Review

Formation, release and control of dioxins in cement kilns

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Abstract

Co-processing of hazardous wastes in cement kilns have for decades been thought to cause increased emissions of PCDD/PCDFs – a perception that has been evaluated in this study. Hundreds of PCDD/PCDF measurements conducted by the cement industry and others in the last few years, on emissions and solid materials, as well as recent test burns with hazardous wastes in developing countries do not support this perception. Newer data has been compared with older literature data and shows in particular that many emission factors have to be reconsidered. Early emission factors for cement kilns co-processing hazardous waste, which are still used in inventories, are shown to be too high compared with actual measurements. Less than 10 years ago it was believed that the cement industry was the main contributor of PCDD/PCDFs to air; data collected in this study indicates however that the industry contributes with less than 1% of total emissions to air.

The Stockholm Convention on POPs presently ratified by 144 parties, classifies cement kilns co-processing hazardous waste as a source category having the potential for comparatively high formation and release of PCDD/PCDFs. This classification is based on early investigations from the 1980s and 1990s where kilns co-processing hazardous waste had higher emissions compared to those that did not burn hazardous waste. However, the testing of these kilns was often done under worst case scenario conditions known to favour PCDD/PCDF formation.

More than 2000 PCDD/PCDF cement kiln measurements have been evaluated in this study, representing most production technologies and waste feeding scenarios. They generally indicate that most modern cement kilns co-processing waste today can meet an emission level of 0.1 ng I-TEQ/m^3, when well managed and operated. In these cases, proper and responsible use of waste including organic hazardous waste to replace parts of the fossil fuel does not seem to increase formation of PCDD/PCDFs.

Modern preheater/precalciner kilns generally seems to have lower emissions than older wet-process cement kilns. It seems that the main factors stimulating formation of PCDD/PCDFs is the availability of organics in the raw material and the temperature of the air pollution control device. Feeding of materials containing elevated concentrations of organics as part of raw-material-mix should therefore be avoided and the exhaust gases should be cooled down quickly in long wet and long dry cement kilns without preheating.

PCDD/PCDFs could be detected in all types of solid samples analysed: raw meal, pellets and slurry; alternative raw materials as sand, chalk and different ashes; cement kiln dust, clinker and cement. The concentrations are however generally low, similar to soil and sediment.

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1. Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) entered into force on 17 May 2004 and aims among others to prevent and minimise as much as possible formation and releases of unintentional POPs such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). Four main source categories are listed in the Annex of the Stockholm Convention as "having the potential for comparatively high formation and release of these chemicals to the environment" (UNEP, 2001; Richter and Steinhauser, 2003). Cement kilns co-processing hazardous waste is one of these.

The Cement Sustainability Initiative (CSI) was launched in 1999 under the auspices of the World Business Council for Sustainable Development (WBCSD); it is supported by 16 of the leading companies in the cement industry operating in more than 70 countries (WBCSD, 2005). The cement industry is today distributed throughout the world and in 2003 produced approximately 1940 million tons of cement (Cembureau, 2004). The cement industry consumes billions of tons of raw materials and more than 300 million tons of coal, and is believed to contribute to about 5% of the global anthropogenic CO_2 emissions (Worrell et al., 2001; WBCSD, 2002; Oss and Padovani, 2003). Approximately 60% of the CO_2 originates in calcination of limestone; the remaining 40% is due to combustion of fossil fuel.

One of the main routes towards sustainability in the cement industry is to reduce the use of non-renewable fossil fuels and virgin raw materials by substituting these with high caloric waste and alternative raw materials. The perception that cement kilns substituting parts of its fossil fuel with waste materials is a potential PCDD/PCDF emitter is taken seriously and the objective of this paper is to present recent data on PCDD/PCDF releases from the industry globally, to compare these with older data and to evaluate the magnitude of their release contribution.

The data presented in this article have been gathered from three main sources: (1) publicly available reports and articles where actual measurements from cement kilns have been conducted, often in test burns, and with complete references; (2) national or regional inventories which present PCDD/PCDF contribution estimates from the cement industry, usually based on emission factors found in literature; and (3) measurements by cement companies performed during last years.

2. Production of cement

Cement production involves heating, calcining and sintering of blended and ground raw materials, typically limestone and clay or shale and other materials to form clinker. Clinker burning takes place at a material temperature of 1450 °C in rotary kilns, i.e. inclined rotating cylinders lined with heat-resistant bricks. After cooling, the clinker is ground with a small amount of gypsum to give Portland cement, the most common type of cement. In addition, blended cements are produced by intergrinding cement clinker with small amounts of materials like fly ash, granulated blast furnace slag, limestone, natural or artificial pozzolanas (Duda, 1985; Roy, 1985; IPPC, 2001).

Depending on how the raw material is handled before being fed to the kiln, basically four different types of rotary kiln processes can be distinguished: the dry, semi-dry, semi-wet and wet processes. In the dry process the feed material enters the kiln in a dry, powdered form. The kiln systems comprise a tower of heat exchange cyclones in which the dry raw material feed is preheated ("suspension preheater kiln") by the rotary kiln's hot exit gases prior to entering

the kiln. The calcination process can almost be completed before the raw material enters the kiln if part of the fuel is added in a secondary combustion chamber, the precalciner. In the wet process, the feed material is grinded with water and the resulting slurry, typically containing 30–40% water, is fed directly into the upper end of the inclined kiln.

In the semi-dry or semi-wet processes water is either added to the ground dry feed material or removed from the slurry, e.g., by filter presses, resulting in a feed material containing about 15–20% moisture. Pellets of feed material are loaded onto a travelling grate where they are preheated by the rotary kiln's hot exit gases. By the time the feed material reaches the kiln entrance, the water has evaporated and calcination has begun.

Preheater kilns usually have four cyclone stages with a capacity of approximately 4000 tons of clinker per day. A considerable capacity increase can be obtained with a second combustion device located between the rotary kiln and the preheater section, the precalciner, were up to 60% of the total fuel of the kiln system can be burnt. Modern preheater/precalciner kiln systems with 5–6-staged cyclone preheater are considered to constitute best available techniques (BAT). Such a configuration will use 2900–3200 MJ of energy per ton of clinker and can have a production capacity up to 10 000 tons of clinker per day (Environment Agency, 2001; IPPC, 2001). The primary fuels used in the cement industry are coal, petcoke, heavy oil and – to a lesser extent – natural gas. The average exhaust-gas volume is 2300 Nm^3/ton of clinker. Dust, or fine particulates, is collected and controlled in air pollution control devices (APCD) like electrostatic precipitators (ESP) and/or bag filters (fabric filters).

Vertical shaft kilns is still the dominating production technology in China accounting for 60% of the Chinese production (approximately 4000 vertical shaft kilns existed in 2005), which was 1065 billion ton in 2005 and accounting for approximately 50% of the world production (Karstensen, 2006b). Vertical shaft kilns are refractory-lined, vertical cylinder, 2–3 m in diameter and 8–10 m high and fed from the top with a mix of dry ground raw material and fuel called black meal, consisting of approximately 13% of coal or coke and produce usually less than 300 tons of clinker per day.

In the cement clinker making process it is necessary to maintain material temperatures of up to 1450 °C in order to ensure the sintering reactions required. In addition, the clinker needs to be burned under oxidising conditions; typically 2–4% excess oxygen is required in the combustion gases. A modern rotary cement kiln has many inherent features, which makes it ideal for hazardous waste treatment; such as high temperatures, long residence time, surplus oxygen during and after combustion, good turbulence and mixing conditions, thermal inertia, counter currently dry scrubbing of the exit gas by alkaline raw material, fixation of the traces of heavy metals in the clinker structure, no generation of by-products such as slag, ashes or liquid residues and complete recovery of energy and raw material components in the waste (Chadbourne, 1997) (see Fig. 1).
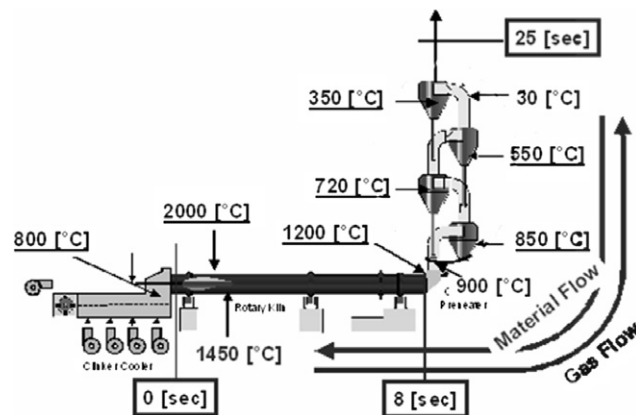

Fig. 1. Temperatures and gas residence time in a four-stage preheater kiln; gas temperature is underlined (Waltisberg, 2001).

