, to the secondary firing or, rarely, to the calcining zone of a long wet kiln ("mid-kiln").

- Fuels: alternative fuels are fed to the main burner, to the secondary firing in the preheater/precalciner section, or to the mid-kiln zone of a long wet kiln.

- Mineral additions: mineral additions such as granulated blast furnace slag, fly ash from thermal power plants or industrial gypsum are fed to the cement mill. In Europe, the type of mineral additions permitted is regulated by the cement standards.

In addition to regulatory requirements, the cement producers have set up self-limitations such as

- To prevent potential abuse of the cement kiln system in waste recovery operations

- To assure the required product quality

- To protect the manufacturing process from operational problems

- To avoid negative impacts to the environment, and

- To ensure workers' health and safety.

The cement manufacturing process is a large materials throughput process with continuous operation and comprehensive operational control. Therefore, it has a large potential for co-processing a variety of materials from industrial sources.

2.11 Cement production in developing countries

Cement plants in developing countries are usually perceived to be of older and polluting technologies only. This is however not entirely true. 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 often impose their internal standards on business ethics, labour rights, corporate responsibility, health, safety and environment. When these companies build new plants in any country, usually the best available techniques (BAT) applies. This is also the most economically 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.

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

Wastes and hazardous wastes in the environment represent a challenge for many countries, but cement kiln co-processing can constitute a sound and affordable recovery option. Cement kilns can destroy organic hazardous wastes in a safe and sound manner when properly operated and will be mutually beneficial to both industry, which generates such wastes, and to the society who want to dispose properly of such wastes in a safe and 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 material temperature at approximately 1450 ^{o}C and kiln gas temperatures up to 2000 ^{o}C, long residence time up to 8 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 1000 ^{o}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 1200 ^{o}C and 2 sec residence time.

In order to co-process organic hazardous wastes in cement kilns properly, it is important to know and control the parameters given in Table 6.

Table 2 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 AFR use in the cement industry

Since the early 1970s, and particularly since the mid 1980s, alternative – i.e. non-fossil – raw materials and fuels derived mainly from industrial sources have been beneficially utilised in the cement industry for economic reasons. Since that time, it has been demonstrated both in daily operations and in numerous tests that the overall environmental performance of a cement plant is not impaired by this practice in an appropriately managed plant operation.

Cement kilns make full use of both the calorific and the mineral content of alternative materials. Fossil fuels such as coal or crude oil are substituted by combustible materials which otherwise would often be landfilled or incinerated in specialised facilities.

The mineral part of alternative fuels (ashes) as well as non-combustible industrial residues or by-products can substitute for part of the natural raw materials (limestone's, clay, etc.). All components are effectively incorporated into the product, and – with few exceptions – no residues are left for disposal. The use of mineral additions from industrial sources substituting clinker saves both raw material resources and energy resources as the energy intensive clinker production can be reduced.

With the substitution of fossil fuels by (renewable) alternative fuels, the overall output of thermal CO_2 is reduced. A thermal substitution rate of 40 % in a cement plant with an annual production of 1 million tons of clinker reduces the net CO_2 generation by about 100,000 tons. Substitution of clinker by mineral additions may be more important as both thermal CO_2 from fossil fuels and CO_2 from the decarbonation of raw materials is reduced.

Since only moderate investments are needed, cement plants can recover adequate wastes at lower costs than would be required for landfilling or treatment in

specialised incinerators. In addition, public investment required for the installation of new specialised incinerators would also be reduced.

Substitute materials derived from waste streams usually reduce the production cost in cement manufacturing, thus strengthening the position of the industry particularly with regard to imports from countries with less stringent environmental legislation. It will also facilitate the industry's development of technologies to further clean up atmospheric emissions.

3.3 Co-processing of hazardous wastes

Cement kilns have utilised hazardous wastes for energy replacement since the early 1970s. However, such practice imposes strict permit requirements. In Europe, cement kilns utilising hazardous 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 National Emission Standards for Hazardous Air Pollutants (Federal Register, 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 % can be 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.

3.3.1 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 has to be determined. In other words, what happens to the components in the combustion process?

3.3.2 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 sulfur, 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 should not be 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 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).

3.3.3 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 was considered to be 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).

3.3.4 Results from trial burns conducted in the 1980s

Trial burns conducted in the 1980s continued to demonstrate that high DREs 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 DREs. 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 3 Average DREs 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 %

3.3.5 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 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 kiln inlet (i.e. cool end) of the kiln along with tyres. DREs obtained were greater than 99.999 % for carbon tetrachloride and greater than 99.996 % for trichlorobenzene.

DRE testing conducted at a cement kiln owned by United Cement supports the foregoing results. Sulfur 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.

3.3.6 Results from newer trial burns

In 1999 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 carried out in Vietnam in 2003. The DRE for the introduced insecticides was >99.99999 %.

3.3.7 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 once widely used but were

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 in several countries. Since PCBs are such thermally 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. However, the majority of cement kilns burning hazardous waste as fuel have chosen not to burn PCB wastes for the reasons of perception and possible bad publicity.

3.3.8 Trial burns – a summary

Earlier data which indicated cement kiln DRE results below 99.99 % are most probably either from outdated sources or improperly designed tests, or both. In the early years of development of this concept 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. 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 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 caution.

In some cases however, 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 possible to avoid today. Trial burn 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 very crucial.

4. Regulatory framework

Regulation of POPs emissions from cement kilns has mainly been confined to PCDD/F emissions and developed first of all in countries like the European Union (EU) and the United States of America (US). In many developing countries regulation and adequate legislation is not yet in place, were it is enforcement is weak or lacking. 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). The EC requested the European Committee for Standardization (CEN) to prepare well-validated and harmonized European Standard (EN 1948) to monitor several pollutants; special attention was paid to PCDD/Fs. The directive entered into force in December 1994 and 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 the end of 1996. In the directive a PCDD/F limit value of 0.1 ng TEQ/m³ was set as an average value measured over the sample period of a minimum of six hours and a maximum of eight hours. Apart from the emission limit value of 0.1 ng TEQ/m^3, the following restrictions were also valid:

- Even under the most unfavourable conditions a temperature of > 850 °C has to be maintained for at least two seconds to destroy PCDD/Fs and to avoid precursors. 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 PCDD/Fs 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 twelve 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, 10 % 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 TEQ/m³), $C_{process}$ 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.

- Any member state of the EU is allowed to maintain or introduce more stringent measures for the protection of the environment.

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 in cement kilns; the existing two Directives on waste and waste incineration shall be repealed 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 as well as the following important amendments:

- 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 TEQ/m^3.

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

- EC shall decide, as soon as appropriate measurement techniques are available, the date from which 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 twelve 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 TEQ/l. The measurements shall not exceed the limit value.

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

In all EU Directives the principles of integrated pollution prevention and control (IPPC), specifically laid down in Directive 96/61/EC, covering all aspects of environmental performance in an integrated manner, shall be taken into account. Also Best Available Technique Reference Documents (BREFs) established by the European IPPC Bureau have to be taken into account by the authorities for issuing permits.

Also the Protocol on persistent organic pollutants signed by the EU within the framework of the United Nations Economic Commission for Europe (UN-ECE) Convention on long-range transboundary air pollutions sets a legally binding PCDD/F

emission limit value of 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 ton per hour of medical waste, and 0.2 ng TEQ/m^3 for installations incinerating more than 1 ton 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 EU under the so-called Air Framework Directive 84/360/EEC (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 or substitute fuels. The European cement industry has argued that prescriptive regulations designed to ensure combustion 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 sulfur dioxide are set according to the sulfur 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 IPPC, 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 EU environmental quality standards to be breached.

Notwithstanding the derogations on emissions of substances such as sulfur dioxide and carbon monoxide, the cement industry has accepted the emission standard for dioxins of 0.1 ng TEQ/m^3 generally applied throughout EU 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.

4.1.2 Sampling and analysis

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

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 10 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.

II1. 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.

II1.1. C — total emission limit values

Pollutant	C
Total dust	30
HCl	10
HF	1
NO_2 for existing plants	800
NO_2 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_2 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_2 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_2 of not more than 1200 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.

II1.2. 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.

II1.3. Emission limit value for CO

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

Figure 11 Special provisions for cement kilns co-incinerating waste given in the EU Directive 2000/76/EC.

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.

The EN 1948 also requires the gas to be sampled iso-kinetically in the duct. The PCDD/Fs both adsorbed on particles and in the gas phase, is 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 German VDI Dilution Method 3499, an option in EN 1948, 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 ^{o}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 are 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, the accuracy of the sampling method it not possible to determine (EN 1948, 1996).

4.1.2.1 Development and validation of the EN-1948

At the end of the 1980s 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. the German VDI Dilution Method 3499, were partly validated for monitoring limit values of 0.1 ng TEQ/m^3. CEN started therefore to develop a European Standard with reliable performance characteristics.

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 (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 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. Due to discrepancies a third field test at a municipal waste incinerator followed and 19 laboratories in 11 European countries were involved. One of the challenges was to find an incineration plants with PCDD/F emissions as near 0.1 ng TEQ/m³ as possible. If the concentrations were above 0.1 ng TEQ/m³, EC would not accept them because they were out of the monitoring concentration range. Also, the PCDD/F concentration in the cross section of the duct had to be identical; otherwise the six sampling trains (two duplicate measurements by each of the three sampling teams) would collect different PCDD/F concentrations. 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. Iso-kinetic sampling had to be applied and minimum resolution of the MS had to be fixed. And last but not least, at that time, some laboratories were not well trained for this concentration range.

The 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 has been accepted by all EU and EFTA states.

4.1.2.2 Analysis and recovery

PCDD/F analysis is usually 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.

4.1.3 Detection/quantification limits and interferences

The Lower Detection Limit (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 0.035 ng I-TEQ/m^3. Taking into account the toxic equivalence factors for the individual congeners the resulting over all detection limits varies between 0.001 and 0.004 ng I-TEQ/m^3. It's

reasonable to assume that concentrations lower than 0.001 ng I-TEQ/m^3 should be considered as being below the detection limit.

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).

4.1.4 HCB and PCBs

Hexachlorobenzene and PCBs are for the time being not required to be monitored on a routine basis in cement plant emissions in the EU or the US.

4.2 PCDD/F emission standards in the US

Under the authority of the Clean Air Act, EPA promulgated national emission standards for new and existing cement kilns burning non-hazardous waste in May 1999 (Federal Register, 1999a; 2004). The regulations are specific to the I-TEQ concentration in the combustion gases leaving the stack. Existing and new cement kilns either combusting or not combusting hazardous waste as auxiliary fuel cannot emit more than 0.2 ng I-TEQ/m^3 (corrected to 25 ^{0}C, 7 % O_2 and dry gas). In addition, the temperature of the combustion gases measured at the inlet to the air pollution control device cannot exceed 232 °C. The rule requires owners or operators of facilities to test for PCDD/Fs every 2½ years and the Office of Air Quality Planning and Standards (OAQPS) expects this rule to reduce I-TEQ PCDD/Fs emissions from existing and new facilities by 36 % over the next few years (Federal Register, 1999a and 2004).

Most air pollution control devices (APCDs) used at cement kilns in the US between 1987 and 1995 were considered to be hot-sided control devices. A hot-sided control device is one that operates at kiln exhaust gas temperatures above 232 °C (some EPA rules use different definitions for hot-sided control devices for different industries). Most APCDs currently used at cement kilns are cold-sided devices (i.e., they operate at kiln exhaust gas temperatures below 232 °C.

The US regulation 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. 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.

EPA is currently developing CKD storage and disposal requirements. In 1999, a proposed rule for the standards for the management of CKD was developed by EPA (Federal Register, 1999b). Under the rule, CKD would remain a non-hazardous waste, provided that proposed management standards are met, which would protect groundwater and control releases of fugitive dust. Additionally, the rule proposes

concentration limits on various pollutants in CKD used for agricultural purposes (Federal Register, 1999c).

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.

5. Formation of PCDD/F

Most of the research done on formation mechanisms is from studies of municipal solid waste incinerators or theoretical laboratory studies. Formation of PCDD/F involves many complex reactions and a complete understanding of the reaction chemistry is not yet established.

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 1970s 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 are traces of PCDD/Fs in the fuel or raw materials, trace amounts can survive and be emitted;

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 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 decompose rapidly at temperatures above 925 °C (Schaub and Tsang, 1983). In cement kilns, the gas phase temperature in the burner zones will be up to 2000 °C, which will ensure that any traces of PCDD/Fs in the fuel fed through burners will be completely destroyed.

Theory (2a) is also believed to play a relatively minor role in the PCDD/F emissions from combustion facilities. Kinetic models have 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 °C 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. Theory (2b) can be distinguished from (3) by reactions involving gas-phase chloroaromatic precursors which might already be present in the fuel, or which could be formed as products of incomplete combustion (Dickson et al, 1992;

Karasek and Dickson, 1987; Dickson and Karasek, 1987). Theory (3) does not require that chloroaromatics precursors be present on fly ash or in the gas stream. Instead, both the chloroaromatics 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 (Stieglitz 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. Dickson postulated the following (Altwicker et al, 1990a):

> "*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 the 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 aromatic PCDD/F precursors through substitution reactions. Chlorination of phenol has 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)

$2\ HCl + ½\ O_2 \Longleftrightarrow Cl_2 + H_2O$, with copper or others metals serving as catalyst.

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). Based upon testing with nine different metals and oxidation states, divalent copper appears 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.

Sulfur 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 conducive to PCDD/F formation. The sulfur/chlorine ratio 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 suggested that sulfur may interfere with PCDD/F formation by 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)

$Cl_2 + SO_2 + H_2O \Longleftrightarrow 2HCl + SO_3$ and:

Equation 3)

$CuO + SO_2 + ½\ O_2 \Longleftrightarrow CuSO_4$

From this background, it is clear that PCDD/F formation involves many complex reactions which are not yet understood in detail. 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 particulates, which allow solid-catalyzed reactions, (2) post-furnace particulate residence time in the critical temperature window (approximately 200 °C to 450 °C), (3) presence of Cl and organic precursors, including chloro-aromatics, and (4) a shortage of formation inhibitors, such as sulfur.

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.

5.2 Possible formation mechanisms in Cement Kilns

The Stockholm Convention is explicitly mentioning cement kilns firing hazardous waste as a fuel substitute as a potential source category for the formation and release of PCDD/Fs. 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 ng TEQ/m^3 to nearly 50 ng TEQ/m^3 (Chadbourne, 1997). 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 (Chadbourne, 1997).

5.2.1 Effect of operating variables and the APCD temperature

The most detailed studies examining the influence of cement kiln design and operating conditions during the combustion of hazardous waste have been undertaken

by the 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. No correlation between the PCDD/F emissions and the following parameters could be found for the same type of ESPs:

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

Not enough data exist to compare the effect of different types of APCDs on the PCDD/F emissions. One positive correlation identified both in US and German studies were that between PCDD/F emission concentration and ESP/stack temperature, at high temperatures. The dioxin emissions were highest at 400 ^{o}C, and decreased 50-fold at 255 ^{o}C. This correlation was generally observed across all facilities tested (Schreiber, 1993). At temperatures lower than 250 ^{o}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.

Data presented in numerous other 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 °C to 450 ^{o}C). Most APCDs used at cement kilns in the US between 1987 and 1995 were considered to be hot-sided control devices, one that operates at kiln exhaust gas temperatures above 232 °C. Most APCDs currently used at cement kilns in the US are cold-sided devices.

Reducing the temperature at the inlet of the APCD is one factor that has been shown to have a significant impact on limiting dioxin formation and emissions at cement kilns (EPA, 1997). Emissions testing at a Portland cement kiln showed that PCDD/Fs were almost entirely absent at the inlet to a hot-sided ESP, but

measurements taken at the exit showed conclusively that dioxins were formed within the hot-sided ESP (EPA, 1997). Reducing the kiln exhaust gas temperature in the APCD to below 232 °C has been shown to substantially limit PCDD/Fs formation. Lower temperatures are believed to prevent the post-combustion catalytic formation of PCDD/Fs. Consequently, a number of cement kilns have added exhaust gas-quenching units upstream of the APCD to reduce the inlet APCD temperature, thereby reducing PCDD/Fs stack concentrations. A quenching unit usually consists of a water spray system within the flue duct.

5.2.2 Effect of combustion conditions

Parameters related to combustion quality are generally less relevant for cement kilns than for incinerators and boilers, primarily because the operating envelope of cement kilns is dictated largely by standard specifications for their final product. Cement kilns operate at high temperatures to achieve material temperatures of 1450 ^{o}C and gas phase temperatures even higher. 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 of limestone 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 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 of the main burner. However, facility-specific DRE testing should generally be sufficient to reveal such design problems.

Wastes injected at mid- or feed-end locations do not experience the same elevated temperatures and long residence times as 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 PICs (Dellinger et al, 1993). Increased PICs, or precursor organics, may enhance formation of PCDD/Fs.

5.2.3 Effect of total hydrocarbons

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 cement kiln (Schreiber and Strubberg, 1994). The chlorination of these hydrocarbons can be 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 role in governing the production of PCDD/Fs (Sidhu and Dellinger, 1997).

PCDD/F precursors are expected to be dominated by precursors in the cement kiln raw materials, rather than precursors in the waste. 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 and low oxygen at the raw material feed end of the kiln. However, excess oxygen is necessary in the sintering zone to produce the essential clinker minerals; one exception is the production of white cement which is performed under reduced conditions. Dellinger observed an inverse relationship between total hydrocarbons and stack oxygen concentrations (Dellinger et al, 1993). Also 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 significantly influence the hydrocarbon levels in the exit gas and total hydrocarbon levels are therefore recommended as a control parameter indicating levels of organics within raw

materials that may be chlorinated from any fuel source. Raw material characteristics are largely dictated by quarry location and are not easily controlled.

5.2.4 Effect of chlorine

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 et al (1996) 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. However, equilibrium calculations show lower chlorine capture at high temperatures and conversion of HCl to Cl_2, suggesting that even a highly alkaline chemical species such as calcium hydroxide would not always be expected to effectively control chlorinated hydrocarbon formation (including PCDD/Fs) at temperatures above 200 ^{o}C (Dellinger et al, 1993). Chlorine input levels are usually strictly controlled in cement production due to operational or quality considerations.