2.1. Feeding of hazardous wastes

Cement kilns have proven to be effective means of recovering value from waste materials (Kreft, 1995; Balbo et al., 1998) and co-processing in cement kilns is now, despite perceptions, an integral component in the spectrum of viable options for treating hazardous and industrial wastes, mainly practised in developed countries. Alternative fuel and raw materials (AFR) derived from industrial sources such as tyres, waste oil, plastics, solvents and many more are commonly used by the cement industry as substitute fuels, but also hazardous organic wastes have been used as a co-fuel since the early 1970s (Chadbourne and Helmstetter, 1983; Burton, 1989; Hansen et al., 1996). Many tests have investigated the influence on the emissions and the product quality when waste materials are used to replace either fuels or raw materials in clinker production. So far, no adverse impacts have been identified (Lauber, 1982, 1987; Branscome et al., 1985; Garg, 1990; Karstensen, 1994; Chadbourne, 1997; Balbo et al., 1998).

Proper preparation and selection of appropriate feed points is however essential for environmentally sound co-processing. This means that alternative raw materials free of organic compounds can be added to the raw meal or raw slurry preparation system while mineral wastes containing significantly quantities of organic components must be 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 or dry kiln ("mid-kiln"). Alternative fuels must be fed to the main burner, to the precalciner, eventually to the kiln inlet, or to the mid-kiln of a long wet kiln. Most importantly is to ensure sufficient temperature, oxygen, retention time, and proper mixing conditions.

A stable cement kiln will comply with the US TSCA PCB incineration criteria which require a temperature of 1200 °C and 2 s retention time at 3% oxygen (Dempsey and Oppelt, 1993; Federal Register, 1999; Lee et al., 2000) or the EU Directive 2000/76/EU, requiring a temperature of 850 °C

for at least 2 s for the incineration of non-chlorinated hazardous waste and 1100 °C and 2 s retention time for organic substances containing more than 1% halogen at 2% oxygen (Council Directive, 2000). Another important criterion for environmentally sound destruction and irreversible transformation is to achieve a sufficient destruction efficiency (DE) or destruction and removal efficiency (DRE) (Basel Convention, 2007). The DRE consider emissions to air only while the more comprehensive DE is also taking into account all other out-streams, i.e. products and liquid and solid residues. A DRE value greater than 99.9999% is required for disposal of POPs in the US (Federal Register, 1999).

3. Formation of PCDD/PCDFs in thermal processes

Most of the research done on PCDD/PCDF formation mechanisms in thermal processes is from municipal solid waste (MSW) incinerators. From these we know that PCDD/PCDFs can result from a combination of formation mechanisms, depending on kiln and process configuration, process and combustion conditions, feed characteristics, and type and operation of the APCD (Lustenhouwer et al., 1980; Shaub and Tsang, 1983; Dickson and Karasek, 1987; Karasek and Dickson, 1987; Stieglitz et al., 1989a,b; Kilgroe et al., 1990; Dickson et al., 1992; Altwicker et al., 1994; Gullett and Lemieux, 1994; Sidhu et al., 1994; Stieglitz et al., 1995; Huang and Bue-

kens, 1996; Buekens et al., 2001; Everaert and Baeyens, 2002). From these studies it can be deducted that the possibilities for formation of PCDD/PCDF in cement kilns will be restricted to the "cooler" cyclone preheater zone and the post-preheater zone, comprising the cooler, mill dryer and APCD.

4. Factors influencing formation of PCDD/PCDFs in cement production

The cement production process in a preheater kiln process can be divided in three thermal zones: (1) the high temperature rotary kiln zone, (2) the cyclone preheater zone, and (3) the post-preheater zone (see Fig. 2).

The high temperature rotary kiln zone includes the burning or sintering zone where the combustion gases from the main burner remain at a temperature above 1200 °C for 5–10 s, with peak gas temperatures up to 2000 °C. In the cyclone preheater zone, at the upper end of the kiln where the raw meal is added, the gas temperatures typically range from approximately 850–250 °C and can have a retention time up to 25 s. In this section, moisture is evaporated and the raw material is partly calcined. In modern kilns, a second precalciner burner is installed between the kiln and the preheater. The post-preheater zone constitutes the cooler, the mill dryer and the air pollution control device, with gas temperatures typically in the range from approximately 250–90 °C from the top of the preheater
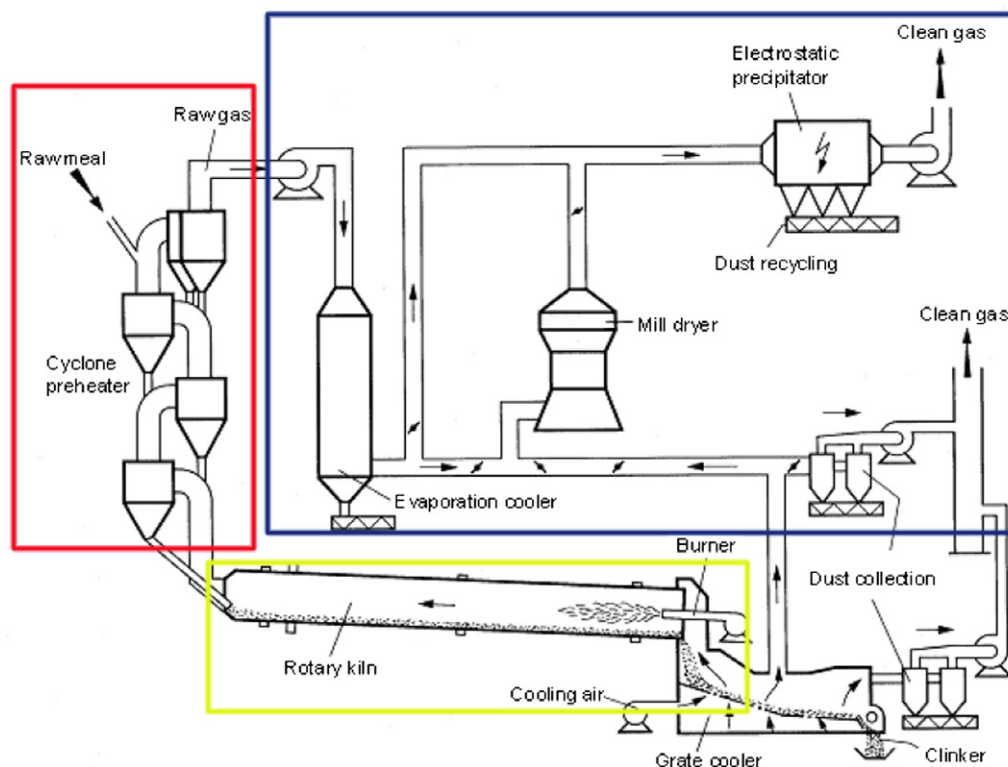

Fig. 2. Rotary kiln with cyclone preheater and gas dust collection. The frames define three distinct thermal zones.

to the exit stack outlet. The retention time of the kiln material in the rotary kiln is 20–30 and up to 60 min depending on the length of the kiln. While the temperature profiles may be different for the various kiln types, the peak gas and material temperatures remain the same for any case.

4.1. Products of incomplete combustion – from the fuel

Organic emissions from cement kilns can have three potential sources: the fuel (including waste), the raw material or be formed as new compounds via reactions in the preheater (products of incomplete combustion, PICs). Fuels are fed finely milled to burners and exposed to the gas-phase temperatures up to 2000 °C and 850–1200 °C in the primary and the precalciner burners, respectively. Combustion theory suggests that cement kilns provide sufficient reaction time, oxygen concentration and high temperatures to destroy all the organic present in the fuel and waste fuel feed and efficient burnout of the organic components should therefore result in limited carryover of PICs to the cyclone preheater zone and the post-preheater zone, potential precursors to PCDD/PCDF (Eduljee and Cains, 1996; Eduljee, 1998). This was to some extent confirmed by Waltisberg (2001) who measured volatile organic carbons (VOC) and benzene at the kiln inlet in a preheater kiln to investigate if organic materials from the fossil fuel could survive the main flame temperature; all the measurements were however below the detection limit. Suderman and Nisbet (1992) investigated emissions with and without fuel substitution and concluded that there is "no significant difference in stack emissions when 20–40% of the conventional fuel is replaced by liquid wastes", implying complete destruction of the fuels. An improper mixing of fuel and oxygen can potentially result in poor combustion and thus leads to emissions, especially from the precalciner were the residence time and temperature is less than in the main burner.

4.1.1. Products of incomplete combustion – DRE of hazardous wastes

Many studies have been measuring the DREs of hazardous wastes fed together with normal fuels. Already in 1975 Mac Donald et al. (1977) carried out test burns with hazardous chlorinated hydrocarbons containing up to 46% chlorine in a wet cement kiln in Canada and concluded that "all starting materials, including 50% PCBs, were completely destroyed to at least 99.98% efficiency in all cases" and emissions of high molecular weight chlorinated hydrocarbons were not detected. Similar tests with chlorinated and fluorinated hydrocarbons conducted in a wet kiln in Sweden showed that the destruction and removal efficiency of PCBs was better than 99.99998% and that there were no change in product quality or any influence on process conditions with a chlorine input up to 0.7% of the clinker production (Ahling, 1979).

Viken and Waage (1983) carried out test burns in a wet kiln in Norway feeding 50 kg PCBs/h, showing a DRE better than 99.9999% and no traces of PCB in clinker or dusts could be detected. Benestad (1989) carried out two studies in a dry preheater cement kiln in Norway and concluded that the "type of hazardous waste used as a co-fuel" does not influence the emissions and that the destruction of PCBs was better than 99.9999%. "0.2 ng N-TEQ/m^3 and 0.1 ng N-TEQ/m^3 were measured when feeding hydrocarbon waste (fatty acid esters, solvents and paint residues) and PCB-waste, respectively".

Thermal stable and refractory materials, such as carbon tetrachloride, perchloroethylene, chlorobenzenes and sulphur hexafluoride have been used to demonstrate that cement kilns can achieve the best DREs when fed at the hot end of cement kilns and earlier data which indicated cement kiln DRE results below 99.99% for hazardous wastes are believed to be due to either outdated sources or improperly designed tests, or both (Chadbourne, 1997; Cement Kiln Recycling Coalition, 2002).

4.1.2. Products of incomplete combustion – formation in the preheater

Trenholm and Hlustick (1990) investigated organic emissions from a preheater/precalciner kiln when feeding liquid wastes to the main burner and solid wastes spiked with monochlorobenzene (MCB) to the kiln inlet. Organic concentration in the alkali by-pass located at the kiln inlet, was generally much lower than in the main stack, reflecting the high temperature conditions and destruction ability in the kiln. Organic emissions in the main stack were believed to be related to organic material in the raw meal (raw material mix) and/or the coal combustion in the precalciner forming PICs. A strong correlation between MCB and the chlorine concentration was established; the MCB concentration increased with increasing input of chlorine when benzene was present.

That MCB can be formed in the preheater was confirmed in another study, where tests on the preheater stack measured a greater quantity of MCB coming out than introduced into the preheater (Lamb et al., 1994). Also, a strong correlation between the emissions of MCB and the input chlorine was observed experimentally, concluding that MCB was formed in the preheater as a result of surface-catalyzed chlorination of organic compounds.

Eduljee (1998) postulated that both chlorobenzenes and chlorophenols can be formed as PICs within the preheater, but due to oxygen concentration, chlorobenzenes may be formed in preference to chlorophenols. A reaction pathway dominated by chlorobenzenes would tend to favour the higher chlorinated congeners of PCDDs at the expense of the lower chlorinated congeners, and hence lower the I-TEQ value of the emission sample relative to a reaction in which chlorophenols dominated (Eduljee, 1998). However, Abad et al. (2004) found that the major contribution

to total TEQ came from the lower chlorinated congeners of PCDFs, especially 2,3,7,8-tetrachlorodibenzofuran and 2,3,4,7,8-pentachlorodibenzofuran.

4.2. Feeding of hazardous waste

Krogbeumker (1994) compared the emissions with the burning of coal only and the use of substitute fuels like solvents with varying amounts of chlorine. The tests resulted in an increase in PCDD/PCDF emissions, from a low base of 0.002–0.006 ng TEQ/m^3 to 0.05 ng I-TEQ/m^3 for chlorinated solvents, and to 0.08 ng I-TEQ/m^3 in the case of used tyres.

PCDD/PCDF emissions data are available for most hazardous waste burning cement kilns in the US. The US EPA has during the last 25 years published extensive sets of data from testing of cement kilns; approximately 750 measurements can be found in various databases (Federal Register, 1999, 2000, 2002a,b). The results range from 0.004 to approximately 50 ng TEQ/m^3 and are highly variable among different kilns and in some multiple tests on a single kiln; the US EPA states that the confidence to many of the results is low (Chadbourne, 1997; EPA, 2000; HWC MACT Data Base NODA Documents, 2002).

Emissions testing of US cement kilns in the 1980s and 1990s often showed that cement kilns co-processing hazardous waste as a co-fuel had much higher PCDD/PCDF emissions than kilns co-processing non-hazardous wastes or using fossil fuel only. One reason for this difference can be attributed to the fact that cement kilns burning hazardous waste were normally tested under "worst" scenario test burn conditions to identify the outer control limits, while cement kilns burning non-hazardous waste or fossil fuel only were tested under normal operating conditions, no "worst" scenario conditions, making a comparison difficult. Worst case conditions often implied testing with high temperature in the APCD, conditions known today to increase the risk for higher emissions of PCDD/PCDF. Another reason is that the dominating technology at that time was long wet and long dry kilns, often without exit gas coolers.

The Thai Pollution Control Department and UNEP carried out a joint emission inventory of Thai industry and among the facilities selected for sampling was a dry process cement plant with two kilns tested, with and without co-processing of liquid hazardous waste and/or tyres (UNEP/IOMC, 2001). PCDD/PCDF measurements were performed at both kilns under baseline operation at full load when fuelled with a blend of lignite and petroleum coke as primary and secondary fuel, and with waste tyres or liquid hazardous waste (waste oils and contaminated solvents) to replace a certain percentage of the secondary fuel at the precalciner. The concentrations measured were all below 0.02 ng I-TEQ/m^3 and as low as 0.0001 ng I-TEQ/m^3; the means were 0.0105 ng I-TEQ/m^3 and 0.0008 ng I-TEQ/m^3 for the baseline operation conditions and 0.003 ng I-TEQ/m^3 and 0.0002 ng I-TEQ/m^3 for the

test performed with substitute fuels, respectively. The report concluded that "2,3,7,8-Cl$_4$DD 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".

A Heidelberg cement kiln in the South of Norway (3500 ton clinker/day) has been fired with a mix of coal, liquid and solid hazardous wastes, refuses derived fuel, petcoke and used oil, accounting for approximately 40% of the heat input, for the last 15 years (Haegermann, 2004). Annual PCDD/PCDF measurements have been performed since 1992 and the concentration has varied between 0.025 and 0.13 ng N-TEQ/m^3 at 10% O$_2$. Studies have not been able to establish any influences on the PCDD/PCDF emissions.

Holcim Colombia (Herrera, 2003) carried out a test burn with 900 tons of POPs contaminated soil (DDT, aldrin, dieldrin and pentachlorbenzene) fed to the kiln inlet of a 58 m long five-stage preheater kiln with a clinker production capacity of 3350 ton/day (fired with bituminous coal). The three PCDD/PCDF measurements performed during the test burn, including one blank measurement under baseline operation ranged 0.00023–0.0031 ng I-TEQ/Nm^3 at 10% O$_2$ and showed no influence of the POPs feeding.

A test burn with used industrial solvents was carried out in Egypt (Farag, 2003). A baseline test was carried out before and after the test burn and all three results showed a PCDD/PCDF concentration less than 0.001 ng TEQ/m^3.

A test burn with and without a mix of two expired toxic chlorinated and fluorinated insecticide compounds (Fenobucarb and Fipronil) introduced at a rate of 2 tons/h through the main burner was carried out in a preheater/precalciner cement kiln in Vietnam (Karstensen et al., 2006). The test burn showed destruction efficiency better than 99.999997% and 99.999985% for Fenobucarb and Fipronil, respectively, and the PCDD/PCDF results for both days were below the detection limit for all the 17 PCDD/PCDF congeners. HCB was also below the detection limit ($<$31 ng/m^3 and $<$35 ng/m^3) for the baseline and the test burn, respectively. None of the non-*ortho* and mono-*ortho* PCB congeners could be quantified.