5.2.5 Effect of waste 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 burning of coal only, 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. The number of measurements is limited and it is questionable if the difference is real or within the normal variability of the kiln investigated. Many other and more recent studies have concluded that the use of alternative fuels and raw materials doesn't influence or affect the emissions of PCDD/Fs (see chapter 6). In general, it seems that the ranges of PCDD/Fs emission concentration resulting from the use of conventional fuels such as coal and petcoke overlap with the ranges obtained with the use of secondary fuel, regardless of the type of secondary fuel.

The UNEP Standardized Toolkit for Identification and Quantification of Dioxin (2003) and Furan releases gives the following summary about the effect of waste feeding:

"*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*".

5.2.6 Effect of feeding alternative fuels and secondary raw materials

The German cement research institute VDZ carried out approximately 160 PCDD/F emission measurements of German cement kilns between 1989 and 1996;

see figure below (VDZ, 2003). The measurements was carried out under baseline conditions (only fossil fuel) and when feeding alternative fuels and secondary raw materials. VDZ concludes that no influence on the PCDD/F emissions can be identified. The substitution of fossil fuel and normal raw materials with alternative fuel and raw materials (AFR) increased in German cement kilns from an average of 23 % in 1999 to nearly 35 % in 2002 (see figure 17).

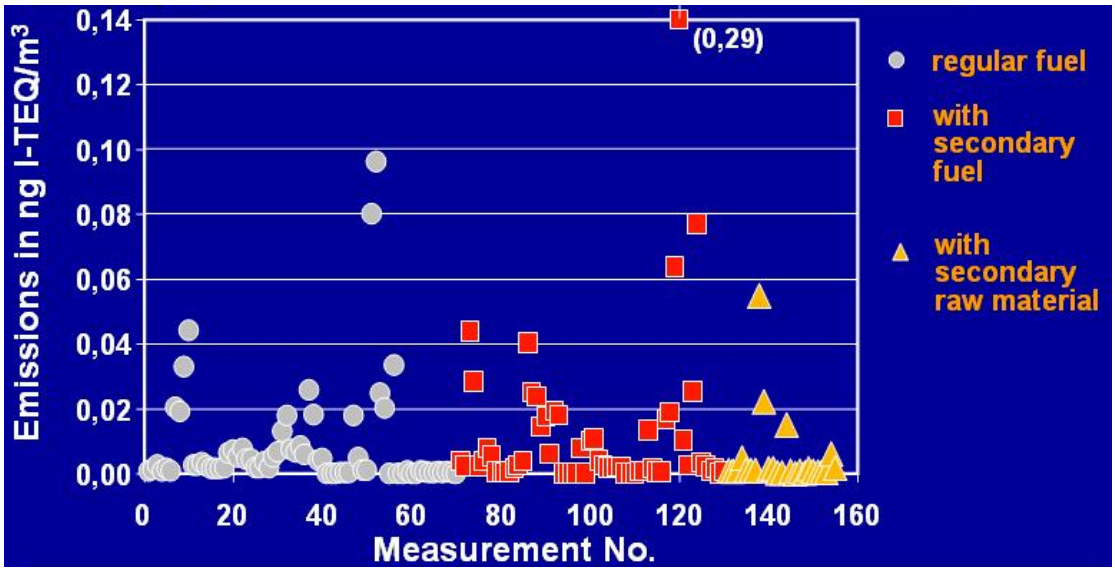

Figure 12 PCDD/F-emissions of German cement kilns between 1999 and 2002

5.2.7 Effect of feeding alternative fuels to the preheater/precalciner

As mentioned earlier, wastes injected at mid- or feed-end locations do not experience the same elevated temperatures and long residence times as wastes introduced at the hot end. When modern cement kilns, i.e. suspension preheater and precalciner kilns, increase the use of alternative fuel, it's normal to feed more to the preheater/precalciner. The possible effect of feeding different alternative fuels to the lower temperature preheater/precalciner was investigated by Lafarge. The concentration level of PCDD/F seems to be low in all measurements and doesn't seem

to be influenced by the feeding to the preheater/precalciner; see table below (Chahine, 2003 b).

Table 4 Feeding of alternative fuels to the preheater/precalciner and the 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	Sludge's	<0.011	1
12	2002	Car waste and sludge's	0.0036 & 0.07 & 0.0032	3

A similar study was carried out by Holcim where 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 (Lang, 2004). 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 % (see figure below).

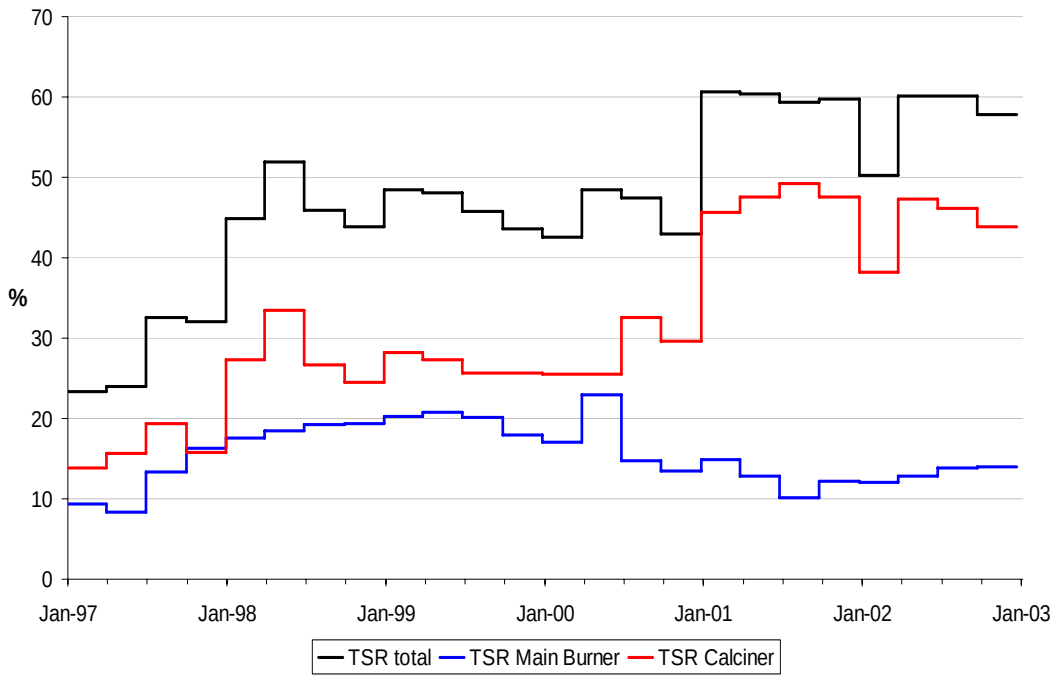

Figure 13 Increase in thermal substitution rate from 1997 to 2003

The AFR used in the Holcim study was solvents, animal meal, bleaching earth, rubber, waste oil, paper and film plastics, fly ash and ferrocarbon/wood.

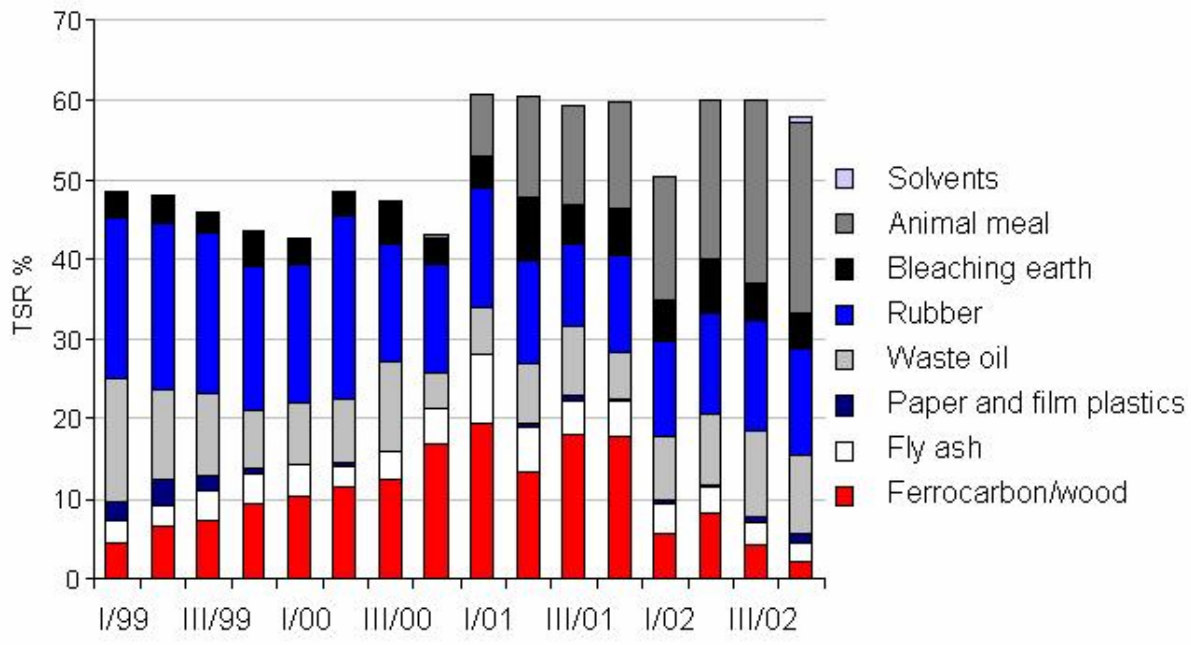

Figure 14 AFR used in the Holcim study

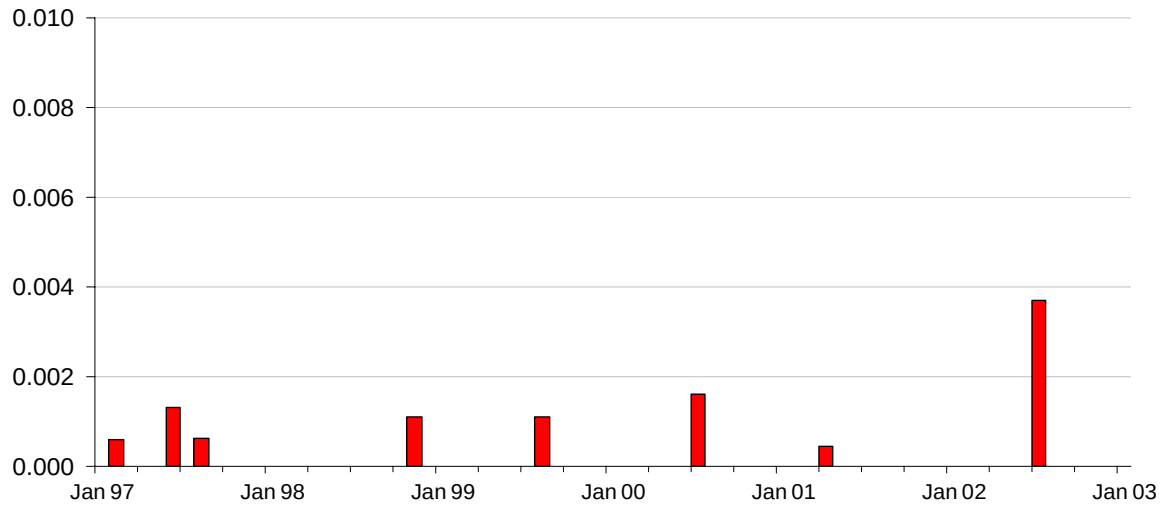

Figure 15 PCDD/F levels measured in the Holcim study (ng TEQ/Nm^3)

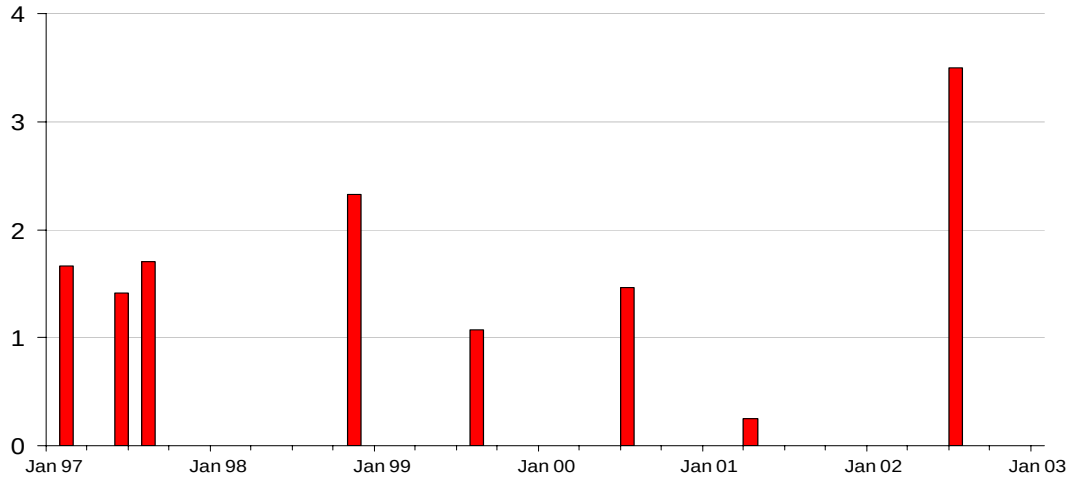

Figure 16 PCB levels measured in the Holcim study (µg/Nm^3)

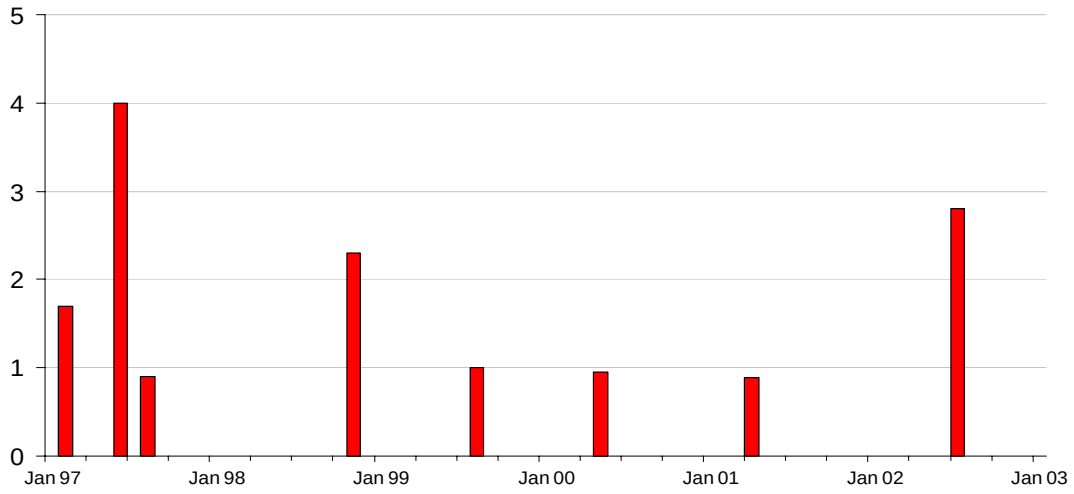

Figure 17 HCB levels measured in the Holcim study (ng /Nm^3)

The increased substitution rates of AFR to the precalciner and the main burner in the period 1997 to 2003 seems to have no influence or effect on the emission concentration of PCDD/Fs, PCBs and HCB.

5.2.8 Effect of catalysts

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

5.2.9 Effect of catalysts

Naturally occurring PCDD/F inhibitors, such as sulfur, are expected to be present in the coal used for firing a cement kiln. Since the alkaline 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 present in the raw materials. In some cases, sulfur 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 sulfur was added to the raw materials to increase the stack concentrations of SO_2 from less than 20 ppm to above 300 ppm and when Na_2CO_3 was injected at the fuel feed end to react with chlorine in the system (Schreiber, 1995).

5.2.10 Effect of carbon injection

No cement kilns are currently utilizing carbon injection for sole PCDD/F control. To effectively utilise carbon injection, the carbon injection system may have to be installed after the APCD, along with a second APCD to collect the carbon.

6. POPs releases from cement production

The general releases of POPs from the production of cement are to air from the exhaust gases, i.e. the kiln, the clinker cooler and any bypass system. There may also be releases of POPs from dusts captured in the various APCDs (generally called CKD, or cement kiln dust) depending on how the CKDs are managed. The composition of the CKDs is more or less similar to the raw material composition and in most cases CKDs are recovered in the process. Release of POPs to water is not expected and release through the product, i.e. clinker and cement is low.

Data on POPs releases to air are presented from different countries and cement companies in an alphabetically order in chapter 6.1 and 6.2 respectively. Chapter 6.3 presents POPs release to air from international and national inventories, chapter 6.4 POPs releases through solids and chapter 6.5 presents a summary. Most of the POPs data are concerning PCDD/Fs; few data are available on the release of PCBs and almost none for HCB. The information is from three main source categories:

1) Publicly available reports and articles where actual measurements from cement kilns have been conducted by an independent party, often in trial burns, and with complete references;

2) Actual measurements from cement companies and individual cement plants especially gathered for this study, performed by an independent party or by themselves;

3) National or regional inventories which present POPs contribution estimates from the cement industry, usually based on emission factors found in literature, i.e. no actual measurements.

Unfortunately, many reports have gaps in the information which makes it difficult or sometimes impossible to evaluate the accuracy of the data provided. Often

information about TEF systems, correction procedures, sampling methodology or recoveries are lacking. This report will contain duplication of some data, for example data from cement companies will in some instances also be included in country reports and inventories.

6.1 PCDD/F and PCB levels established by actual measurements

In this subchapter information on POPs releases in publicly available reports and articles are presented. These studies have involved actual measurements from cement kilns, often in trial burns performed under worst case scenario conditions. The measurements have normally been conducted by an independent party.

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 fuel 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; Pacific Air and Environment, 2002).

Repeated measurements over a decade (1991-2001) 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 source contributions in Australia. Comparison with all sources, places cement and lime manufacturing in the 14'Th place among 19 source categories identified to emit PCDD/F in Australia. The 55 measurements of PCDD/Fs in stack gases cover the range 0.001-0.07 ng I-TEQ/m^3 and 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 23 PCDD/F measurements for 5 Belgian kilns in 1999-2000 (Febelchem, 2001). All measurements was below 0.1 ng TEQ/m^3 and some of the measurements were performed during the co-processing of low PCB contaminated animal meal and fat.

6.1.3 Canada

In an effort at establishing a virtual elimination target of PCDD/Fs and HCB, the Environment Canada (1999) suggested to use the Limit 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 TEQ/m^3.