4.3. Feeding of non-hazardous wastes

Kuhlmann et al. (1996) reported approximately 160 emission measurements at German cement kilns in the period 1989–1996 and covered 16 different dry preheater kilns, i.e. suspension preheater kilns and Lepol kilns, all equipped with electrostatic precipitators. Gas temperatures in the ESP typically ranged from 95 °C to 205 °C (suspension preheater kiln) and 120 °C to 150 °C (Lepol kilns). Secondary fuels such as used oil, bleaching earth, used car tyres or waste-derived fuels were used in some kilns and secondary raw material substitutes like, e.g., fly ash, or contaminated sand were used in others. The average concentration was about 0.02 ng I-TEQ/m^3 at 10% O$_2$. No significant differ-

ence in emissions from the type of fuel being used or any temperature correlation with the PCDD/PCDF concentration in stack could be established. Examinations also showed that the oxygen content as well as the dust concentration in stack did not correlate with the reported emission concentrations. The general level of substitution of fossil fuel and raw materials with AFR increased in German cement kilns from 23% in 1999 to nearly 35% in 2002 but no effects have been observed on the PCDD/PCDF emissions. In another study, 106 PCDD/PCDF measurements of 37 kilns showed that all values were below 0.065 ng I-TEQ/m^3 (10% O$_2$), and in seven cases no PCDD/PCDF was detected (VDZ, 2002).

Environment Australia (2002) has measured a range of Australian cement plants representing different operating and process conditions, different fuel sources and different raw materials. Both wet and dry process kilns have been investigated, as plants using gas and coal as primary fuels sources as well as plants using waste-derived fuels. No significant difference in PCDD/PCDF emissions due to use of waste-derived fuels have been observed within plants. Results of repeated measurements over a decade showed that levels of PCDD/PCDF emissions from Australian cement manufacturing have consistently been below 0.1 ng I-TEQ/m^3. Fifty-five measurements showed the range 0.001–0.07 ng I-TEQ/m^3, with subsequent emissions factors covering the range 0.0032–0.216 µg I-TEQ/ton cement.

The Japanese cement industry utilizes a broad range of alternative fuels and raw materials (AFR) in their cement production and approximately 78 million tons of clinker was produced in 62 dry suspension preheater kilns in Japan in 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; all measurements corrected to 10% O$_2$ (Japan Ministry of Environment, 2003).

In the first phase of the Spanish PCDD/PCDF inventory, 20 cement kilns (18 dry and 2 wet processes) were measured for PCDD/PCDF emissions under baseline 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. In the period 2000–2003 samples from 41 kilns were collected, representing 69.5% of the industry and 40.2 million ton cement. Fifty-eight samples were taken when using conventional fuels and 31 when alternative fuels were used. No evidence of higher PCDD/PCDF emissions when using alternative fuels could be found (Fabrellas et al., 2004).

Heidelberg cement (Haegermann, 2004) made a comparison between kilns using a high substitution rate of alternative fuels and kilns using fossil fuel only. Nine plants with a substitution rate of minimum 40% showed an average value of 0.007 ng TEQ/m^3 (minimum 0.001 ng TEQ/m^3, maximum 0.016 ng TEQ/m^3) while the average of eight kilns using fossil fuel only was 0.016 ng TEQ/m^3 (minimum 0.002 ng TEQ/m^3, maximum 0.031 ng TEQ/m^3). Five measurements from two German preheater kilns feeding a mix of coal and plastics to the main burner and tyres to the kiln inlet showed concentrations from <0.0021 ng TEQ/m^3 up to 0.0057 ng TEQ/m^3 (Haegermann, 2004). Measurements from five European dry kilns using waste fuel (3 ton/h) and/or tyres (1.7–3 ton/h) done in 2003 varied between 0.001 and 0.062 ng I-TEQ/Nm^3, with an average of 0.011 ng I-TEQ/m^3 at 10% O$_2$. The subsequent emission factors varied between 0.002–0.025 µg TEQ/ton clinker (Haegermann, 2004).

The effect of increasing the total thermal substitution rates with different alternative fuel and raw materials on the emissions of PCDD/PCDF, PCB and HCB was investigated in one suspension preheater/precalciner kiln by Holcim (Lang, 2004). The total thermal substitution rate increased from 23% in 1997 up to 60% in 2003 and covered solvents, animal meal, bleaching earth, rubber, waste oil, paper and film plastics, fly ash and waste wood; the thermal substitution rate to the precalciner increased in the same period from approximately 14% up to near 50% and the thermal substitution rate to the main burner remained more or less stable around 10%. All measurements ($N = 8$) were unaffected by the increased substitution and showed that all PCDD/PCDF measurements were <0.004 ng I-TEQ/m^3, PCB < 4 µg/m^3 and HCB < 4 ng/m^3.

Holcim Chile (Jensen, 2004) reported measurements of a kiln fed with 25% petcoke and 75% coal showing a concentration of 0.0059 and 0.0194 ng I-TEQ/m^3; one measurement was done with coal only, showing 0.0100 ng I-TEQ/m^3, and two measurements done when introducing liquid alternative fuel: one with 20% liquid alternative fuel, 6% tyres, 18.5% petcoke and 55.5% coal showed a PCDD/PCDF concentration of 0.0036 ng I-TEQ/m^3; another test with 12% liquid alternative fuel and 88% coal showed a PCDD/PCDF concentration of 0.0030 ng I-TEQ/m^3; all corrected to 10% O$_2$.

Five dry preheater cement kilns were measured for PCDD/PCDF in the Philippines showing a concentration of 0.0073, 0.0093, 0.0059, 0.013 and 0.011 ng I-TEQ/m^3 at 10% O$_2$ (Lang, 2004). A test burn with 1200 tons out-of-spec dog food containing 1.28% of chlorine was carried out in a 5500 ton clinker/day preheater/precalciner kiln (80 m long and 5 m diameter) in the Philippines in 2004. Three test runs were performed with sampling of PCDD/PCDFs; one with coal only, one with 1750 kg/h and one with 3500 kg/h dog food fed to the precalciner. All runs were performed in compound mode and showed a concentration of 0.00038, 0.0012 and 0.0013 ng I-TEQ/m^3 at 10% O$_2$, respectively (Schimpf, 2005).

Abad et al. (2004) investigated the influence of feeding waste materials to three Spanish dry preheater/precalciner kilns. The alternative fuels were fed to the preheater/precalciner at a rate of 4.8–14% of the heat input and consisted of meat meal and used tyres. The emission of PCDD/PCDFs ranged from 0.001 to 0.042 ng I-TEQ/m^3 and the authors

concluded that the levels were similar to those emitted during the use of conventional fuel.

Capmas (2003) did 40 PCDD/PCDF measurements from cement plants using meat meal as a secondary fuel in France and compared with measurements from 22 plants using fossil fuel only; no differences could be established. Conesa et al. (2006) investigated the emissions of acid gases, heavy metals, PCDD/PCDF, PAHs and VOCs when feeding various amounts of sewage sludge and tyres. The

authors could not identify any influence of any of the emissions, which were all in compliance with EU and Spanish regulation.

Lafarge investigated the effect on PCDD/PCDF emissions of feeding different alternative fuels to the kiln inlet/precalciner (Table 1); feeding rates were not available (Reiterer, 2004).

The European Cement Association reported 230 PCDD/PCDF measurements (some of these data may be included in other reports in this article) from 110 cement kilns and 11 countries in 2003 (van Loo, 2004). The countries covered by the survey were Belgium, Czech Republic, Denmark, France, Germany, Hungary, Italy, Norway, Spain, the Netherlands and United Kingdom; most countries practise co-processing of wastes. The measurements showed that the average concentration was 0.017 ng I-TEQ/m^3 for all measurements. The lowest and highest concentrations measured were <0.001 and 0.163 ng I-TEQ/m^3, respectively. Overall, 98% of the 230 kilns had emission concentrations below 0.1 ng TEQ/m^3 and the majority of the kilns emitted concentrations lower than 0.01 ng TEQ/m^3 (see Figs. 3 and 4).

Eight international cement companies reported more than 500 recent PCDD/PCDF measurements (some of these data was included in the previous overview) representing a large number of countries, a production of more

Table 1
Feeding of alternative fuels to the kiln inlet/precalciner in Lafarge kilns and influence on PCDD/PCDF emissions (single or mean value) (Reiterer, 2004)

| Type of alternative fuel	ng I-TEQ/m^3	N
Animal meal, plastics and textile	0.0025	4
Animal meal and impregnated saw dust	0.0033	4
Coal, plastic and tyres	0.0021, 0.0041	2
Tyres	0.002, 0.006	2
Petcoke, plastic and waste oil	0.001	1
Petcoke, sunflower shells and waste oil	0.012	1
Tyre chips	0.004, 0.021	2
Solvents	0.07	1
Impregnated saw dust and solvents	0.00003, 0.00145	2
Solvents	0.00029, 0.00057	2
Sludge's	<0.011	1
Car waste	0.0036, 0.07, 0.0032	3
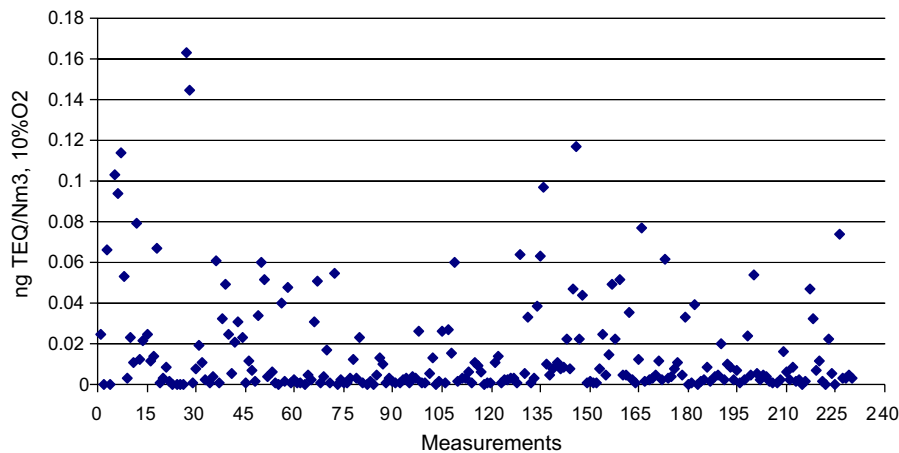
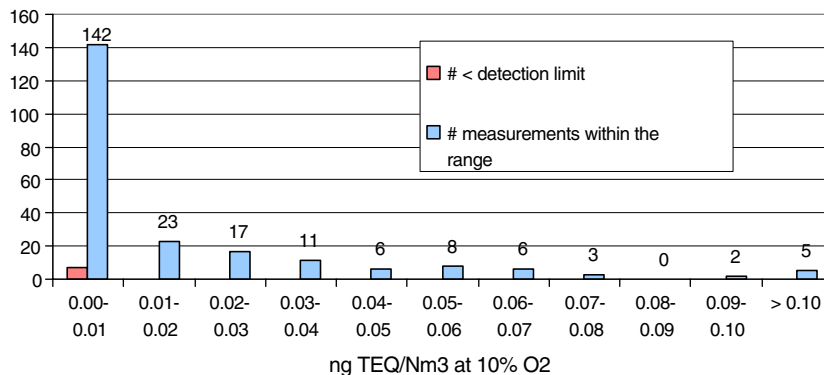Fig. 3. 230 measurements in 110 kilns and 11 European countries (van Loo, 2004).

Fig. 4. Concentration distributions of 230 measurements (van Loo, 2004).

Table 2
Cement company emission measurements of PCDD/PCDF ng I-TEQ/m^3

Cement company	N	Concentration range (average)	Reference
Cemex 1999–2003	16	0.00049–0.024	Quiroga (2004)
Heidelberg 2001–2004	>170	0.0003–0.44 (0.020)	Haegermann (2004)
Holcim 2001	71	0.0001–0.2395 (0.041)	Lang (2004)
Holcim 2002	82	0.0001–0.292 (0.030)	Lang (2004)
Holcim 2003	91	0.0003–0.169 (0.025)	Lang (2004)
Lafarge 1996–2003	64	0.003–0.231 (0.0207)	Reiterer (2004)
RMC 2000–2004	13	0.0014–0.0688	Evans (2004)
Siam 2003	4	0.0006–0.022	Siam Cement (2004)
Taiheiyo	67	0.011	Izumi (2004)
Uniland	2	0.002–0.006	Latorre (2004)

than 300 million tons of clinker, most production technologies and the use of wide variety of AFR. The concentration distribution showed that approximately 98% of the measurements are below 0.1 ng TEQ/m^3 (see Table 2).

Cimpor reported 14 PCDD/PCDF measurements done in Portugal, Spain and South Africa in the period from 1997 to 2003; see Table 3 (Leitao, 2004).

4.4. PCDD/PCDFs in solid materials

One cement kiln study in the US concluded that "naturally occurring PCDD/PCDF found in the raw materials constitute a majority of all the PCDD/PCDF emitted from the system" (Schreiber et al., 1995). Liske et al. (1996) confirmed the identification of PCDD/PCDFs in the raw material feed.

Solid materials used and produced in the cement industry were also analysed for PCDD/PCDFs in this study. The main purpose was to confirm the possibility of having naturally occurring PCDD/PCDFs in the raw meal feed, but also to look into the general concentration levels of release through products and dusts. Dusts are as much as possible reintroduced back to the process, often together with the raw material feed, and can potentially represent a source of PCDD/PCDFs.

Dyke et al. (1997) estimated that approximately 30 kg of CKD are produced per ton of clinker in long kilns; but this will 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 due to high content of sodium and potassium (Riney and Yonley, 1994). A range of concentrations of PCDD/PCDFs has previously 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 kilns. US EPA characterized a wide range of cement kiln dusts in a Report to Congress (CKD, 1995). The average TEQ concentration in the CKD from kilns burning hazardous waste was 35 ng I-TEQ/kg; these results were influenced by a high concentration in one sample (UNEP, 2005). For kilns that did not burn hazardous waste, the average concentration in the CKD was 0.03 ng I-TEQ/kg. Sixty-four percent of the CKD was recycled directly back into the kiln or raw feed system in the US.

US EPA could not find organics, volatile and semi-volatile compounds in CKD and PCDD/PCDF could not be detected in any clinker samples (CKD, 1995). This was however not the case in this study – PCDD/PCDFs could

Table 3
PCDD/PCDF measurements in Cimpor kilns (Leitao, 2004)

Country	Plant	Kiln	Date	ng I-TEQ/m^3 10% O$_2$	Production process/type of kiln	Air pollution control system	Gas T (°C)
Portugal	Souselas	2	16.07.2001	0.0008	Dry kiln; cyclone preheater	Electrostatic precipitator/bag filter	117
		3	13.12.1997	0.0009	Dry kiln; separated SLC-D precalcinator	Electrostatic precipitator/bag filter	106
	Alhandra	6	08.12.1997	0.0009	Dry kiln; cyclone preheater	Electrostatic precipitator/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 ILC-E 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 precalcinator	Electrostatic precipitator	–
	Cordoba	1	06.06.2001	0.0243	Dry kiln; in line ILC-E precalcinator	Bag filter	90
	Niebla	1	2001	0.006	Semi-dry; lepol preheater	Bag filter	117
South Africa	Simuma	1	11.07.2002	0.00053 0.001	Dry kiln; cyclone preheater	Electrostatic precipitator	113 114

Table 4
PCDD/PCDF in solid materials from the cement industry

Sample type	N	Average concentration ng I-TEQ/kg	Highest concentration ng I-TEQ/kg	Samples below detection limit
Kiln raw material feed	11	1.4	7.1	1
Alternative raw material	10	0.99	3.3	1
CKD	90	6.7	96	5
Clinker	57	1.24	13	7
Cement	49	0.91	6.9	7

be detected in all solid sample categories analysed. The kiln feed samples comprised raw meal, pellets and slurry; alternative raw materials comprised sand, chalk and different ashes. Samples of CKD, clinker and cement were also analysed, with CKD not surprisingly having the highest concentrations (Table 4).

4.5. Organics in the raw material (raw meal)

Field studies conducted at full-scale kilns have shown that total organics/hydrocarbon emissions are not very sensitive to the changes in combustion conditions (Trenholm and Hlustick, 1990; Dellinger et al., 1993). It has also been shown that organics present in the raw materials (e.g., clay, shale, gypsum, etc.) are the major sources of organic emissions from cement kilns. These hydrocarbons are volatilized from the raw materials prior to entering the high temperature regions of the kiln (Dellinger et al., 1993; Schreiber and Strubberg, 1994).