30 PCDD/F measurements from 8 cement kilns burning hazardous and non-hazardous waste were included in the study and covered the range 0.0054 - 0.057 ng I-TEQ/m^3 at 11 % O_2 (Environment Canada, 1999).

In a recent report by the Canadian Council of Ministers of the Environment (CCME, 2003) on activities related to dioxin Canada Wide Standards (CWS), data from the cement industry indicate that all releases of dioxins and furans are below 0.08 ng/m^3, with one exception. To date, 0.08 ng/m^3 is the lowest emission limit established by a CWS based on available technology and feasibility (CCME, 2003).

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 Environmental Protection Agency, 2003).

The largest kiln is heated by a mixture of petcoke, coal and industrial waste including plastic (non-PVC), and sludge from paper manufacturing and textiles from tyres. Meat and bone meal is now also being used as alternative fuel for the kiln. Waste containing more than 0.1 % chlorine is not accepted. The air emission from this kiln is cleaned in an electrostatic precipitator at 130 ^{0}C before being directed to the chimney. Coal and oil only heat the other grey kilns, and the off-gases are cleaned by an electrostatic precipitator at around 250 ^{0}C. The air emission from the 4 kilns used for white cement is cleaned first in an electrostatic precipitator at around 300 ^{0}C and afterwards by a scrubber. Approximately 2.6 million tonnes of cement were manufactured in 2001. In the largest kiln approximately 1.7 million tonnes cement with airflow of 3150-3500 million Nm^3/year was manufactured. In the other kilns approximately 0.9 million ton cement with airflow of around 3200 million Nm^3/year was manufactured, and a discharge of cleaned scrubber water of approx. 400,000 m^3 water/year. Filter dust from electrostatic precipitators is recycled into the largest kiln. Scrubber water is cleaned and the content of solids used for gypsum manufacturing (Danish Environmental Protection Agency, 2003).

Measurements of dioxin emission to air from the large kiln have 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. In 2001 a new measurement was carried out at the same kiln. The sample was made while using meat and bone meal as a part of the fuel. The measurement resulted in an emission of 0.035 ng I-TEQ/m^3 or 0.0001 mg I-TEQ/ton manufactured. The annual emission calculated on the basis of this measurement is approximately 167 mg I- TEQ/year, and this indicated that the dioxin emission increases, when meat and bone meal is used as an alternative fuel in the cement production. This conclusion is however not definitive, as only one measurement has been taken - there may be other influencing conditions (Danish Environmental Protection Agency, 2003).

In 1995 a measurement was made on one of the smaller kilns. The measurement showed a dioxin emission of 0.15 ng N-TEQ/m^3, which means an annual emission of 162 mg N-TEQ/year. The emission factor is approximately 0.0005 mg N-TEQ/ton. There have not been any measurements on the relevant kiln since 1995. No measurements have been undertaken for the other kilns and scrubber water. The best possible estimate is assumed to be based on the company's own measurements, although only one measurement has been made on one of the small kilns back in 1995. Using the value from this measurement at the 0.9 million tonnes manufactured on the smaller kilns and the emission factor 0.00001 mg I-TEQ/ton for the 1.7 million tonnes manufactured at the large kiln, the total annual emission is estimated to be in the range of 156-1401 mg I-TEQ/year. This interval is calculated assuming an uncertainty of ± factor 3. Best estimate is 467 mg I-TEQ/year (Danish Environmental Protection Agency, 2003).

6.1.5 Europe

In a survey performed by the European Cement Association CEMBUREAU (van Loo, 2004) 230 PCDD/F measurements from 110 cement kilns and 11 European countries were presented. The countries covered 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.

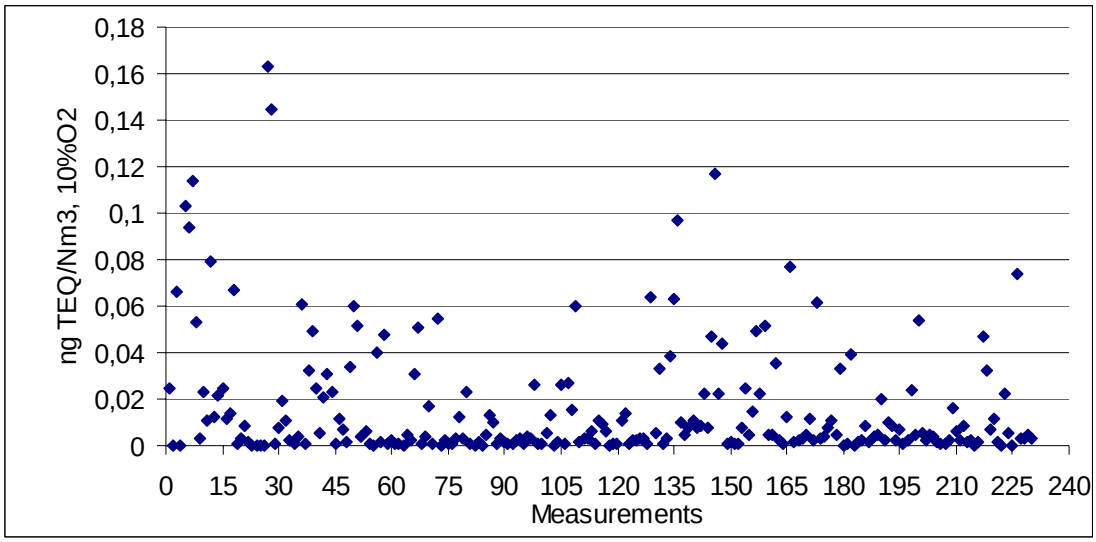

Figure 18 230 measurements in 110 kilns and 11 European countries

The concentration distribution of the 230 measurements is presented in the figure below and shows 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 have lower emissions than 0.01 ng TEQ/m^3.

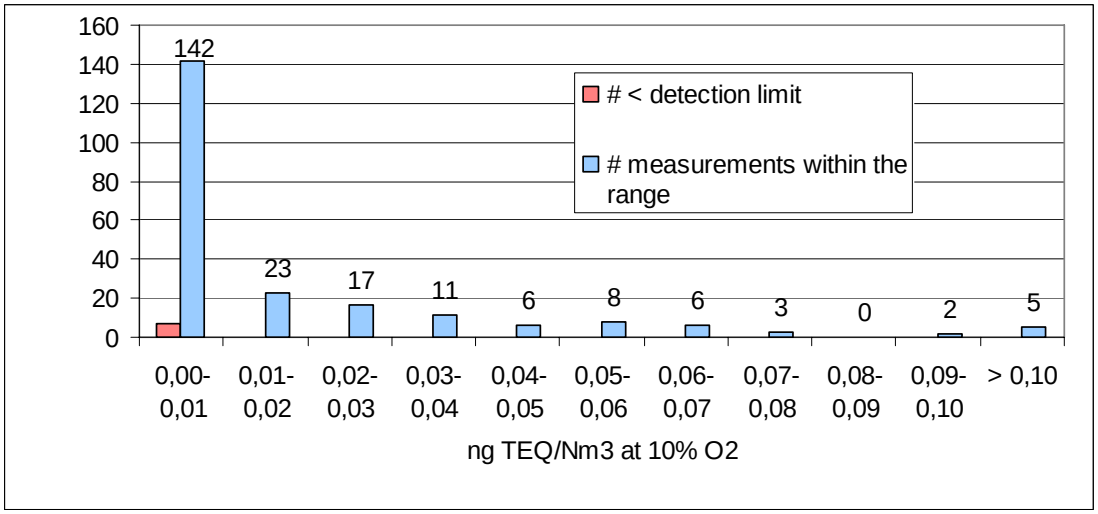

Figure 19 Concentration distributions of 230 measurements in 110 kilns and 11 European countries

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 preheater and precalciner; se table below (VDZ, 2002).

		As at: 01.01.2000			As at: 01.01.2001			As at: 01.01.2002		
		Number	Capacity t/d	%	Number	Capacity t/d	%	Number	Capacity 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 5 Process types and capacity in Germany 2000-2002 (VDZ, 2002).

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, 2002).

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 6 Fuel types and energy consumption in Germany 2000-2002 (VDZ, 2002).

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	8	13
- Oil mud		
- Organic distillation residues		

Table 7 Alternative fuel types used in Germany 2001 (VDZ, 2002).

6.1.6.1 PCDD/F results before 1996

The Verein Deutscher Zementwerke (VDZ) reported PCDD/F data from more than 150 single emission measurements at German cement clinker kilns during the period 1989–1996 (Schneider; 1996). The measurements covered 16 different dry preheater kilns, i.e. suspension preheater kilns and Lepol kilns, all equipped with ESPs for dedusting.

All samples were collected using the filter/cooler sampling method according to the VDI Guideline (1996). Sampling ports were always downstream of the ESP where the flue gas had been dedusted. Sampling time was about 6 hours and 20-25 m^3 flue gas was extracted from the stack gas. During sampling the kilns were in a representative mode of operation, i.e. the raw meal 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 was 0.02 ng I-TEQ/m^3 at 11 % O_2. No significant difference was indicated from the type of fuel being burnt. Gas temperatures in the ESP typically ranged from 95 ^oC to 205 ^oC (suspension preheater kiln) and 120 ^oC to 150^oC (Lepol kilns) and there was no indication that temperature correlated 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.

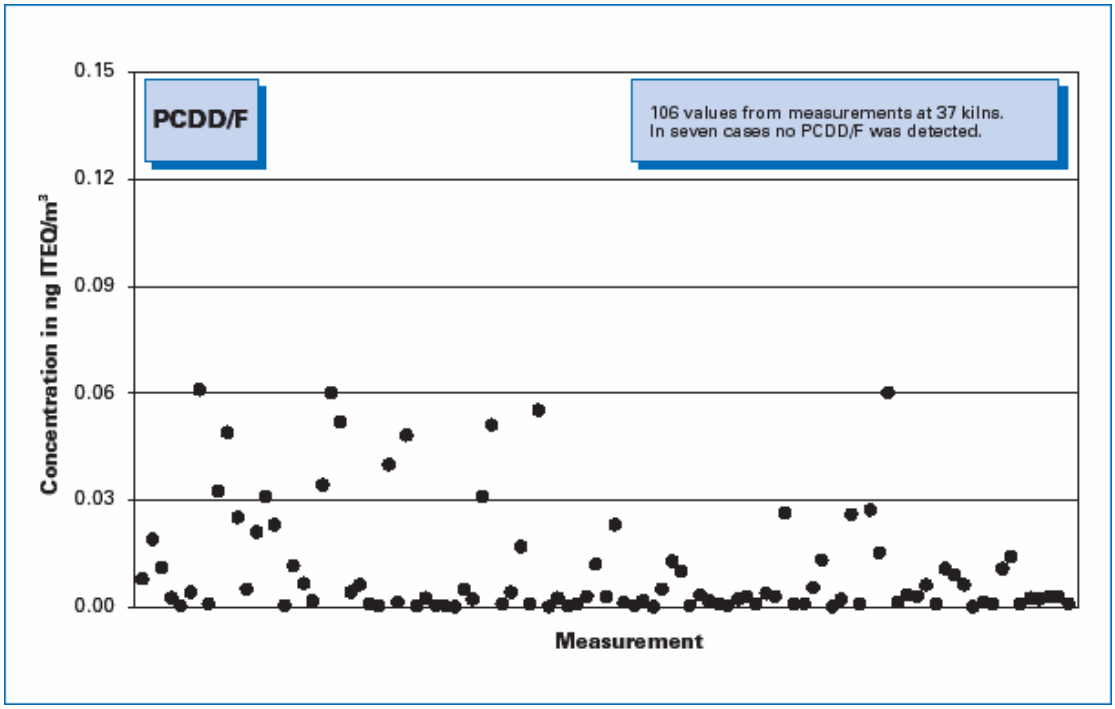

Figure 20 PCDD/F levels in 37 cement kilns in Germany 2001 (VDZ, 2002).

A summary of all PCDD/F-emissions of German cement kilns during 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). There seems to be no impact of the use of alternative fuels on the emissions of PCDD/F.

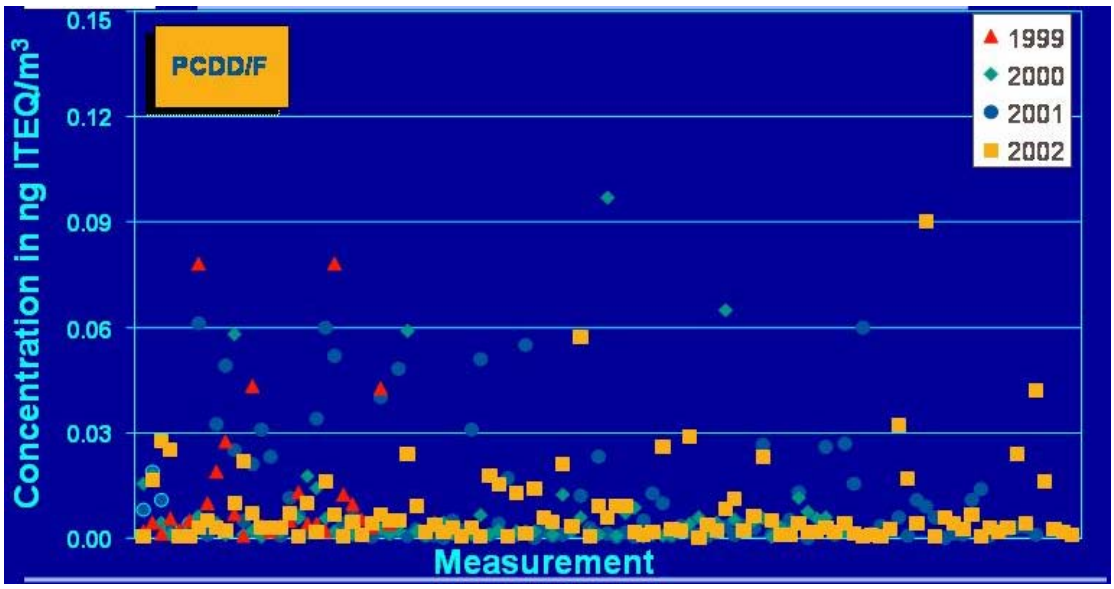

Figure 21 PCDD/F-emissions of German cement kilns between 1999 and 2002

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, 2002). It seems to be no impact of the use of alternative fuels on the emissions of PCBs.

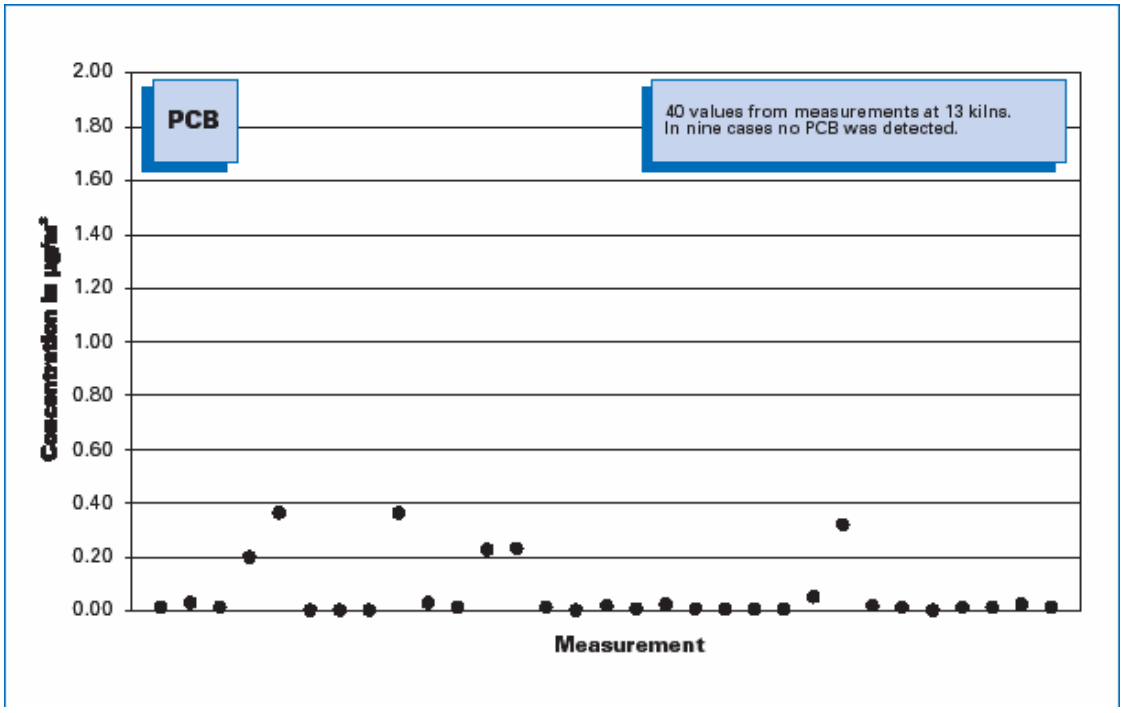

Figure 22 PCB levels in 13 cement kilns in Germany 2001 (VDZ, 2002).

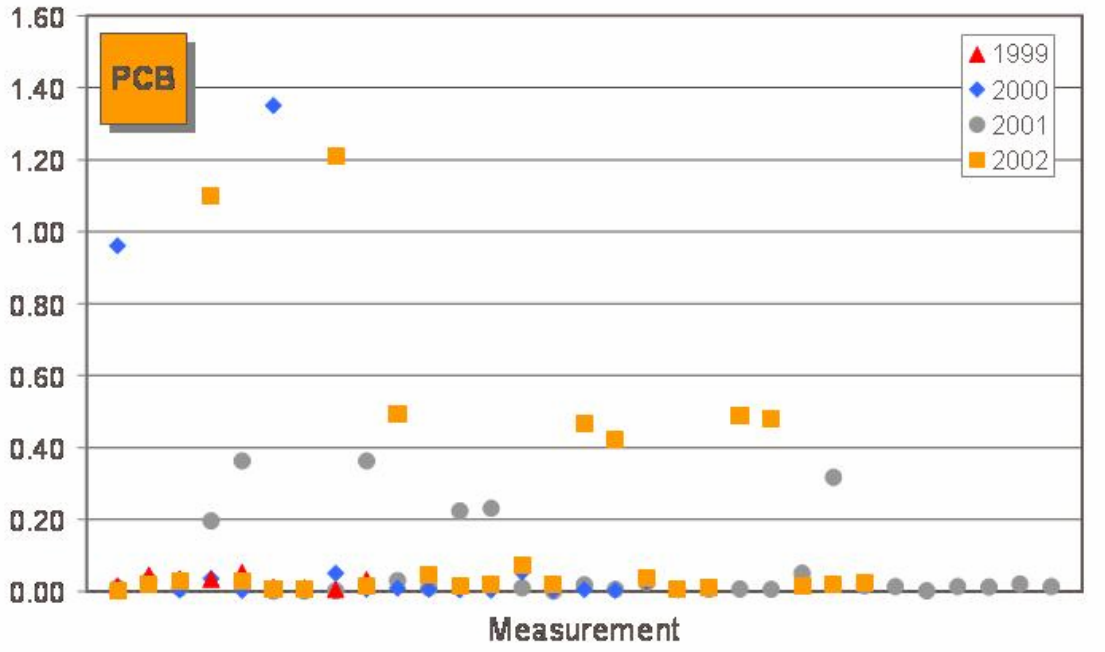

Figure 23 PCB-emissions of German cement kilns between 1999 and 2002

6.1.7 Japan

The Japan Ministry of the Environment compiled the Dioxins Emission Inventory of Japan from 1997 through 2003. Dioxin emission decreased year on year by 95 % between 1997 and 2003 (Japan Ministry of Environment, 2004)

In 2003 approximately 78 million tonnes of clinker were produced in a total 62 dry suspension preheater kilns in Japan (Sakai, 2003). 54 measurements performed in 2000 showed 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 influence the PCDD/F emissions from a Polish cement kiln Dudzinska et al carried out a test in 1998. There are no details about the process type, operating conditions or waste composition used in the test. The article claims that Polish cement plants are mostly using high content sulfur coal as fuel and that this probably disturbs the formation of PCDD/F. The wastes introduced during the test consisted of 10 % “inorganic wastes” from metal finishing processes containing 0.08 % copper (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 and the PCDD/F emissions were 0.0515 ng I-TEQ/m^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 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 with light heating oil; the pesticide content represented 11.5 %, 29.4 % and 30.5 % 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 were 0.009 ng I-TEQ/m^3 with coal only and 0.015, 0.053 and 0.068 ng I-TEQ/m^3 when feeding the three alternative fuels mixes with pesticides respectively.

6.1.9 Spain

In the first phase 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/m^3 and the mean emission factor 0.014464 µg I-TEQ/ton cement. Spain had in 2000 36 cement plants with 58 kilns - 6 wet, 4 semi-dry and 48 dry processes. The industry produced 32 million ton of clinker and contributed in total an estimated 0.578 g I-TEQ in 2001 (Fabrellas et al, 2002).

In the period 2000-2003 89 samples from 41 kilns were collected, which represents 69.5 % of the industry. Apart from conventional fuels (petroleum coke and coal), the use of residue-derived materials such as waste oil, tyres, organic liquid mixtures, plastics, sewage sludge, or saw dust, is gaining in importance within cement manufacturers (Fabrellas et al, 2004). In 2002 production figures reached 40.2 million tonnes of finished product. Currently, the sector comprises 36 facilities owned by 21 different companies. Petroleum coke (88 %), coal (8 %) and gas (< 5%) are the dominating fuels. Of the 89 samples, 58 were taken when using conventional fuels and 31 when alternative fuels were used. The results are presented in the figure below.

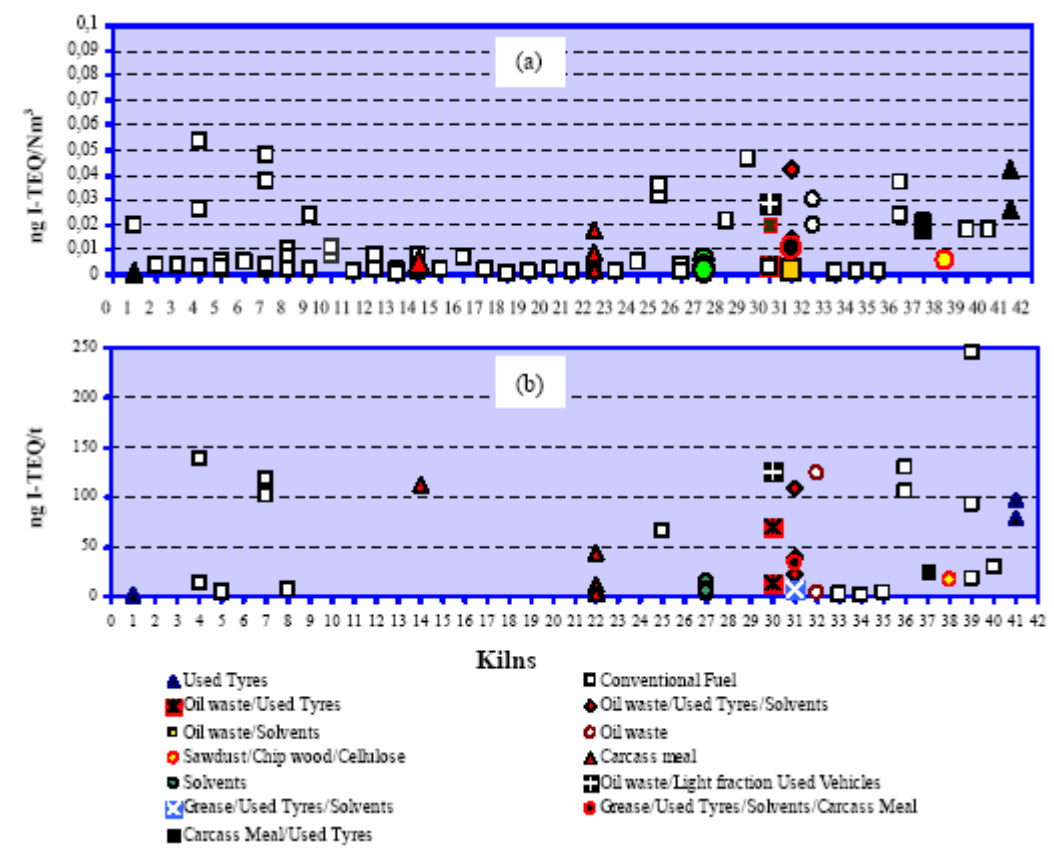

Figure 24 **(a) PCDD/F emission (ng I-TEQ/Nm3) and (b) Emission Factor (ng I-TEQ/t clinker) (Fabrellas et al, 2004)**

No evidence of higher PCDD/F emissions when using alternative fuels could be found (Fabrellas et al, 2004). Considering annual production figures of 30 and 40 million tonnes of clinker and cement, respectively (data of year 2002), the annual emission obtained was 1.07 g I-TEQ/yr. Although higher than that reported in 2002, 0.578 g I-TEQ/yr (Fabrellas et al, 2002), it should be considered as more representative since number of facilities has been substantially enlarged. Compared with other European countries with similar production figures, Germany, 4.88 g I-TEQ/yr, United Kingdom, 1.71 g I-TEQ/yr, the Spanish value is between 1.7 and 4.9 fold lower (Fabrellas et al, 2004).

Emission factors per ton of clinker and cement were also calculated, average value being 36.53 and 28.82 ng I-TEQ/t respectively. Emission factors are plotted in part b of the Figure above. No higher values for plants co-incinerating waste materials were recorded. The authors of the report consider "*cement manufacture*

sector as a non-relevant source of PCDD/F in Spain" and that "*there is no evidence of higher PCDD/F emissions when residue derived materials are incorporated into the clinker kiln as alternative fuel*" (Fabrellas et al, 2004).

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, 2001). Among the facilities, a dry process cement plant with two kilns, with and without co-processing of liquid hazardous waste and/or tyres was 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 (raw material feeding to kiln A, 270 t/h, and kiln B, 330 t/h) 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 mean values 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. 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 subsequent emission factors when feeding wastes was approximately one third of those without waste.

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 (UNEP/IOMC, 2001).

Table 8 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 clinker
Kiln 1 mean value - no AFR feeding	**No**	**0.0105**	**0.017**
1	No	0.018	
2	No	0.009	
3	No	0.005	
Kiln 1 mean value - with feeding of tyres	**Tyres**	**0.0029**	**0.005**
1	Tyres	0.004	
2	Tyres	0.003	
3	Tyres	0.001	
Kiln 2 mean value - no AFR feeding	**No**	**0.0008**	**0.0010**
1	No	0.0018	
2	No	0.0004	
3	No	0.0001	
Kiln 2 mean value - with feeding of hazardous waste	**Hazardous waste**	**0.0002**	**0.0003**
1	Hazardous waste	0.0001	
2	Hazardous waste	0.0001	
3	Hazardous waste	0.0006	

6.1.11 United Kingdom

An improved atmospheric emission inventory for UK of PCDD/F and PCB was presented by Alcock et al in 1999. The inventory also investigated 5 cement plants. 14 measurements were performed and covered the range 0.012 - 0.423 ng N-TEQ/m^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 between 0.29-10.4 grams TEQ per year, which constitute 0.04-4.7 % of the total UK emissions.

Table 9 ng PCB TEQ/m^3 from a UK cement plant using waste fuel

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 study also included sampling and analysis of PCBs from one cement kiln. Dioxin-like PCBs are those with the highest toxicological significance. The three day measurements were generated during a test burn with substitute liquid fuel; see table below.

The range in measured TEQ emission for PCBs was small (0.013 to 0.025 ng/m^3), suggesting a consistent sampling method and a 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

Portland cement clinker production in the United States is estimated to have been 75.2 million tons in 2000 (PCA, 2001) and 15 cement plants were using hazardous waste as co-fuel; representing about 15% of all plants (CKRC, 2005). Organic hazardous wastes used in the US include diverse substances, such as waste oils, spent organic solvents, sludge's from the paint and coatings industry, waste paints and coatings from auto and truck assembly plants, and sludge's from the petroleum refining industry (Greer et al, 1992). The heating values of these wastes are comparable to that of coal.

Cement kiln operators in the US began recovering energy from organic waste materials 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 the US kilns are permitted to replace up to 100 % of their conventional fuels with waste-derived fuels (CKRC, 2002). Trial burns have consistently shown that destruction and removal efficiencies of 99.99 to 99.9999 % can be achieved for very stable organic wastes, including chlorinated compounds, using cement kilns (Greer et al, 1992). Other types of supplemental fuel commonly used include natural gas, fuel oil, automobile tires, used motor oil, sawdust, and scrap wood chips.

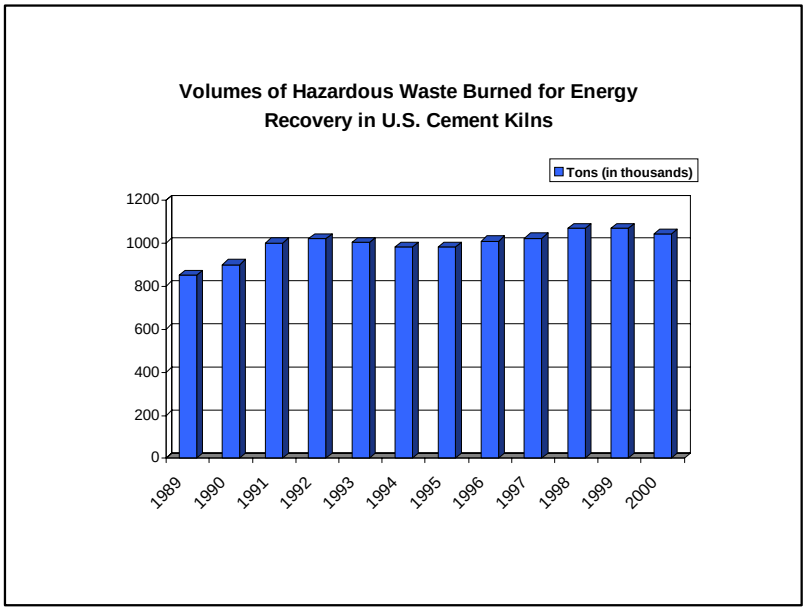

Figure 25 Volumes of hazardous waste used in US cement kilns 1989-2000

Trial burns in the US are usually designed to determine how effectively a cement kiln is able to operate under specifiable worst case conditions and must fulfil three major requirements regarding combustion performance, of which the DRE is the most important: Principle Organic Hazardous Constituents (POHCs) must be destroyed and/or removed in the waste stream to a DRE of 99.99 % or better; PCDD/Fs and PCBs wastes must achieve a DRE of 99.9999 %. The other requirements involve emissions of particulates and gaseous hydrogen chloride (Federal Register, 1999). The operating conditions selected for the trial burn should represent the worst case conditions to establish the outer limits of where the kiln should be permitted to operate. The conditions typically include high waste feeding rates, high concentrations of all POHCs, minimum O_2 level in stack gas, low combustion temperature, high temperatures in the APCD etc. (Niessen, 1995).

Cement kilns in the US co-processing hazardous waste must operate in compliance with the stringent and comprehensive US EPA regulation (Federal Register, 2002a and 2002b). The US EPA and the cement industry have done numerous studies to investigate the potential influence of co-processing hazardous wastes on the emissions from cement kilns. The detailed results from these studies

are publicly available in databases that describe the environmental performance. Examples of such data can be found in the database "*Sources of Environmental Releases of Dioxin-like Compounds in the United States*", developed by EPAs Office of Research and Development (ORD) to be a repository of certain specific chlorinated PCDD/F emissions data from all known sources in the US (EPA, 2001)

PCDD/F emissions data from tests conducted between 1989 and 1996 were obtained for 16 cement kilns burning hazardous waste and 15 cement kilns burning non-hazardous waste (EPA, 1996e). More recent PCDD/F emissions data were also obtained from tests conducted in 2000 at 3 cement kilns burning hazardous waste (EPA, 2002) and from tests conducted in June and July of 1999 at one facility burning non-hazardous waste (Bell, 1999). According to EPA (2005b) "*The majority of stack emissions data from cement kilns burning hazardous waste were derived during trial burns and may overestimate the PCDD/F emissions that most kilns achieve during normal operations. Stack emissions data from kilns burning non-hazardous waste were derived from testing during normal operations.*"

According to Chadbourne (1997) the US EPA published PCDD/F testing results of cement kilns in May 1994, showing that five kilns exceeded 50 ng TEQ/m^3 at 7% O_2; the five lowest were less than 0.02 ng TEQ/m^3 at 7 % O_2. The US EPA suggested already in 1994 that PCDD/F from cement kilns could be controlled by a combination of low temperature in the APDC, low carbon monoxide and elevated oxygen (EPA, 1994d). Later results have shown that carbon monoxide and oxygen levels are relatively unimportant (Chadbourne, 1997).

EPA continued to develop their database as part of the 1996 proposed "*Maximum Achievable Control Technology*" (MACT) standards for hazardous waste combustors (HWCs) (Federal Register, 1997). The 1996 database contains information from facilities in three source categories which burn hazardous wastes, including 40 cement kilns (multiple testing). The database contains stack gas emissions data (including data on metals, chlorine, particulate matter, chlorinated dioxins and furans, carbon monoxide (CO), and hydrocarbons (HC), process operating data (including waste, fuel, and raw materials compositions and feed rates), and facility equipment design and operational data (including combustor and air

pollution control device temperatures, pressures, etc.). The databases have been revised and updated and used to develop revised MACT standards (Federal Register, 1999). The current databases contain test results for numerous cement kilns with multiple testing campaigns for the years 1992, 1995, and 1998 (Federal Register, 2002c).

Based on testing at non-hazardous-waste (NHW) kilns, with NHW fuels at kilns that normally burn hazardous waste (HW), and under worst-case conditions at kilns that burn HW, US EPA concluded in 1998 that *"Based on the test results for both NHW and HW kilns, the predominant factor affecting PCDD/F emissions is the temperature of gases at the inlet to the APCD. The highest PCDD/F emissions (near 40 ng TEQ/m^3) occurred at the highest gas temperatures (between 260 ^{0}C and 370 ^{0}C) while the lowest emissions (near 0.02 ng TEQ/m^3) occurred at the lowest temperature (at approximately 100 ^{0}C)"* (Federal Register, 1998). Data from testing fourteen NHW kilns under different test conditions is presented in the figure below. Stack temperatures are presented since inlet APCD temperature data are not typically recorded during stack emissions testing (stack temperatures will be lower than inlet APCD temperatures).

Kiln type	APCD type	Kiln fuel	Avg Gas T (°F)	Avg TEQ ng/dscm	Kiln location
PH/PC	FF	Natural gas; main stack tested	183	0.011	Capital Aggregates—San Antonio TX.
PC	FF	Coal,tires, pulp/paper mill sludge	220 →	0.0063	Calaveras Cement—Redding CA.
PH/PC	FF	Natural gas; raw mill on	221	0.042	Ash Grove—Seattle WA (kiln/in-line mill).
PH/PC	ESP	Not reported	226	0.00087	RMC Lonestar—Davenport CA.
PC	FF	Coal & tires	233 →	0.21	Calaveras Cement—Redding, CA.
PH/PC	FF	Natural gas; bypass stack tested	299	0.054	Capital Aggregates—San Antonio TX.
WET	ESP	Coal	305	0.0024	Holnam—Florence CO.
WET	ESP	Coal & natural gas	315	0.072	Ash Grove—Montana City MT.
WET	ESP	Coal	346 ⇨	0.37	Lehigh—Union Bridge MD.
WET	ESP	coal & tires	358 ⇨	1.2	Lehigh—Union Bridge MD.
WET	ESP	Coal/coke	366	0.032	Holnam kiln #1—Holly Hill SC.
DRY	FF	Coal, gas, tire derived fuel	396	0.0035	Riverside—Oro Grande CA.
WET	ESP	Natural gas	397	0.020	Capital Aggregates—San Antonio TX.
DRY	FF	Coal & natural gas	403	0.0084	Riverside—Oro Grande CA.
WET	ESP	Coal	417	0.12	Lone Star—Greencastle IN.
WET	ESP	Coal/coke	418	0.04	Holnam kiln #2—Holly Hill SC.
DRY	ESP	Coal, coke, & tires	450	0.074	Lone Star—Oglesby IL.
WET	ESP	Coal	482	0.55	Continental Cement—Hannibal MO.
WET	ESP	Coal	518	1.0	Holnam—Clarksville MO.