The chlorination of these organics is a potential source of PCDD/PCDF precursors, such as MCB. Bench-scale, as well as full-scale tests by the industry has confirmed that organics from raw materials play a significant role in governing the production of PCDD/PCDFs (Sidhu and Dellinger, 1995). Although the operating conditions necessary for achieving high total organics 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. Dellinger et al. (1993) observed an inverse relationship between total hydrocarbons and stack oxygen concentrations and Schreiber and Strubberg (1994) observed that raw-material-generated hydrocarbons decrease as kiln oxygen increases. However, raw material characteristics, i.e. the organic content are largely dictated by quarry location and are not easily controlled.

Heating of eight raw meal samples from different process points (before and after each cyclone, bag house, grinding mill and silo) under inert helium atmosphere showed that most of the organics were desorbed between temperatures of 250–500 °C (Sidhu and Dellinger, 1995; Sidhu et al., 2001). To speciate these organics, cement kiln raw meal samples were desorbed under cement kiln preheater zone conditions (4% O_2, temperature range of 30–500 °C) showing that cement kiln raw meal contains a wide range organics including benzene, toluene, naphthalene, alkanes, C14–C18 carboxylic acids, phthalates and their derivatives and natural products like cholesterol (Saiz-Jimenez, 1994; Schulten, 1995; Sidhu and Dellinger, 1995; Sidhu et al., 2001).

Alcock et al. (1999) showed that TEQ concentrations in stack emissions of a cement kiln collected within a few hours of each other on the same day could, in some cases, be very different. For example, the first sample collected measured 4.2 ng and the second, collected 5 h later, 0.05 ng I-TEQ/m^3. During the time period stack gas was sampled the plant was running normally and spike recoveries of both samples were within the normal range. One possible explanation of this variability in emissions would be unevenly distribution of raw material organics.

4.6. Chlorine

The input of chlorine in cement production needs to be monitored and controlled carefully to be able to comply with standard product quality criteria and to avoid process related problems. The availability of chlorine does not seem to be a limiting factor, i.e. there will be enough chlorine in the raw materials or in the fossil fuels (Bragg et al., 1991) to form PCDD/PCDFs under unfavourable conditions.

It has been believed that the highly alkaline environment in cement kilns scavenges available chlorine, making it unavailable for chlorination of organic material (Eduljee, 1998). Data presented by Lanier from testing a full-scale facility showed 97% acid gas capture by the alkali material, and no effect on PCDD/PCDF emissions due to variations in chlorine feed rate (Lanier et al., 1996). Equilibrium calculations show on the other side that chlorine capture is not effective at high temperatures and that HCl is converted to Cl_2, suggesting that even a highly basic chemical species such as calcium hydroxide would not always be expected to effectively control chlorinated hydrocarbon formation (including PCDD/PCDFs) at temperatures above 200 °C (Dellinger et al., 1993). Lamb et al. (1994) confirmed the availability of chlorine and that this led to increased production of MCB in the lower part of the preheater.

Any chlorine in the fuel enters the preheater zone as HCl and Cl_2, eventually organic chlorides (Sidhu et al., 2001). The HCl to Cl_2 ratio seems to be important, as Cl_2 is a much superior chlorinating agent than HCl. Chlorine may also be initially present in the raw meal or may be captured from the gas-phase by alkali reactions of the raw meal (Sidhu et al., 2001). Chlorine can therefore be present in the preheater zone as organic chlorides, HCl, Cl_2, alkali and alkaline earth chlorides, and transition metal chlorides and the chlorination of hydrocarbons can be catalyzed by the alkali metal oxides and hydroxides present in the feed

material at the temperatures normally found in preheaters (Eduljee, 1998). Consequently, higher temperatures and oxygen concentration downward the preheater will increase conversion rate of HCl to Cl_2 by pushing the Deacon reaction towards molecular chlorine, and hence potentially the yield of PICs such as MCB (Dellinger et al., 1993). For more on the role of chlorine in the formation of PCDD/PCDFs see Griffin (1986), Stieglitz et al. (1989a), Gullett et al. (1990), Bruce et al. (1991) and Gullett et al. (1992, 2000a,b).

4.7. Catalysts

Catalytic metals such as copper play an important role in the formation of PCDD/PCDF but spiking wastes with copper was not observed to affect PCDD/PCDF emission rates during full-scale testing of a US cement kiln (Lanier et al., 1996). Dudzinska et al. (1988) carried out a test in a Polish cement kiln feeding 10% inorganic (containing 0.08% copper) and 10% organic hazardous waste without copper. The authors claim that Polish cement plants are mostly using coal with high sulphur content and that this may have disturbed the formation of PCDD/PCDF. The kiln was operated at 6% oxygen and the PCDD/PCDF emissions were 0.0515 ng I-TEQ/Nm³ with coal only, and 0.0819 and 0.0698 ng I-TEQ/Nm³ when feeding inorganic and organic waste, respectively.

4.8. Particulates

Schreiber et al. (1995) conducted a test with activated carbon injection between the kiln inlet and the electrostatic precipitator inlet on a cement kiln burning coal, liquid waste fuel and solid waste fuel. A reduction in PCDD/PCDF levels was anticipated, but the result gave a 100-fold increase in the PCDD/PCDF level in the CKD, from 0.5 to 34 ng/kg, and no improvement in stack emissions (0.32 ng/m³) and the authors concluded that "addition of activated carbon as a control technology in cement kilns does not reduce PCDD/PCDF emissions".

This test actually added to the particulate loading of the ESP, which also was operated at a temperature of 270 °C, and thereby increasing the available surface area for heterogeneous surface-catalyzed reactions, as shown by the increase of PCDD/PCDFs in the CKD and actually confirms the theories regarding PCDD/PCDF formation. For a cement kiln to effectively utilize carbon injection, the carbon injection system must be installed after the APCD, along with a second APCD to collect the carbon (Eduljee, 1998).

It has been suggested that capture and removal of particulate matter would result in a corresponding reduction in PCDD/PCDF emissions (Eduljee, 1998). A number of studies have however shown that the correlation between PCDD/PCDF emissions and particulate emissions is not necessarily observed in full-scale plant under all operating conditions, owing to the conflicting influence of a number of operating variables (Eduljee and Cains, 1996). When operating temperatures are reduced, the PCDD/PCDF present in the gas stream will adsorb onto the surface of particulate matter and a combination of reduced temperature and improved particulate abatement may result in lower PCDD/PCDF emissions. The data to support this contention on cement kilns has yet to be systematically collected, but it is instructive that within the EPA study (1994), the kilns operating with fabric filters show both lower particulate emissions and lower PCDD/PCDF emissions than the kiln operating with ESP's (Eduljee, 1998). Whether this result is due to the lower operating temperature of the fabric filter relative to an ESP (therefore minimising PCDD/PCDF formation within the pollution control device) or due to increased adsorption onto and removal of particulate matter within a fabric filter operating at a lower temperature than an ESP has not been elucidated (Eduljee, 1998).

4.9. Temperature and operating conditions

The operating envelope of cement kilns is dictated largely by standard specifications for their final product and these conditions are conducive to efficient organic destruction, which makes parameters related to the temperature of the burning zone generally less relevant for cement kilns than for incinerators. Although some cement kilns operate at elevated carbon monoxide levels, these levels are not necessarily indicative of poor combustion. The calcination process releases large quantities of carbon dioxide, which can subsequently decompose into carbon monoxide at the extremely high temperatures in the kiln. In addition, carbon monoxide may be formed at the kiln gas exit end where total hydrocarbons are volatilized from the raw materials and are partially oxidized.

A study examining the influence of kiln design and operating conditions during the combustion of hazardous waste was undertaken by US EPA (1994). Data from 23 separate kilns (predominantly wet kilns with ESP pollution abatement equipment, comprising 86 data points) was analysed for correlations against various emissions and operational parameters. No correlation could be established between PCDD/PCDF emissions and the stack concentration of HCl, total hydrocarbons, oxygen or particulates for the same type of electrostatic precipitator. One positive correlation identified both in US and German studies (Kuhlmann et al., 1996) was that between PCDD/PCDF concentration and ESP/stack temperature, at high temperatures. This was confirmed by Schreiber (1993) which tested a cement kiln with the ESP temperature between 255 °C and 400 °C; the PCDD/PCDF emissions were highest at 400 °C, and decreased 50-fold at 255 °C. Harris et al. (1994) and Lanier et al. (1996) demonstrated that PCDD/PCDF emissions from cement kilns increase exponentially with increases in inlet temperatures to the air pollution control device APCD within the PCDD/PCDF formation window (250–450 °C).