Abbreviations:
PH/PC = preheater/precalciner.
ESP = electrostatic precipitator.
PC = precalciner.
FF = fabric filter.

Figure 26 Average PCDD/F TEQ emissions (at 7 percent oxygen) and average stack gas temperatures for NHW cement kilns tested under NHW conditions (Federal Register, 1998).

The US EPA stated the following with regards to the impacts of feeding hazardous waste to a cement kiln (Federal Register, 1999):

> *"Notwithstanding our decision to divide the Portland cement manufacturing source category based on the kiln's waste burning status, we considered both hazardous waste burning cement kiln and non-hazardous waste burning cement kiln data together because both data sets are adequately representative of general dioxin/furan behaviour and control in either type of kilns. This similarity is based on our engineering judgement that hazardous waste burning does not have an impact on dioxin/furan formation; dioxin/furan is formed post-combustion. Though the highest dioxin/furan emissions data point from MACT (i.e., operating control device less than 200 ^{0}C) hazardous waste and non-hazardous waste burning cement kiln sources varies somewhat (0.28 versus 0.37 ng TEQ/m^{3} respectively), it is our judgment that additional emissions data, irrespective of hazardous waste burning status, would continue to point to a floor of within the range of 0.28 to 0.37 ng TEQ/ m^{3}. This approach ensures that the floor levels for hazardous waste burning cement kilns are based on the maximum amount of relevant data, thereby ensuring that our judgment on what floor level is achievable is as comprehensive as possible. We estimate that approximately 70 percent of test condition data from hazardous waste burning cement kilns are currently emitting less than 0.40 ng TEQ/m^{3} (irrespective of the inlet temperature to the particulate matter control device). In addition, approximately 50 percent of all test condition data are less than 0.20 ng TEQ/m^{3}".*

In 1999 EPA concludes that hazardous waste burning in cement kilns does not have an impact on PCDD/F formation as it is formed post-combustion, probably exclusively in the APDC. Today, in 2005, the US EPA is working with the Year 2000 Update of the Inventory of Sources and Environmental Releases of Dioxin-

Like Compounds in the United States (EPA, 2005b) and the following statement can be found on hazardous waste burning in cement kilns:

> *"These data show that the average emission factor for kilns burning hazardous waste is about 90 times greater than that for kilns burning non-hazardous waste. However, it should be noted that the average emission factor for kilns burning hazardous waste was derived from "near worst case" testing of hazardous waste-burning kilns. Although the average emission factors for the two groups of kilns differ substantially, the emission factors for individual kilns in the two groups overlap. Therefore, other aspects of the design and operation of the kilns - in particular, the temperature of the APCD equipment - are likely affecting PCDD/F emissions. Previous attempts to understand these differences using parametric testing of cement kilns yielded mixed results. EPA conducted a limited comparison (EPA, 1997) of PCDD/F TEQ stack gas concentrations (ng TEQ/m^3) between cement kilns burning hazardous wastes and those not burning hazardous wastes. Those comparisons were made at 14 cement kilns. With the exception of the fuel being burned, operating conditions (e.g., APCD temperature) were the same or similar for each set of comparisons. Baseline conditions used coal as the only primary fuel. The results of these comparisons found:*
>
> - *Seven kilns in which the baseline (i.e., no combustion of hazardous waste) PCDD/F TEQ stack gas concentrations were about the same as those for the burning of hazardous wastes,*
>
> - *two kilns in which the baseline PCDD/F I-TEQ stack gas concentrations were about double those for the burning of hazardous wastes, and*
>
> - *five kilns in which the hazardous waste PCDD/F I-TEQ stack gas concentrations were substantially greater (3- to 29-fold greater) than those for the baseline operating conditions.*

Further, the report says "*Given the strong empirical evidence that real differences exist, ORD decided to address the kilns burning hazardous waste separately from those burning non-hazardous waste to develop a PCDD/F emissions inventory and to subdivide the hazardous waste-burning category into subcategories by APCD inlet temperature (i.e., less than 232 °C and greater than 232 °C). APCD inlet temperature data were available for 88 test runs at 14 cement kilns. The number of test runs conducted at individual kilns ranged from 1 to 26*".

It's difficult to explain why EPA chooses to use calculated emission factors to estimate the annual release from the different source categories when complete data of actual emissions is available in databases. It's also difficult to understand why EPA in 2005 treat cement kilns burning hazardous waste differently than they did in 1999, especially when "empirical evidence" seems to be given greater weight than statistic. Also when "*the majority of stack emissions data from cement kilns burning hazardous waste were derived during trial burns and may overestimate the PCDD/F emissions that most kilns achieve during normal operations. Stack emissions data from kilns burning non-hazardous waste were derived from testing during normal operations*" (EPA, 2005b).

When it comes to the confidence of the emission factors used in the inventory update US EPA states the following (EPA, 2005b):

"The TEQ emission factors are given a low confidence rating for all subcategories and all years. The emission factor for non-hazardous waste-burning kilns was given a low rating because test data were available for only 16 facilities. The tested facilities may not be representative of routine PCDD/F emissions from all kilns burning non-hazardous waste. Although a higher percentage of the kilns burning hazardous waste (with reported APCD temperature data) had been tested, greater uncertainty exists about whether the emissions are representative of normal operations because the tests used trial burn procedures and because a greater majority of the operating facilities had reduced their APCD temperatures to below 232 °C.

Accordingly, a low confidence rating was also assigned to the estimated emission factors for kilns burning hazardous waste."

It is demanding to get a good overview and complete understanding of the content of the various databases available in the US. More than 750 measurements can be found in various documents and databases; some of these may be from the same source (EPA, 2005b). Many measurements have also been collected by the US cement industry, which have conducted comprehensive testing to investigate the specific origins of PCDD/F emissions.

The early US EPA publications over-estimated the PCDD/F emissions from cement kilns that burn hazardous wastes for energy recovery. 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), a cement industry "association", 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. Based on their investigations the industry also identified emissions reduction opportunities, and voluntarily implemented modifications to realize these reductions.

In 1996, EPA further revised its PCDD/F emissions estimate for hazardous waste burning cement kilns to 23 g TEQ/year. In the 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*." (Federal Register, 1999).

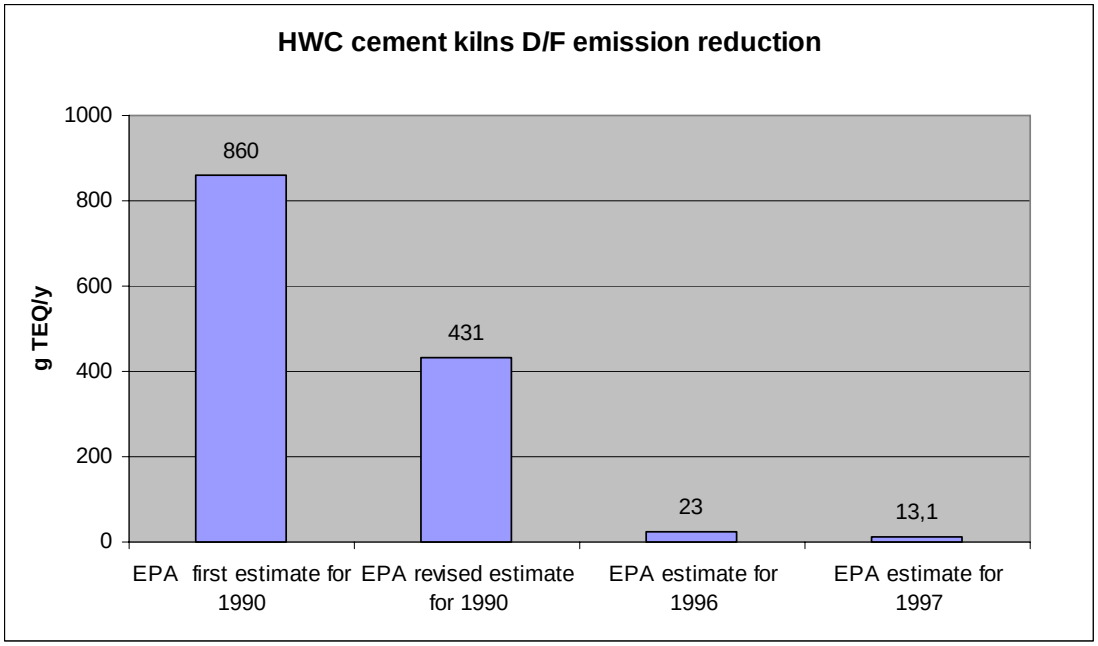

Figure 27 US EPA PCDD/F contribution estimates for cement kilns co-processing hazardous waste.

The figure shows EPAs estimated contributions from cement kilns co-processing hazardous waste in the USA from 1990 until 1997 and illustrates the uncertainties introduced by solely using emission factors estimates. The PCDD/F emissions will probably diminish even further as hazardous waste burning cement kilns achieve compliance with the new National Emission Standards for Hazardous Air Pollutants from Hazardous Waste Combustors, scheduled for promulgation in September 2005 (EPA, 2005a).

6.1.12.1 The Great Lakes

In a joint Canadian and US project on PCDD/F reduction options from the Great Lakes Binational Toxics Strategy (GLBTS, 2000) they conclude that burning

hazardous waste in cement kilns doesn't seem to influence the formation and emission of PCDD/F. 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 specifically gathered for this study from the CSI cement companies and individual cement plants. The data is reported as received from the different companies; some have submitted entire independent laboratory reports, others figures only. The data has been received in numerous reports over the last couple of years which cannot be referred to individually. The environmental coordinator in each company has been responsible for reporting the data and the web addresses or contact details are given below. The World Business Council for Sustainable Development, Cement Sustainability Initiative, (www.wbcsdcement.org) has coordinated the effort and been responsible overall.

www.cemex.com/

www.cimpor.pt/

www.holcim.com/

www.heidelbergcement.com/

www.lafarge.com/

RMC House, Coldharbour Lane, Thorpe Surrey TW20 8TD, United Kingdom

www.siamcement.com/

www.taiheiyo-cement.co.jp/

www.titan.gr/

www.uniland.es/

6.2.1 Cemex Cement Company

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

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 TEQ/m^3 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 ng/m^3 TEQ 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 ng/m^3 TEQ and 0.007 ng/m^3 TEQ at 10 % O_2.

Table 10 PCDD/F measurements in Cemex kilns

Country	Results PCDD/F (ng TEQ/Nm^3)	Emission limit (ng TEQ/Nm^3) 10 % O_2	Year
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 reported 14 PCDD/F measurements done in Portugal, Spain and South Africa in the period from 1997 – 2003 (Leitao, 2004); see table below.

Table 11 PCDD/F measurements in Cimpor kilns

Country	Plant	Kiln	Date	ng I-TEQ/m3 10 % O_2	Production process / type of kiln	Air pollution control system	Gas 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 exit gas temperature between 106–122 ^{o}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 TEQ ng/m^3 at 10 % O_2. All kilns are equipped with electro precipitators or bag-house filters and has exit gas temperature between 90–117 ^{o}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 TEQ /m^3 at 10 % O_2. The kiln is equipped with electro precipitator and has an exit gas temperature of 113 ^{o}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 the Holcim kilns (Holcim, 2001).

The average PCDD/F value for 2001, 2002 and 2003 are 0.041 ng TEQ/m^3 (71 kilns), 0.030 ng TEQ/m^3 (82 kilns) and 0.025 ng TEQ/m^3 (91 kilns) respectively (Lang, 2004). 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/m^3; the minimum and maximum value was 0.0001 and 0.292 ng TEQ/m^3 respectively, with 9 long wet kilns being above 0.1 ng TEQ/m^3.

29 of these measurements performed in 2001 and 2002 were from non-OECD countries with an average value of 0.0146 ng TEQ/m^3; the minimum and maximum value measured was 0.0002 and 0.074 ng TEQ/m^3 respectively, with no measurements being above 0.1 ng TEQ/m^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 12 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/m^3	Minimum PCDD/F ng TEQ/m^3	Maximum PCDD/F ng TEQ/m^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

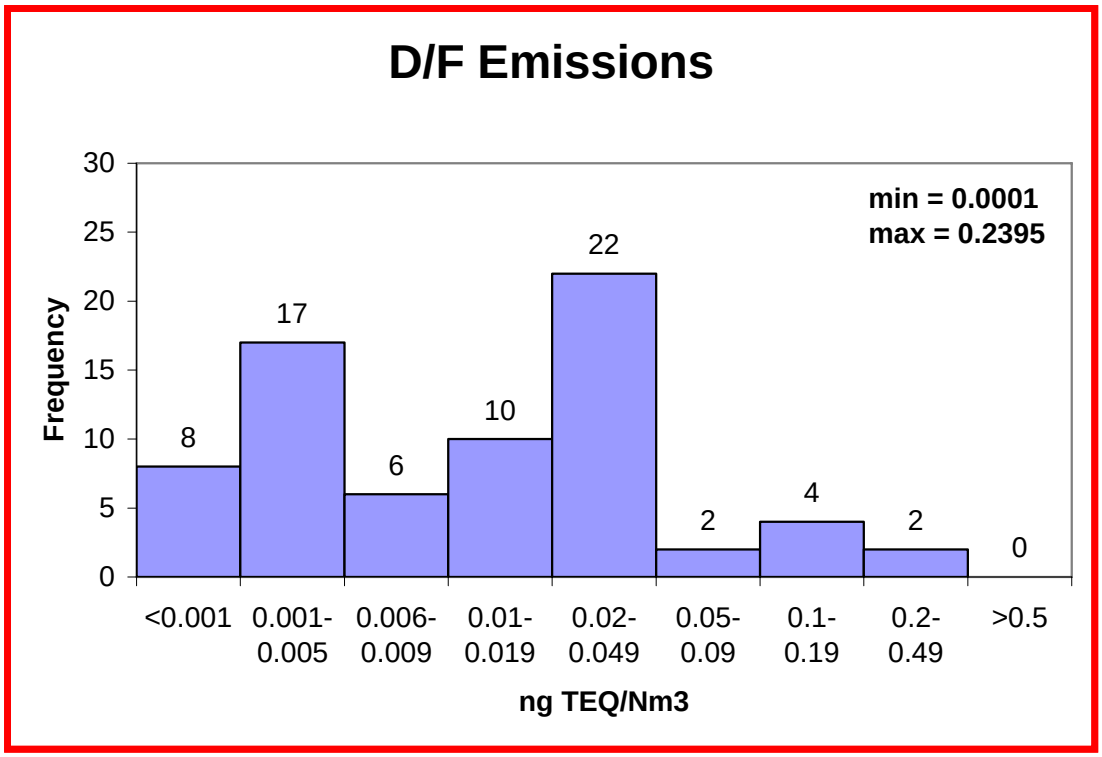

Figure 28 Holcim PCDD/F data from 2001 representing 71 kilns

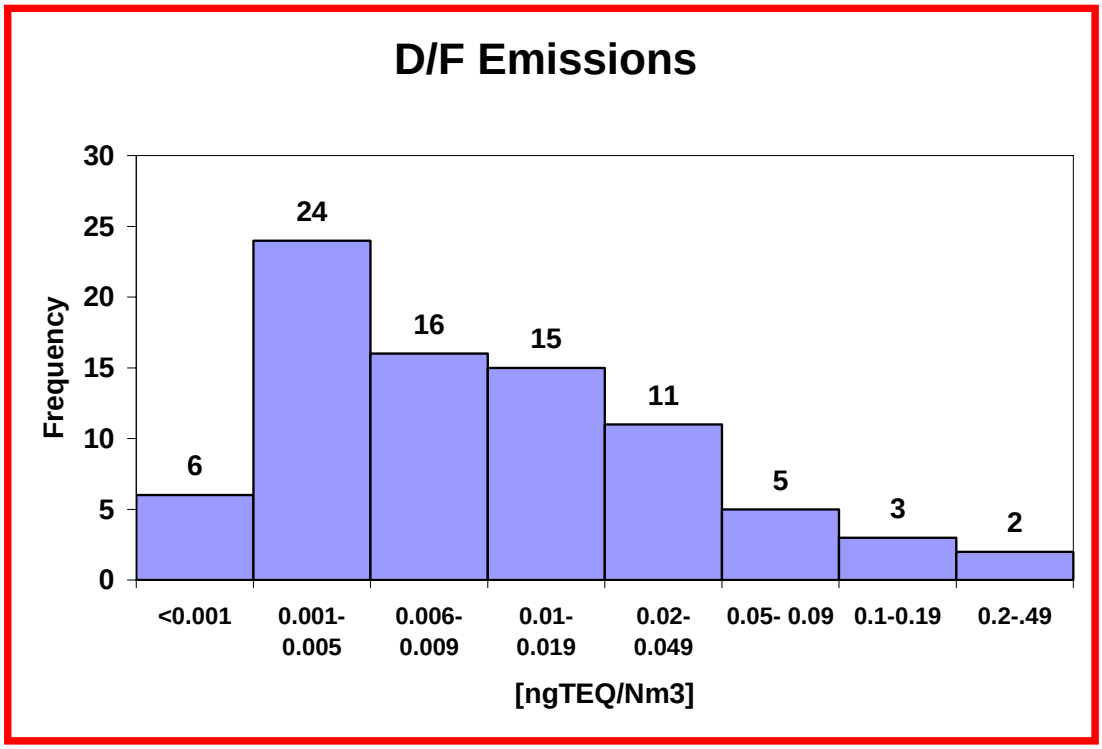

Figure 29 Holcim PCDD/F data from 2002 representing 82 kilns

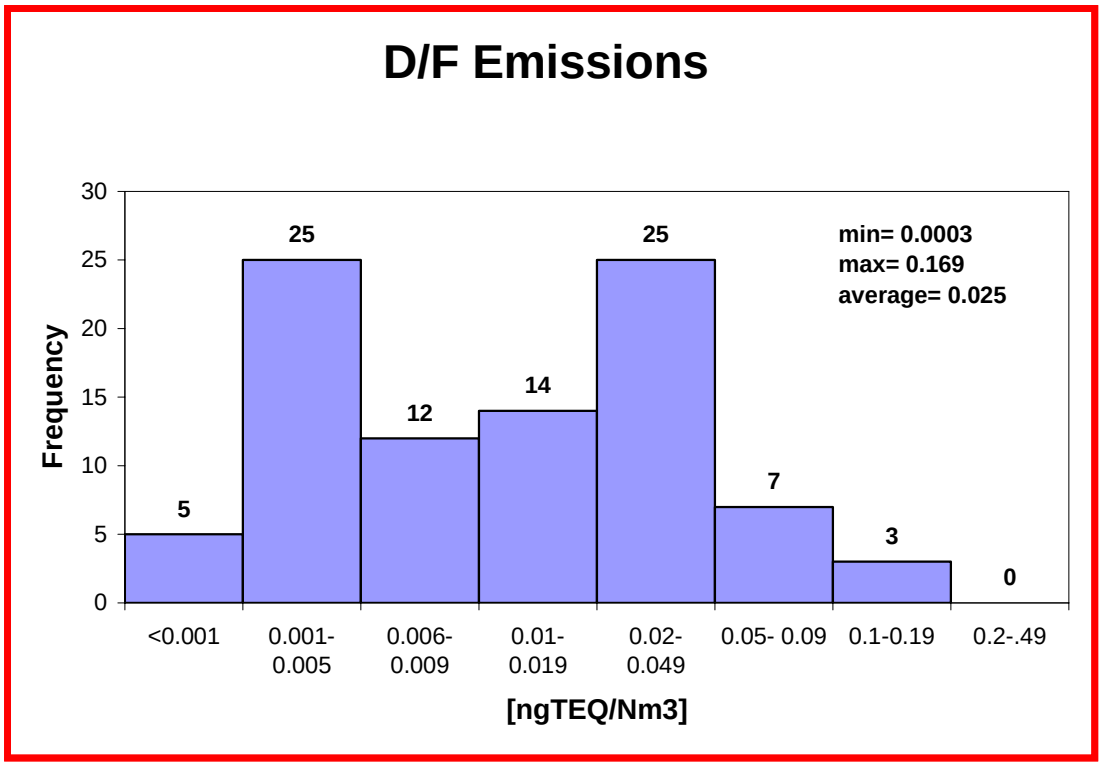

Figure 30 Holcim PCDD/F data from 2003 representing 91 kilns

6.2.3.1 Holcim Chile

Five PCDD/F measurements were reported from a cement company in Chile, during 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/m^3 at 10 % O_2; one measurement is done with coal only, showing 0.0100 ng I-TEQ/m^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/m^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/m^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 3350 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/m^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 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/m^3.

6.2.3.4 Holcim Philippines

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/m^3 at 11 % O_2.

6.2.3.5 Holcim Vietnam

A test burn with two expired chlorinated insecticide compounds introduced simultaneously at a rate of 2 tons per hour through the main burner was carried out in Vietnam in 2003. 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/m^3 for the baseline and the test burn respectively.

HCB were measured to be below the detection limit, < 31 ng/m^3 and < 35 ng/m^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 13 PCB concentration measured during a test burn in Vietnam

ng PCB/Nm^3		**Baseline study**	**Test burn**
Total "dioxin-like" PCBs	Excluding LOD values	0.00	0.00
	Including half LOD values	0.78	0.78
Total 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 insecticides 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 Heidelberg Cement (Haegermann, 2004).

Data of 152 PCDD/F measurements from 43 kilns at 37 plants measured in 2001-2004 showed an average value of 0.020 ng TEQ/m^3 (see figure below). A comparison made between kilns using a high substitution rate of alternative fuels and kilns only using fossil fuel indicates that the use of alternative materials have 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/m³ (minimum 0.001 TEQ/m³, maximum 0.016 ng TEQ/m³) while the average of eight kilns not using any secondary fuels was 0.016 ng TEQ/m³ (minimum 0.002 TEQ/m³, maximum 0.031 ng TEQ/m³).

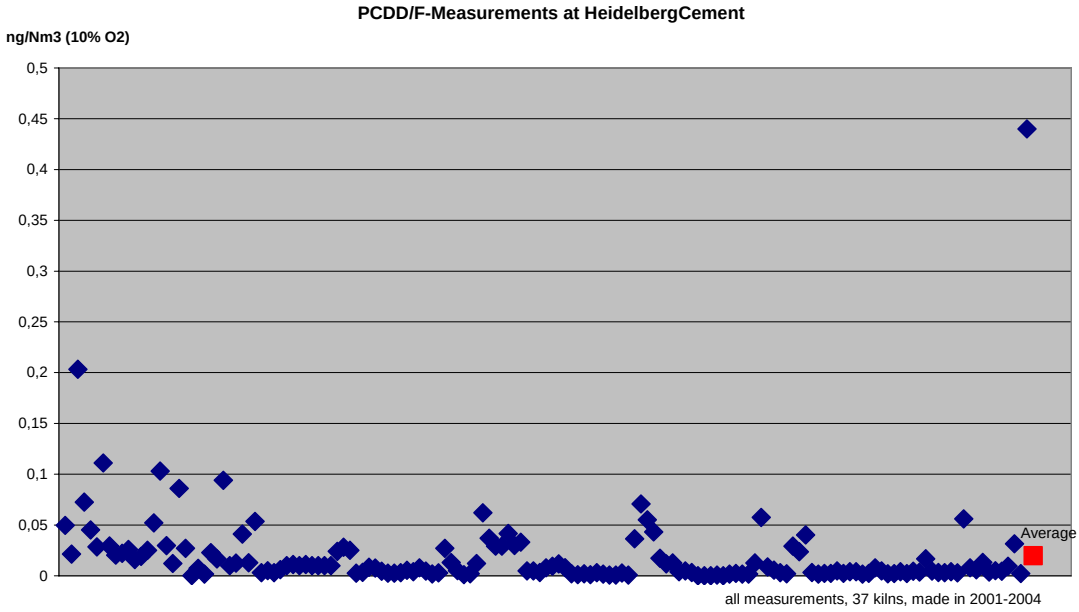

Figure 31 152 PCDD/F measurements from 43 Heidelberg kilns in 2001-2004

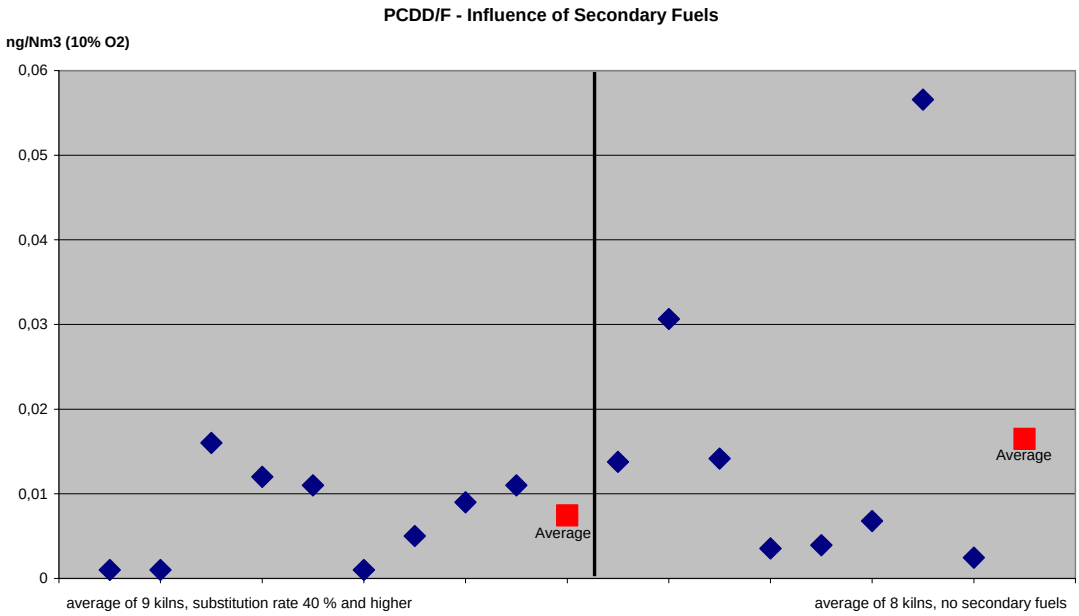

Figure 32 Heidelberg kilns using more than 40% alternative fuel compared with kilns using fossil fuel only

The highest value, 0.44 ng TEQ/m³ 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 TEQ/m³, 0.0041 TEQ/Nm³ and 0.0018 ng TEQ/m^3;

Kiln 2: <0.0041 TEQ/m³ and <0.0021 ng TEQ/m^3.

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

Table 14 PCDD/F emission data and emission factors from 5 dry European kilns using waste fuel and/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/m^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/m^3 at 10 % O_2 was: 0.0099 TEQ/m^3, 0.0125 TEQ/m^3, 0.041 TEQ/m^3, 0.0128 TEQ/m^3 and 0.0535 ng/m^3.

Plant 2:

Operates a double-string 4-stage preheater kiln with planetary coolers and a production capacity of 2000 tons per day. The concentration measured has varied in the range off 0.03-0.05 ng I-TEQ/m^3 at 10 % O_2.

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 has varied in the range off 0.03-0.06 ng I-TEQ/m^3 at 10 % O_2.

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 370 ^{o}C to about 150 ^{o}C 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 220 ^{o}C before pre-dedusting and utilization for drying in the raw mill department where after a repeated dedusting takes place at about 100 ^{o}C 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 wastes, refuses derived fuel, petcoke and used oil fed through the main burner and kiln inlet.

Table 15 Mean PCDD/F concentration in a Norwegian cement plant using a wide range of alternative fuel and raw materials (ng N-TEQ/m^3 at 11 % O_2)

Year	1995	1996	1997	1998	1999	2000	2001	2002	2003
ng/ Nm^3	0.055	0.13	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 between the Nordic Toxicity Equivalency Factor N-TEFs and the International I-TEFs is negligible as the two schemes differ only in a single congener; the N-TEF scheme gives 1,2,3,7,8-Cl_5DF a TEF of 0.01 whereas the I-TEF a value of 0.05.

6.2.4.2 Heidelberg UK

Heidelberg 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 TEQ/m^3. The results of 8 measurements of the two long wet kilns showed a

maximum concentration of 0.44 ng I-TEQ/m^3. The current authorized limit for the wet kiln is 0.8 ng TEQ/m^3.

6.2.5 Lafarge Cement Company

In a 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 with 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 operates 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 over nearly 10 years. 13 measurements were carried out over the last 4 years and covered the range 0.0014-0.0688 ng N-TEQ/m^3 at 11 % O_2.

Table 16 64 PCDD/F measurements from Lafarge Cement Company

	Data from	Main kiln type	Filter type	AF & ARM	Clinker production [t/year]	Stack emissions [ng/Nm³]
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

6.2.7 Siam Cement Company

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

Table 17 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 currently operates 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 18 Emission levels of Taiheiyo Cement plants (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 report from the Spanish cement company Uniland Cementera (Latorre, 2004) the measurements from two dry preheater kilns were reported. A 3100 ton clinker/day kiln had a PCDD/F concentration of 0.006 ng I-TEQ/m^3 at 10 % O_2 in a measurement conducted in 2000 and a 2100 t clinker/day kiln had a PCDD/F

concentration of 0.002 ng I-TEQ/m^3 at 10 % O_2 in a measurement conducted in 2002. The calculated emission factors were 0.011 and 0.005 µg I-TEQ/t clinker, respectively.

6.3 PCDD/F release levels established by estimations

Many country wide inventories are solely based on emission factors. Emission factors estimates the release of PCDD/F, often given in micrograms, when one ton of cement or clinker is produced. An emission factor is originally based on real emission measurements from a specific cement kiln but is often used to estimate the annual release from the entire industry by multiplying with the total production volumes. With great variability in raw material composition, process technology, APDC, operation etc. such extrapolation is questionable. The accuracy of such inventories can be low and not reflect the real emission situation. Emission factors published in earlier studies have a tendency to be used irresponsible by others and may lead to exaggerated estimates. Many recent inventories haven't looked up the latest and most updated information but used figures from early studies. As reflected in the next chapters, the emission factors in use are highly variable.

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 by 2005 is achievable. The upper estimate contribution of the European Cement Industry was 21 grams in 1985, i.e. 0.15 % of the total contribution. For 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% of the total release. In some inventories, the cement industry is not even mentioned (Eduljee, 1996). Emissions factor generally used in Europe range from 5 to 0.001 µg PCDD/F per ton 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 an average PCDD/F concentration in the flue gas of a dry kiln to be 0.02 ng TEQ/m^3. If an exhaust-gas volume of 2300 m^3/ton clinker and a clinker/cement ratio of 0.8 are assumed, this calculation gives an emission factor of 0.037 µg TEQ/ t cement, i.e. one quarter of the value used in the European inventory.

6.3.2 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 an exit gas flow rate of 7000 m^3/min. The contribution from the cement industry would constitute between 0.96-1.39 percent of total emissions.

6.3.3 Krasnoyarsk, Russia

According to two poster-articles by Kucherenko et al (2001a; 2001b) "*Russia is the only industrial country which does not estimate its annual dioxin emission*". The articles describe local monitoring of industrial emissions of PCDD/Fs in the city of Krasnoyarsk, a large industrial centre in Siberian region, being the main producer of aluminium metal in Russia. "*A program directed toward the decrease of the level*

of dioxins and dioxin-like compounds in the environment started in Krasnoyarsk region in 1998. A total of 80 samples were studied; 21 air samples, 35 solid waste samples, 22 sewage sludge samples and 2 samples of end products. Sample collection was carried out during normal functioning of the plants using methods certified in the Russian Federation". Emissions to air from the major industrial sources were equal to 560 g I-TEQ in 1999. An emission factor of ~ 200 µg TEQ/t was derived for the cement plant; constituting 6.5 % of the total release (see discussion in chapter 7).

6.3.4 Lombardy region, Italy

In a PCDD/F emissions inventory of the Lombardy region of Italy, Caserini and Monguzzi used the emission factors proposed by US EPA 1996, 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. 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.

6.3.5 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 POPs. Kakareka and Kukharchyk published emission estimates of PCDD/F and PCB from industrial sources in the Newly Independent States (NIS) and the Baltic countries in June 2002. An emission factor of 0.2 µg TEQ/t was used for the cement industry (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.

Table 19 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%

6.3.6 Taiwan

An inventory of dioxin emissions from major industrial sources was carried out by the Chia-Nan University of Pharmacy and Science in Taiwan in 2003 (Chen, 2004). The university "*used limited data and information to generate the inventory*" and a total of 67.25 g I-TEQ of dioxins was estimated released annually.

By using US EPAs dioxin emission factor of 0.29 ng I-TEQ/kg of clinkers produced (EPA, 1998) and annual cement production of 23.85 million tons in Taiwan in 1999, the emission of this sector was estimated to be 6.92 g I- TEQ, which accounts for over 10 % of the total emission. According to the author, there is no cement kiln taking hazardous waste as auxiliary fuel when this report was prepared, but several are in the process of such application.

6.3.7 UK Inventory 1995

In an inventory of PCDD/F sources in UK, Eduljee and Dyke (1996) used emissions factors of 0.025-1.08 μg I-TEQ/t product to estimate the release from the cement industry. The emission factors were 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 stated 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.

The UK cement industry was estimated to contribute 0.2-11 grams I-TEQ per year in 1995, which constitute 0.018-1.96 % of total emissions.

6.3.8 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 the internet and personal communication.

The report categorizes the PCDD/F sources to air into nine major sectors, wherein cement production is covered as a subcategory under Mineral Products Production. Cement production is 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 20 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			19.1	0.17	11314

Atmospheric Emission Inventory (38 countries)					
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

6.3.9 UNEP Standardized Toolkit

The UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases (UNEP, 2005) 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 of its default emission factors rather than using own measured data of questionable quality.

6.3.9.1 UNEP Standardized Toolkit default emission factors for cement production

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

The UNEP Standardized Toolkit has proposed four classes of default emission factors for cement production, differentiating between type of kiln and ESP temperature and refers to the US EPA statement in 1999 "*that hazardous waste burning does not have an impact on PCDD/F formation, PCDD/F is formed post combustion*" (Federal Register, 1999).

The Toolkit states 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 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), where the results demonstrated that the addition of tyre and/or liquid hazardous waste had no effect on the emissions results*".

Table 21 UNEP default emission factors for cement production (UNEP, 2005)

Classification	**Emission factors - µg TEQ/t of cement**				
	Air	Water	Land	Product	Residue
1. Shaft kilns	5.0	ND	ND	ND	ND
2. Wet kilns with ESP temperature >300 °C	5.0	ND	ND	ND	NA
3. Rotary kilns with ESP temperature 200-300 °C	0.6	ND	NA	ND	NA
4. Wet kilns with ESP temperature <200 °C Dry kilns preheater/precalciner, T<200 °C	0.05	ND	NA	ND	NA

The Toolkit states 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/m^3, temperatures over 300 °C increase the likelihood of finding higher emissions, typical concentrations would be 0.3 ng TEQ/m^3 and above. In some cases much higher emissions may be found and these seem 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 emission factor of 5 µg TEQ/t of cement is applied to vertical shaft kilns and wet kilns with dust collectors over 300 °C. In some Asian countries, vertical shaft kilns (VSK) are used to produce clinker. These plants are relatively small with a daily capacity from 50 t/d up to around 300 t/d. However, no measurements of PCDD /F concentrations can be found in the literature. Thus for the purpose of this Toolkit and to make a first release estimate, the same emission factor as developed for old wet

kilns (Class 2) will be applied to these plants. An emission factor of 0.6 µg TEQ/t is applied to wet kilns where the dust collector is between 200 ^{o}C and 300 ^{o}C. An emission factor of 0.05 µg TEQ/t is applied to all dry kilns and wet kilns where dust collector temperatures are held below 200 ^{o}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 noting the wastes used, the means used to introduce them to the kiln and any operational control (e.g. prevention of feeding during combustion upsets, etc.).

The Toolkit states 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.

The Toolkit states the following with regards to potential releases to land and through residues (UNEP, 2005):

> *"It should be mentioned that the dusts collected in air pollution control systems, typically electrostatic precipitators (ESP) or cyclones, mainly consist of raw materials fed into the kiln (at the end of the secondary burner). The remainder of the dust consists of emissions from the kiln that has passed the hot zone. Typically, the dusts from the ESPs/cyclones or bagfilters are re-introduced into the kiln. Therefore, the default Table 41 does not contain any emission factors for residues.*
>
> *In cases, where solid residues from flue gas cleaning equipment are not recycled into the kiln, an initial estimate of release of PCDD/PCDF in CKD would be based on the assumption that approximately 30 kg of CKD per ton of clinker (0.03 % of clinker production) is generated. This value is based on a report that gave*

0.4 million tons CKD from 13.5 million tons of clinker/cement production (Dyke et al. 1997).