The US EPA suggested that PCDD/PCDFs from cement kilns could be controlled through a combination of low temperatures in the APCD, low carbon monoxide and elevated oxygen. Attempts by cement manufacturers to achieve the 0.20 ng TEQ/m^3 limit proposed in 1996 clearly demonstrated that carbon monoxide and oxygen levels are relatively unimportant and that reduced APCD temperature gave mixed results (Chadbourne, 1997). A number of wet kilns have however added flue gas quenching to reduce inlet APCD temperature, and these additions have reduced the US PCDD/PCDF emissions (EPA, 2000). Even if this suggests that maximum inlet temperature to the APCD system is a key control parameter related to PCDD/PCDF emissions from wet cement kilns, low temperatures do not necessarily guarantee low results. This indicates that other parameters are important in combination with the temperature and Chadbourne (1997) postulated that the formation of PCDD/PCDFs is proportional to precursor and/or organics concentration and time but exponential with respect to the temperature.

4.10. Inhibitors

Sulphur in coal is believed to be the reason for low PCDD/PCDF emissions from coal-fired power plants (Raghunathan and Gullett, 1996; Gullett and Raghunathan, 1997). Researchers have concluded that sulphur may interfere with PCDD/PCDF formation by SO$_2$ depletion of Cl$_2$, and eventually by SO$_2$ poisoning of copper catalysts to prevent the synthesis of aromatic compounds or to interfere with the Deacon reaction (Griffin, 1986; Gullett et al., 1992, 2000b; Raghunathan and Gullett, 1996).

Sulphur is present in cement production both in the coal and in the raw material. Schreiber et al. (1995) intentionally added sulphur to a cement kiln to achieve PCDD/PCDF control and reductions were documented when the stack concentrations of SO$_2$ increased from less than 20 ppm to above 300 ppm. Schreiber (1993) also documented PCDD/PCDF emissions reductions when Na$_2$CO$_3$ was injected at the fuel feed end to react with chlorine in the system. Since the alkali raw materials may 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/PCDF inhibitors, such as calcium, are already being present in the raw materials.

4.11. Factors influencing formation of PCDD/PCDFs in cement production – a summary

The very low emissions of PCDD/PCDFs from cement kilns, regardless of the type of fuel used can generally be attributed to the high temperatures and long residence times within the kiln (Kreft, 1995; Karstensen, 2004). We have seen evidence, especially from data of newer origin, that fuels and wastes fed through the burners are properly destroyed, also hazardous wastes (Stobiecki et al., 2003). Even if we cannot entirely exclude the possi-

bility of having PICs and precursors formed from these two sources, they will normally be of minor importance compared to organics in the raw material. Raw material organics, seemingly to consist of mainly aromatic compounds, will be volatilized in the preheater and partially oxidized and/or pyrolyzed and made available in the gas stream. There seems to be enough chlorine, in different species and from various sources, which through the temperature gradient in the preheater and the post-preheater region will be available for surface-catalyzed reactions on particulate surfaces. Additional chlorine feed, for example through waste feeding, does not seem to be of major importance. There are studies showing that monochlorobenzenes are formed in the preheater, probably by the chlorination of raw material organics, which again can form potent precursors like chlorophenols and/or PCDD/PCDFs directly.

The preheater region of a cement kiln is unique, with a temperature gradient ranging from approximately 250–850 °C, with high gas volumes and a gas retention time up to 25 s, and abundance of particle surfaces makes it ideal for heterogeneous surface-catalyzed reactions and de novo synthesis (if the post-preheater region is included). The lower parts of the preheater may even constitute a possible place for having homogeneous pure gas-phase formation of precursors and PCDD/PCDFs. We know for the time being nothing about the possible role of wall deposits or soot, but from other studies (Gullett et al., 2000c; Grandesso et al., 2006) it can be assumed to play a role also in cement kiln APCDs.

Modern preheater/precalciner kilns seems to emit slightly less PCDD/PCDF than wet-process cement kilns. This may be attributed to two main differences between the two: the inherent lower temperature of the APCD zone in modern dry kilns and the absence of an in-line raw-mill-dryer in wet kilns. The dominating operational mode, representing the normal low emissions from modern preheater kilns, is to duct the hot exit gas from the kiln and the preheater through the raw-mill-dryer for heating the raw materials, before it enters the APCD and the stack (called compound mode). This mode of operation both reduces the exit gas temperature and seems to absorb PCDD/PCDF. When the raw-mill-dryer is shut off parts of the time (direct mode), the exit gas is cooled with water, as in wet kilns. The absorption seems however to be less effective in such a mode of operation, resulting in increased emissions (authors experience). Such mode of operation resemble wet kilns equipped with coolers and may, at least partly, explain the seemingly higher emissions from wet kilns; absorption on particles in the raw-mill-dryer is more effective than in water coolers. In early days when wet kilns ducted the exit gas directly from the kiln to the APCD without cooling, the temperature would be in the range of 200–400 °C in the APCD, making it an ideal place for de novo synthesis.

Evidence from the US has shown that naturally occurring PCDD/PCDFs in the raw materials can be emitted

from the system, probably through volatilization. This study have identified and quantified two sources of input materials containing PCDD/PCDFs; raw material kiln feed and CKD (Karstensen, 2006a). Raw material kiln feed may potentially contain two sources of PCDD/PCDFs, naturally PCDD/PCDFs and adsorbed PCDD/PCDFs from the raw-mill (when CKD are reintroduced back to the process together with the raw meal). It is therefore plausible that there is a region within the preheater and the raw-mill-dryer where the PCDD/PCDFs, from any origin, are circulating between gaseous and particle adsorbed phases; once they are adsorbed onto particles in the cooler parts, the material flow is moving downwards to higher temperatures, where they again will be volatilized and reintroduced to the hot exit gas from the kiln.

A circulation of PCDD/PCDFs may interact with, and may even be controlled by the known circulation of alkali chlorides and sulphates in the upper parts of the kiln zone and in lower parts of the preheater. Such circulation may exhibit an inhibition effect due to equilibrium reactions between chlorine and sulphur; sulphur is present in both coal and raw material and the alkali materials are in abundance. We know from other studies that sulphur and the presence of alkaline materials has been shown to decrease PCDD/PCDF emissions (Schreiber et al., 1995), and a reverse correlation between the concentration of SO_2 and the concentration of PCDD/PCDF in the flue gas may be expected.

The net formation and release of PCDD/PCDFs in cement production may therefore be due to a complex combination of simultaneous formation and decomposition reactions:

- destruction of PCDD/PCDFs in the kiln region;
- formation of PICs and chlorinated organics in the preheater, basically from raw material organics;
- gas-phase formation reactions between precursors in the lower part of the preheater can form PCDD/PCDFs directly;
- heterogeneous surface-catalyzed formation of precursors and PCDD/PCDFs in the preheater;
- an adsorption–desorption circulation process of naturally and adsorbed PCDD/PCDFs in the preheater and the raw-mill-dryer;
- interaction with equilibrium reactions and circulation of chlorine, sulphur and alkali materials in the upper parts of the kiln zone and lower parts of the preheater may lead to inhibition;
- de novo synthesis and formation of PCDD/PCDFs in the APCD and the post-preheater zone.

The detailed understanding how PCDD/PCDFs are formed in cement production is not yet complete, but it seems that a combination of heterogeneous surface-catalyzed reactions and de novo synthesis in the preheater and the post-preheater zones are the most important. A comprehensive mass balance study would be needed to reveal this hypothesis.

4.12. Controlling emissions of PCDD/PCDFs

For new cement kilns and major upgrades the BAT 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 the energy use (UNEP, 2007). PCDD/PCDF control in cement production becomes a simultaneous effort to reduce the precursor/organic concentrations, preferably by finding a combination of optimum production rate and optimum gas temperatures and oxygen level at the raw material feed end of the kiln, and the reducing the APCD temperature. Feeding of alternative raw materials as part of raw-material-mix should be avoided if it includes elevated concentrations of organics and no alternative fuels should be fed during start-up and shut down. The most important measure to avoid PCDD/PCDF formation in wet kilns seems to be quick cooling of the kiln exhaust gases to lower than 200 °C. Modern preheater and precalciner kilns have this feature already inherent in the process design and have APCD temperatures less than 150 °C. Operating practices such as minimising the build-up particulate matter on surfaces can assist in maintaining low PCDD/PCDF emissions.

5. Emission inventories and release contribution of the cement industry

Emission inventories and release contribution estimates for the cement industry are usually based on two types of information, earlier literature data or real measurements, providing considerably different results.