Concentrations of PCDD/PCDF in the CKD are expected to vary and a range of concentrations from 0.001 to 30 ng TEQ/kg has been reported for UK kilns (Dyke et al. 1997), 1-40 ng TEQ/kg were summarized for German tests (SCEP 1994).

6.4 PCDD/F releases through solid materials

Cement kilns do not produce any by-products such as slag, ashes or liquid residues from exit gas cleaning and releases of PCDD/Fs to water is not expected (UNEP, 2003). The two main solid materials produced in cement production are cement clinker and dust materials trapped in the APCDs.

New analyses of solid materials are particularly gathered for this study from the cement companies participating in the Cement Sustainability Initiative. The data is presented as received and is believed to reflect the real situation on PCDD/F in solids.

There is however a lack of standardised methodology for sampling, sample pre-treatment, preparation and extraction of solid materials and this is a particular problem for clinker, which is hard to crush and difficult to extract, i.e. the risk for contamination is great. The VDI Guideline 3499, part 1 (EN 1948, 1996) contains a section on measurement of PCDD/F in filter dust, potash and slag. Analytical procedures for sample preparation and extraction are also described in EN 1948-2 and EN 1948-3. EPA method 1613 (Federal Register, 2000) is the analytical reference in the US but is not specific for filter dust or cementitious materials.

6.4.1 PCDD/F in cement kiln dust

Dust can be collected from various gas streams in cement production; from the kiln, from the clinker cooler, from any by-pass streams and from mills. The dusts are collected in appropriate APCDs like ESP or bag house filters. As a matter of convenience, the different dusts are commonly referred to as cement kiln dust, or CKD. The composition of dusts from the kiln, clinker cooler and the by-pass will all generally be close to the raw material composition. Dyke et al. (1997) estimated that approximately 30 kg of CKD are produced per ton of clinker, 0.3 %; the production will however vary depending on plant specific factors. Since CKDs are valuable "cement" materials they are recycled and reintroduced into the process to the highest degree possible. However, sometimes CKDs must be removed from the process for product quality reasons due to high content of sodium and potassium (Riney and Yonley, 1994; CKD, 1995).

A range of concentrations of PCDD/Fs has been reported in CKD; 0.001-30 ng TEQ/kg (Dyke et al., 1997) for UK kilns and 1-40 ng TEQ/kg for German tests (UNEP, 2003).

US EPA characterized a wide range of cement kiln dust in a Report to Congress (CKD, 1995). The report was partly based on a 1991 survey of cement manufacturers conducted by the Portland Cement Association (PCA) where data were received from 64 percent of the active cement kilns in the United States. The purposes of the sampling and analysis efforts were to: (1) characterize the PCDD/F content of clinker and CKD; (2) determine the relationship, if any, between the PCDD/F content of CKD and the use of hazardous waste as fuel; and (3) to determine the relationship, if any, between the PCDD/F content of CKD and the use of wet process versus dry process cement kilns (CKD, 1995). Clinker samples were collected from five kilns not burning hazardous waste and six kilns burning hazardous waste. PCDD/F was not detected in any cement kiln clinker samples. Tetra- through octa-chlorinated PCDD/F were detected in the recycled CKD samples obtained from 10 of the 11 kilns and in the wasted CKD samples obtained from 8 of the 11 kilns.

The average TEQ concentration in the CKD from kilns burning hazardous waste was 35 ng I-TEQ/kg; for kilns that did not burn hazardous waste, the average concentration in the net CKD was 0.03 ng I-TEQ/kg. These results were strongly influenced by very high levels in one sample (UNEP, 2003). Total CKD generation was 12.7 million metric tons, where 64 percent was recycled directly back into the kiln or raw feed system. Wasted CKD is usually disposed in piles, quarries or landfills; some is sold for use as a waste stabilizer, liming agent or materials additive. US EPA could not find organics, volatile and semi-volatile compounds in the CKD.

6.4.1.1 Data from the CSI companies on CKD

8 CSI companies reported the PCDD/F concentration in CKDs in 2005. 90 samples showed an average value of 6.7 ng I-TEQ/kg, seemingly strongly influenced by a few high level samples. The CKD samples presented in the figure comes from wet and long dry kilns, from clinker cooling, from by-pass and ESPs in dry suspension preheater kilns. All non-detect TEQ values was designated zero. The highest concentration reported was 96 ng I-TEQ/kg.

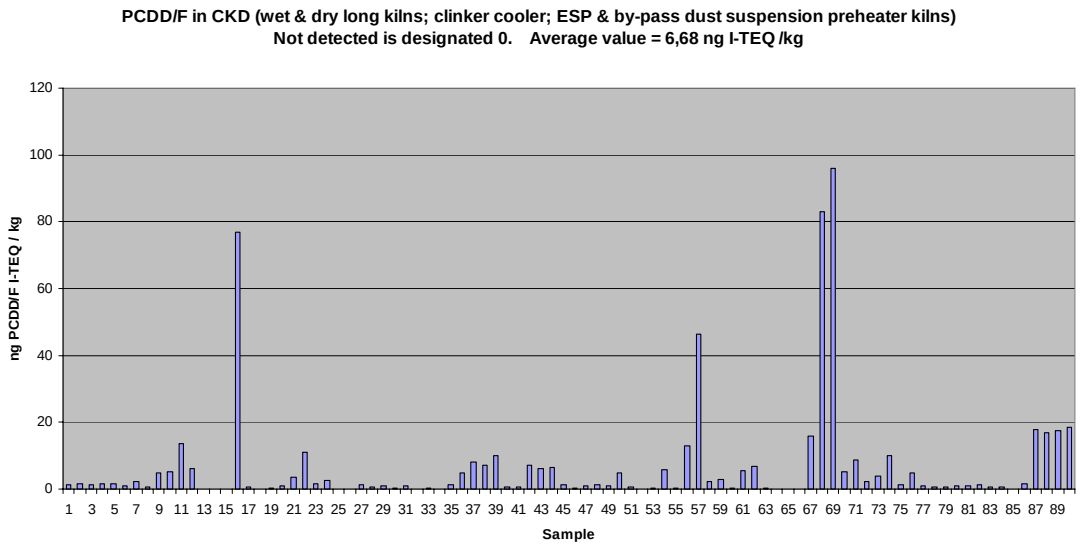

Figure 33 PCDD/F in 90 CKD samples from 8 CSI companies in 2005.

A report from Lafarge provides more details about the process conditions applied in two long wet and one long dry kiln in the US and in one German dry suspension preheater kiln.

Table 22 PCDD/F in CKD measured by Lafarge

Kiln type	Kapacity [t/d]	Fuels	Alternative raw materials	Exit gas temperature [°C]	Filter type	Year	CKD [ng/kg TEQ]
Suspention preheater	950	70% lignite 10% animal meal 20% animal fat	no ARM	150	ESP	2001	7.2
Suspention preheater	950	100% lignite	no ARM	137 - 155	ESP	2001	5
Long wet	619	85% solvents / 15% Coke	4%	185	Bag	2002	1.28
Long wet	614	85% solvents / 15% Coke	4%	185	Bag	2003	0.68
Long wet	608	85% solvents / 15% Coke	4%	185	Bag	2004	0.48
Long dry		coal / pet coke	6%	215-240	Bag	2004	0.14
Suspention preheater	2,060	36% lignite 8% animal meal 15% plastics 41% waste oil	2%	120	ESP	2005	4.51
Suspention preheater	1,350	50% pet coke / coal 6% animal meal 25% tyres 19% plastics	1%	60	ESP	2005	0.47
Suspention preheater	1,920	65% coal 7% impregnated saw dust 7% fuel oil 7% plastics 14% tires	2%	130	Bag	2005	12.3
Long dry	698	68% pet coke / coal 32% recycled liquid fuel	no ARM	200	ESP	2005	42.5
Precalciner	5,140	pet coke / coal	3.7%	100	ESP	2005	2.28

The higher bag-filter temperature of the long dry kiln doesn't seem to influence the PCDD/F concentration. The EPA method 8290 was used for analysis of the US CKD samples; the German used EN 1948.

6.4.2 PCDD/F in clinker and cement

8 CSI companies reported the PCDD/F concentration in 57 clinker samples in 2005. The average value of 1.24 ng I-TEQ/kg seems to be influenced by a few "high" level samples. The clinker samples came from wet and dry suspension preheater kilns. All non-detect TEQ values was designated zero. The highest concentration reported was 13 ng I-TEQ/kg.

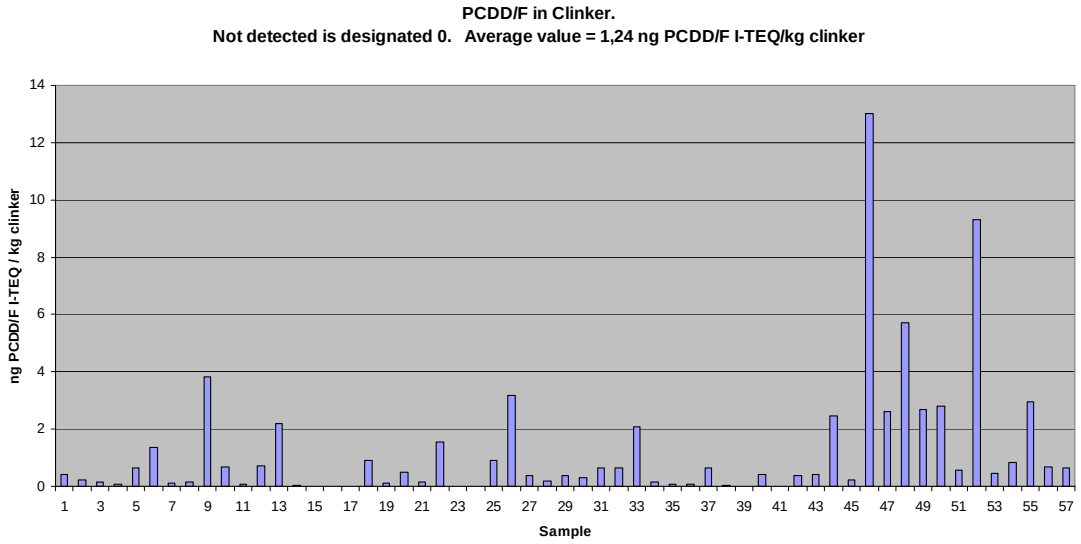

Figure 34 PCDD/F in 57 clinker samples from 8 CSI companies in 2005.

8 CSI companies reported the PCDD/F concentration in 49 cement samples in 2005. The average value of 0.91 ng I-TEQ/kg. The cement samples came from wet and dry suspension preheater kilns. All non-detect TEQ values was designated zero. The highest concentration reported was 6.9 ng I-TEQ/kg.

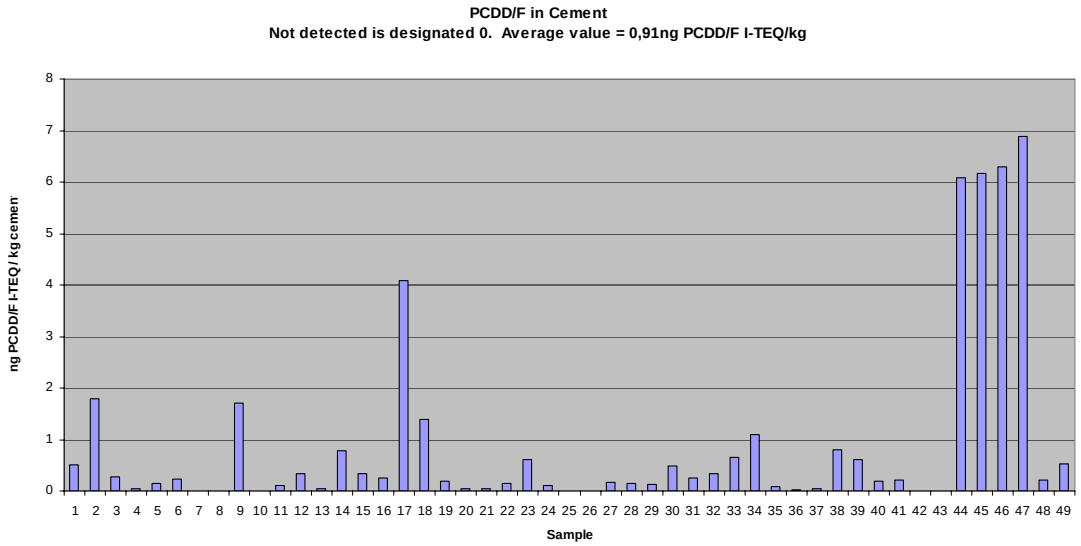

Figure 35 PCDD/F in 49 cement samples from 8 CSI companies in 2005.

6.4.3 PCDD/F in kiln feed

Two CSI companies reported the PCDD/F concentration in 11 kiln feed samples in 2005, consisting of raw meal, pellets, and slurry and raw material components. The average value of 1.4 ng I-TEQ/kg. The kiln feed samples came from wet and dry suspension preheater kilns. All non-detect TEQ values was designated zero. The highest concentration reported was 7.1 ng I-TEQ/kg.

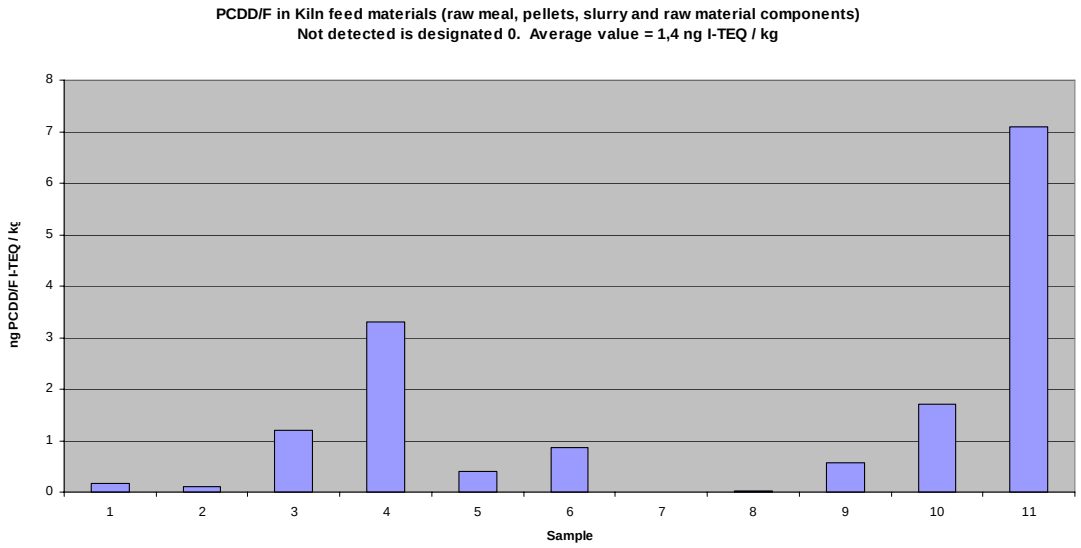

Figure 36 PCDD/F in 11 kiln feed samples from 2 CSI companies in 2005.

One CSI company reported the PCDD/F concentration in 10 alternative raw material samples in 2005, consisting of sand, chalk and different ashes. The average value of 0.99 ng I-TEQ/kg. The kiln feed samples came from wet and dry suspension preheater kilns. All non-detect TEQ values was designated zero. The highest concentration reported was 3.3 ng I-TEQ/kg.

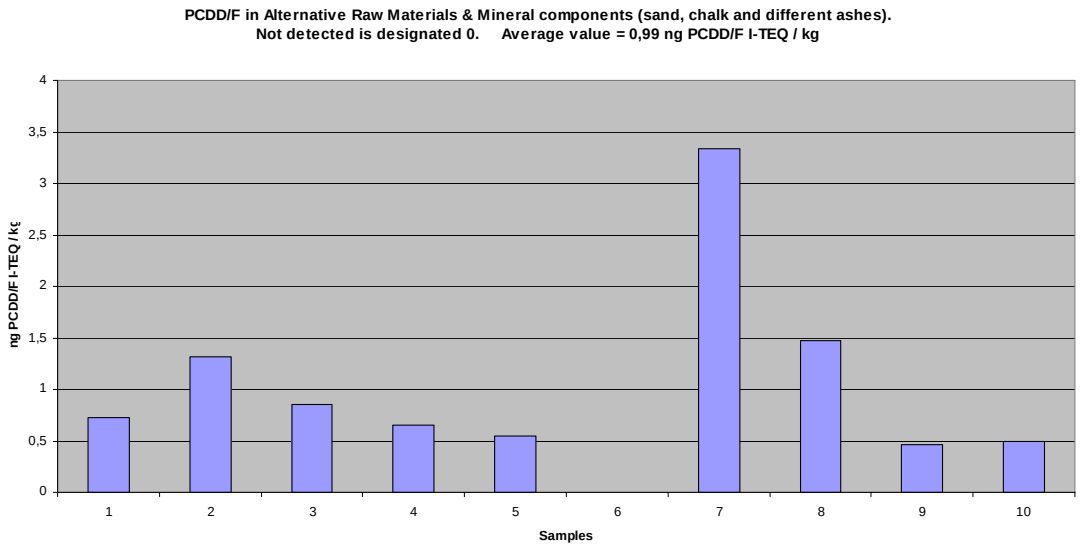

Figure 37 PCDD/F in 10 kiln alternative raw material samples from one CSI company in 2005.

7. Summary of findings and discussion

Since PCDD/F is the only group of compounds currently being regulated in many countries, 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 and show a concentration of a few nanograms per cubic meter to below the detection limit.

The data in chapter 6 indicates that higher confidence should be given to real measurements from actual plants, no matter whether they are few, than to inventories using emission factors only. Real measurements represent actual conditions with respect to raw materials and process conditions.

7.1 POPs release through emissions

A summary of all the PCDD/F measurements presented in this report is presented as average values or ranges for countries or cement companies in the table below. The data represents more than 2200 PCDD/F measurements and covers the period from early 1990s until 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 some developing countries in Africa, Asia and South America but no data however, is available from vertical shaft kilns, which is still the dominating process in China (in number of kilns).

Many of the high US data presented are from trial burns done in the 1990s, often with wet kilns feeding hazardous waste under worst scenario conditions, i.e. high waste feeding rates and high temperatures in the APCD etc. The overwhelming

majority of the data presented in chapter 6 indicates that these higher values now represent the past. The average PCDD/F flue gas concentration in European kilns is approximately 0.02 ng TEQ/m^3, representing hundreds of measurements. In general terms, emissions from the cement industry can be classified as low today, even when wastes and hazardous wastes are used as a co-fuel.

Table 23 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	89	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 - ~ 50	~750	<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 early 1990s; the number of measurements is approximate.

The data compilation is not complete in the sense that not all kilns in the world are covered and there will still be individual plants in operation which have a potential to reduce their emissions significantly. Hopefully the general knowledge about the main causes of formation and the practical measures for controlling PCDD/F emissions will enable all cement industry to get their emissions below 0.1 ng TEQ/m^3. Dry preheater/precalciner kilns generally seem to emit slightly lower levels of PCDD/F than wet kilns and data indicates that co-processing of waste and alternative raw materials in these kilns does not influence the emissions.

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/m^3 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.

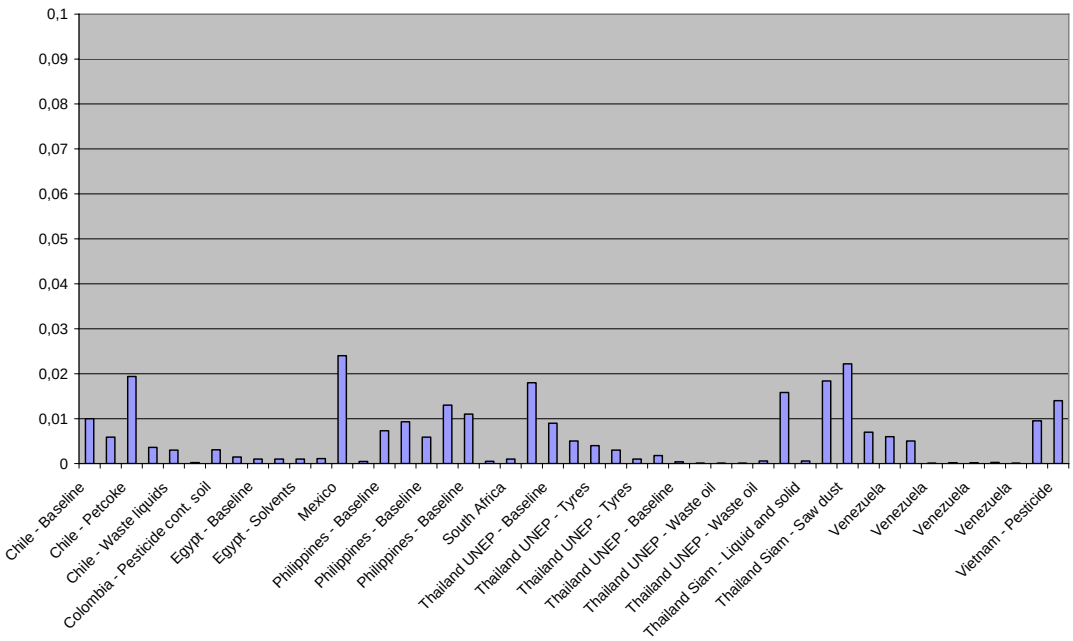

Figure 38 47 PCDD/F measurements from various developing countries (ng TEQ/m^3.

7.2 Release estimates using emissions factors

The typical dioxin contribution of the cement industry in national European inventories is about 0.5 %, using emission factors in the range 0.001-5 µg/ton cement, but the cement industry is not even mentioned in some inventories (Eduljee, 1996). The European dioxin inventory was based on a flat emission factor of 0.15 µg/t cement; the emission factors were not differentiated according to kiln technology, temperature in the APDC or waste feeding.

Data from Europe indicates that an average PCDD/F concentration in the flue gas of European dry kiln could be set to approximately 0.02 ng TEQ/m^3. If an average exhaust-gas volume of 2300 Nm^3/ton clinker is assumed and a clinker/cement ratio of 0.8, this would give an emission factor of 0.037 µg TEQ/ton cement, i.e. one quarter of the value used in the European inventory (Van Loo, 2004). This approach was used in Hong Kong assuming 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 from the local cement kiln, giving a maximum contribution of 1.4 %.

The UNEP global dioxin emission inventory for 1996 (UNEP, 1999) applies an emission factor for hazardous waste burning cement industry of 2600 µg TEQ/t, i.e. indicating a global cement industry contribution of 4.9-6.07 % of the total dioxin emissions. The emission factor for non-hazardous waste burning cement industry is 200 µg TEQ/t and the subsequent global contribution would be 2.3-2.86 % of the total emissions.

By assuming the same average exhaust-gas volume of 2300 Nm^3/ton clinker as above this figure would constitute an exit gas concentration of 1130 ng TEQ/Nm^3 and 87 ng TEQ/m^3 for hazardous waste burning and non-hazardous waste burning cement industry respectively. This is very unlikely; the highest concentration reported in the literature is approximately 50 ng TEQ/m^3 from a US wet kiln tested under worst case conditions in the early 1990s (Chadbourne, 1997). Compared with the average PCDD/F concentration in European kilns, 0.02 ng TEQ/m^3, this emission factor would give a 56,000 times higher contribution estimate for hazardous waste burning kilns. This seems unlikely, also because most European kilns substitute fossil fuel with waste materials and many are using hazardous waste on a regular basis.

The two poster-articles by Kucherenko et al (2001a; 2001b) presented in chapter 6.3.3 seem to be incomplete. There is no information about the cement production process or the process conditions, and no information about the number of samples taken or the concentration of the PCDD/F measured in the stack, only the derived emission factor, 20,2231 ng I-TEQ/t clinker, or ~ 200 µg TEQ/t. The experimental description is unfortunately split between the two poster-articles, which makes it difficult to get an overview of what has really been done and how. It seems that the stack gas sampling lasted between 5-20 minutes and was done with a "high-volume-air-sampler". To be regarded "representative" in Europe and USA you would need to sample the exit gas for 6-8 hours and to use certified sampling equipment with proper nozzle and absorbents; high-volume-air-samplers are normally used for ambient air sampling in Europe and USA.

If however we assume a dry preheater kiln with an average exhaust-gas volume of 2300 m^3/ton clinker this figure would constitute an exit gas concentration of 88 ng TEQ/m3. If we on the other hand assume a wet kiln with an average exhaust-gas volume of 4000 m^3/ton clinker this figure would constitute an exit gas concentration of 50 ng TEQ/m^3; the last assumption is the most probable. The highest flue gas concentration reported in the literature is approximately 50 ng TEQ/m^3 from a US wet kiln tested under worst case conditions in a trial burn; this kiln was supposed to run under normal conditions. The emission factor obtained in the study may be real but the information provided really doesn't support the message; also to conclude that this emission factor is representative for the cement industry (based on one measurement?) in the Russian Federation is dubious.

When UNEP investigated industrial facilities and source categories in Thailand 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 emission factor was 0.017 μg I-TEQ/t and 0.005 μg I-TEQ/t for the kilns not using waste and 0.001 μg I-TEQ/t and 0.0003 μg I-TEQ/t for the kilns co-processing hazardous waste.

The UNEP Toolkit (UNEP, 2003) provides emission factors for all source categories and processes that are listed in Annex C, Parts II and III of the Stockholm Convention. The Toolkit differentiates the 10 main source categories according to their performance and Class 1 refers to low technology (with no APC system), Class 2 refers to newer technology/controlled combustion (with minimal APC system) and finally Class 3 and 4 refers to latest technology (with sophisticated APC system). For cement kilns the following emission factors are suggested: 5 μg I-TEQ/t for vertical shaft kilns and wet cement kilns with dust collector temperatures over 300 ^{o}C; 0.6 μg I-TEQ/t for wet kilns with temperatures 200 and 300 ^{o}C; and 0.05 μg I-TEQ/t for all dry kilns and wet kilns where APCD is held below 200 ^{o}C. Compared with all the other industrial source categories given in the Toolkit, the cement industry emission factors are among the lowest (UNEP, 2003).

Many of the inventory data presented in chapter 6 have used the emission factors published by the US EPA (1998), i.e. 16.7 and 0.216 μg I-TEQ/ton cement for cement kilns co-processing and not co-processing hazardous waste, respectively, for example the Italian inventory from Lombardy.

7.3 POPs release through solid materials

When US EPA and PCA analysed clinker from US cement kilns in the beginning of the 1990s PCDD/F could not be identified (CKD, 1995). However, data from the CSI companies in this study showed an average value of 1.24 ng I-TEQ/kg for clinker and 0.91 ng I-TEQ/kg for cement. Cement is often mixed with CKDs and a higher value for cement than clinker could be expected; not the opposite.

The PCDD/F concentration in clinker was expected to be very low due to the high material temperatures inside the kiln (1450 ^{o}C). If we assume that the PCDD/F comes with the raw material (an average value of 1.4 ng I-TEQ was found in the feed materials) and/or the fuel, we end up with a dilemma: It should be physically impossible for PCDD/F to survive the temperatures inside the kiln; the PCDD/F must be due to other reasons. One possible explanation for the PCDD/F in clinker could be contamination through ambient air in the cooling process. Thousands of cubic meter of ambient air are used for cooling and investigations from 8 EU countries have shown concentrations from 1 to 705 fg (femtogram) I-TEQ/m^3 for both urban and rural air (Fiedler, 2003). A second possible explanation could be contamination through adsorption of dust and material residues in the cooler; the possibility for adsorption of dust layers is great. A third possibility which cannot be ruled out for the time being is contamination through the sample preparation for the analysis. Clinker is hard spheres which are difficult to crush and contamination during sample preparation in the laboratory is not impossible.

A range of concentrations between 0.001-40 ng TEQ/kg has been reported for PCDD/F in CKDs in the literature. The data from 8 CSI companies collected for this study showed an average value of 6.7 ng I-TEQ/kg for 90 samples; the highest

concentration reported was 96 ng I-TEQ/kg. The CKD samples constituted different dust sources from wet and long dry kilns, from clinker cooling, from by-pass and ESPs in dry suspension preheater kilns. Kiln feed samples showed an average value of 1.4 ng I-TEQ/kg and alternative raw material an average value of 0.99 ng I-TEQ/kg.

Comparison with other known materials may put the figures in perspective. For example residues from municipal waste incineration (MSWI) and other combustion processes have shown levels up to 13,000 ng PCDD/F TEQ/kg in fly ash from MSWI; up to 5,800 ng PCDD/F TEQ/kg have been found in fly ash from wood combustion and up to 42,000 ng PCDD/F TEQ/kg have been found in soot from home heating systems.

Contaminated soils within the EU have concentrations from several hundred to around 100,000 ng PCDD/F TEQ/kg dry matter. The highest concentrations were found in Finland at sites contaminated with wood preservatives and the Netherlands close to a scrap car and scrap wire incinerator. US EPA has estimated mean TEQ values for background urban and rural soils to be 13.4 and 4.1 ng I-TEQ/kg of soil, respectively (Fiedler, 2003).

Sediments within the EU normally range from a few ng PCDD/F TEQ/kg up to 50 ng TEQ/kg dry matter. However, hotspots have been identified in many countries where concentrations exceed 1000 ng PCDD/F TEQ/kg; up to 80,000 ng I-TEQ/kg were reported from Finland downstream from a wood preservative producing site. Cores from 11 lakes/reservoirs located in various geographic locations throughout the United States were selected to represent background conditions (i. e., no known PCDD/F sources nearby). Based on the most recently deposited sediments, the PCDD/F TEQ concentrations ranged from 0.11 ng TEQ/kg to 15.6 ng TEQ/kg with a mean of 5.3 ng TEQ/kg (Fiedler, 2003).

Austria and Germany have established a maximum permissible concentration of 100 ng PCDD/F TEQ per kg dry matter for sewage sludge applied to agricultural land. The concentrations within several EU countries range from below 1 ng PCDD/F TEQ/kg to around 200 ng TEQ/kg dry matter, with levels in Germany reaching over

1000 ng PCDD/F TEQ/kg. Average concentrations of PCDD/F in sewage sludge are quite similar for each country, lying between 10 and 40 ng PCDD/F TEQ/ kg (Fiedler, 2003).

Fish bio-accumulate PCDD/Fs and several hundred ng TEQ/kg fat have been detected, which is higher than found in terrestrial animals, such as cattle, pig, or chicken. Top-predators like sea eagles or guillemots also showed high concentrations of PCDD/F: as an example in Finland, 830 to 66,000 ng TEQ/kg fat were found in white-tailed sea eagles. The Swedish Dioxin Database reported a wide range of dioxin concentrations in the blubber of ringed seal: 6.3 to 217 ng TEQ/kg fresh weight (Fiedler, 2003).

Santillo et al (2001) analyzed butter samples randomly collected from 24 countries; the median of this survey was 0.51 ng TEQ/kg for PCDD/F and 1.02 ng WHO-TEQ/kg for dioxin-like PCBs. The annual means of PCDD/F (ng TEQ/kg fat) in breast milk from mothers in Germany, from a total of 2,438 samples during the year 1985 – 1998 dropped by approximately 60 % during ten years from ca. 30 ng TEQ/kg fat to 12.9 ng TEQ/kg fat (Fiedler, 2003).

This comparison shows that products and residues from the cement industry has dioxin levels in the same magnitude as foods like fish, butter, breast milk, and less than the maximum permissible concentration of 100 ng TEQ per kg for sewage sludge applied to agricultural land.

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

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

- ✓ Particulate surfaces, i.e. sites which can catalyse the formation;
- ✓ Hydrocarbons and chloride(s);
- ✓ Appropriate temperature window between 200 °C and 450 °C, with a maximum at around 350 °C;
- ✓ Appropriate residence time, probably more than 2 seconds.

8.1 Principle control measures

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.

8.2 Best available techniques and best environmental practise

The cement production process has an impact on the energy use and the emissions to air. For new plants and major upgrades the best available techniques (BAT) for the production of cement clinker is a dry process kiln with multi-stage

preheating and precalcination. The following general primary measures (integrated process optimisation) seem to be sufficient to comply with an emission level of 0.1 ng PCDD/F I-TEQ/Nm^3:

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

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

  - The use of modern 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 sulfur, nitrogen, chlorine, metals and volatile organic compounds should be selected.

Expert judgement by the European IPPC Bureau has played a key role in identification of Best Environmental Practice (BEP) and BAT for the cement industry (IPPC, 2001). In the Best Available Technique Reference (BREF) document, 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.

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.

8.3 Critical measures – a summary

The following primary measures are considered to be most critical in avoiding the formation and emission of PCDD/F from cement kilns:

- ✓ Quick cooling of kiln exhaust gases to lower than 200 ^{o}C in long wet and long dry kilns without preheating. In modern preheater and precalciner kilns this feature is already inherent.

- ✓ Limit or avoid alternative raw material feed as part of raw-material-mix if it includes organic materials.

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

- ✓ Monitoring and stabilisation of critical process parameters, i.e. homogenous raw mix and fuel feed, regular dosage and excess oxygen.

9. Conclusion

This report evaluates around 2200 PCDD/F measurements made from the late 1970s until recently. The data represent emission levels from large capacity processing technologies, including wet and dry process cement kilns, performed under normal and worst case operating conditions, with and without the co-processing of a wide range of alternative fuel and raw materials and with wastes and hazardous wastes fed to the main burner, to the rotary kiln inlet and to the preheater/precalciner. Vertical shaft kilns, regarded to be an obsolete technology and still common in many countries, have not been dealt with in this report due to lack of emission data. The PCDD/F data presented in this report shows that:

- Most cement kilns can meet an emission level of 0.1 ng TEQ/Nm^3 if primary measures are applied;

- Co-processing of alternative fuels and raw materials, fed to the main burner, kiln inlet or the precalciner does not seem to influence or change the emissions of POPs;

- Data from dry preheater cement kilns in developing countries presented in this report show very low emission levels, much lower than 0.1 ng TEQ/Nm^3.

The emissions from modern dry preheater/precalciner kilns seem generally to be slightly lower than emissions from wet kilns. A common practise in many countries today is to co-process waste and alternative raw materials in dry preheater kilns, thereby saving fossil fuel and virgin raw materials. One example illustrates this: a UNEP project measured emissions between 0.0001-0.018 ng TEQ/m^3 from a dry preheater kiln in Thailand replacing parts of the fossil fuel with tyres and hazardous waste; the lowest concentration was found when the kiln was co-processing hazardous waste, 0.0002 ng TEQ/m^3.

Emission data from US cement kilns in the 1980s and first part of the 1990s stands in contrast to these findings. They often indicated that cement kilns co-processing hazardous waste as a co-fuel had much higher PCDD/F emissions than kilns co-processing non-hazardous wastes or using conventional fuel only. In all recent documents however, the US EPA has explained the most probable cause for these findings, namely that cement kilns burning hazardous waste were normally tested under "worst" scenario trial burn conditions, i.e. typically high waste feeding rates and high temperatures in the air pollution control device, conditions today known to stimulate PCDD/F formation. Cement kilns burning non-hazardous waste or conventional fossil fuel only were however tested under normal conditions, no "worst" scenario conditions, making comparison between hazardous waste burning and non-hazardous waste burning kilns questionable. Reducing the temperature at the inlet of the air pollution control device is one factor shown to have a significant impact on limiting dioxin formation and emissions at all types of cement kilns, independent of waste feeding, as lower temperatures are believed to prevent the post-combustion catalytic formation of PCDD/Fs.

For new cement plants and major upgrades the best available techniques for the production of cement clinker is 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 for the energy use. The most important primary measures to make sure compliance with an emission level of 0.1 ng TEQ/Nm^3 is quick cooling of the kiln exhaust gases to lower than 200°C in long wet and long dry kilns without preheating. Modern preheater and precalciner kilns have this feature already inherent in the process design. Feeding of alternative raw materials as part of raw-material-mix should be avoided if it includes organic materials and no alternative fuels should be fed during start-up and shut down.

This report also provides a large number of measurements of PCDD/F in products and residues from the cement industry. The levels are normally low and of the same magnitude as found in foods like fish, butter and breast milk as well as soil, sediments and sewage sludge.

Since PCDD/F is the only group of POPs commonly being regulated up to know, there are fewer measurements available for HCB and PCBs. 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 concentrations below the detection limit.

10. References and bibliography

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