Early inventories usually assigned high emission factors based on the literature data, especially to hazardous waste burning kilns. Brzuzy and Hites (1996) estimated the total global annual emission of PCDD/PCDF to air to be 3000 ± 600 kg. The cement industry burning and not burning hazardous waste was assigned an emission factor of up to 4160 μg/ton cement and 320 μg/ton cement, respectively. UNEP assigned in 1999 an emission factor of 2600 μg TEQ/ton and 200 μg TEQ/ton for hazardous waste burning and non-hazardous waste burning cement kilns, respectively (1999). Other examples can be found from Italy (Caserini and Monguzzi, 2002), Russia (Kucherenko et al., 2001a,b) and Taiwan (Chen, 2004). These emissions factors lead to cement industry contribution estimates ranging from 5%, and up to a worst case scenario estimate of 59% of total emissions by Brzuzy and Hites (1996).

The most recent inventories do not longer differentiate if the kiln uses hazardous or non-hazardous waste. The UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases (UNEP, 2005) has suggested three classes of default emission factors for cement production, differentiating between kiln type and the APCD temperature only. An emission factor of 5 μg TEQ/ton is assigned to vertical shaft kilns and wet kilns with APCD temperature over 300 °C; 0.6 μg TEQ/ton is assigned to

wet kilns with APCD temperature between 200 °C and 300 °C, and 0.05 µg TEQ/ton is assigned to all dry kilns and wet kilns where dust collector temperatures is held below 200 °C. The European PCDD/PCDF inventory was based on a flat emission factor of 0.15 µg TEQ/ton cement, not differentiating between kiln technologies or temperature in the APCD (Quaß et al., 2004).

More recent inventories are usually based on real measurements, resulting in significantly lower emission factors and a release contribution estimates, constituting from about 0.5% or less of total emissions. Fabrellas et al. (2002, 2004) used 0.014464 µg I-TEQ/ton cement in the Spanish inventory; 0.2 µg TEQ/ton were used for the Newly Independent States and the Baltic countries (Kakareka, 2002; Kakareka and Kukharchyk, 2002); 0.025–1.2 µg I-TEQ/ton cement was used in the UK, covering also wet kilns burning a mix of fossil and waste-derived fuel (Eduljee and Dyke, 1996; Eduljee, 1998; Alcock et al., 1999). In the absence of real measurements, the Environmental Protection Department Hong Kong (2000) assumed an exit gas concentration of 0.1 ng I-TEQ/m^3, a flow rate of 7000 m^3/min and an operation of 7680 h of per year for their cement plant, leading to a contribution estimate of 0.96–1.39% of total emissions.

The latest and most comprehensive investigations illustrate the gap between earlier literature data and real measurements. The average PCDD/PCDF flue gas concentration in European kilns is approximately 0.02 ng TEQ/m^3, representing hundreds of recent measurements. Assuming an average exhaust-gas volume of 2300 Nm^3/ton clinker (IPPC, 2001) and a clinker/cement ratio of 0.8 would give an emission factor of 0.037 µg TEQ/ton cement. The worldwide measurements performed by Holcim showed an average emission factor of 0.104 µg TEQ, 0.073 µg TEQ and 0.058 µg TEQ/ton clinker, representing a clinker production of 35.1, 46.7 and 57.6 million ton, respectively (Lang, 2004). Taiheiyo cement measured the emission factor to be 0.03 µg TEQ/ton, representing 23.6 million tons of cement in 2001 (Izumi, 2004).

6. Discussion

Many articles used in this study have gaps in the reported information which makes it difficult to evaluate the accuracy and the precision of the data, but also to establish relationships and influences of process conditions. Most reports does not specify fuel, waste or raw material composition, or process conditions, making a systematic and detailed evaluation of the main influencing parameters difficult. Often there is no information of which toxic equivalency factor (TEF) system have been used, or if and eventually how, the referred data has been corrected to normal conditions and oxygen concentration. Generally higher confidence can be given measurements from actual plants than to the literature data from surveys using emission factors only; measurements from actual plants represent local conditions. However, it have not always been

possible to verify the quality and completeness of the received data as some cement companies have submitted complete laboratory reports, others figures only (Karstensen, 2006a).

Information about sampling methodology, spiking recoveries and detection limits are often missing or inadequately reported. Before the first European Standard appeared in 1996 (EN 1948, 1996) different methodologies were used for sampling, extraction, clean-up, identification and quantification. It is reasonable to expect that data published before mid-1990s are less reliable compared to recent data due to absence of standard procedures and sophisticated analysis technology, especially high resolution gas chromatography mass spectrometry. Since no reference materials are available for PCDD/PCDFs in exhaust gases, the accuracy of the sampling method is not possible to determine, only the external and internal variability can be evaluated. The uncertainty for the complete procedure is estimated 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; see EN, 1948 – 3 February 2004. Taking into account the toxic equivalent factors for the individual congeners, the resulting overall detection limits varies between 0.001 and 0.004 ng I-TEQ/m^3 implying that concentrations lower than 0.001 ng I-TEQ/m^3 should be considered as being below the detection limit, but figures lower than this are frequently reported (Environment Canada, 1999). Also, interferences should be expected to occur from compounds that have similar chemical and physical properties to PCDD/PCDFs. All these factors suggests need for caution when using few results or results from early studies to provide emissions factors for the whole industry sector.

This becomes evident when early emission factors referred to in this article are considered, varying from the high 4160 µg TEQ/ton cement (Brzuzy and Hites, 1996) to the low 0.0003 µg TEQ/ton representing actual measurements from a cement kiln in Thailand co-processing hazardous wastes (UNEP/IOMC, 2001) – a factor of almost 14 million times difference. Assuming an average exhaust-gas volume of 2300 Nm^3/ton clinker, an emission factor of 4160 µg TEQ/ton cement would be equivalent to an exit gas concentration of >1800 ng TEQ/m^3; the highest concentration found in the literature is 50 ng TEQ/m^3 (Chadbourne, 1997).

The International POPs Elimination Network claim that the PCDD/PCDF emissions in 2004 from a long dry kiln in the UK reached 136 ng TEQ/m^3 and averaged more 50 ng TEQ/m^3 over the year with total emissions of more than 40 g TEQ. The kiln, now closed, was operating with relatively high temperatures in the electrostatic precipitator and used raw material with high organic content together with waste pulverised fuel ashes. This information cannot be confirmed in scientific literature, but is referred in UNEP (2007).

The contribution estimate made by Brzuzy and Hites (1996) showed that the cement industry were supposed to contribute with 1420 kg PCDD/PCDF/yr, or 59% of estimated total global emissions as a worst case scenario. This

calculation can be redone by using recent data, for example from the UNEP Toolkit (UNEP, 2005). Assuming a global cement production of approximately 2 billion tons and using the highest emission factor of the Toolkit as the worst case scenario, 5 μg TEQ/ton, would imply a contribution from the cement industry of 10 kg/yr. A best scenario estimate would be to use the lowest emission factor of the Toolkit, 0.05 μg TEQ/ton, making the contribution from the cement industry to be 100 g/yr.

A more reasonable contribution estimate would be to assume that the eight international cement companies presented in Table 2, representing approximately 20% of the total clinker production, is currently representative of the global industry. More than 500 recent measurements from around the world, representing all technologies and local raw material conditions as well as feeding AFR, show an average flue gas concentration of 0.021 ng I-TEQ/m^3. Assuming a global cement production of 2 billion ton/yr, or 1.6 billion ton/yr of clinker and an exhaust-gas volume of 2300 Nm^3/ton clinker, the contribution from the cement industry would constitute 77 g/yr. When compared with the 1420 kg estimated by Brzuzy and Hites (1996) in their worst case scenario, it becomes evident how unreliable early emission factors are.

The slightly higher concentration of PCDD/PCDF found in clinker than in cement when analysing the CSI samples in 2005 was a surprise (see Table 4). Cement is often mixed with CKDs and a higher PCDD/PCDF concentration was expected in cement than in clinker due to normally higher concentrations in CKD, not the opposite. The concentration in clinker was expected to be low; because none has identified PCDD/PCDF in clinker earlier (CKD, 1995; Federal Register, 1995) and because of the high material temperatures inside the kiln (1450 °C). One possible explanation could be that the clinker samples had been contaminated 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 TEQ/m^3 for urban and rural air (Fiedler, 2003). A second possible explanation could be contamination through adsorption of dust and material residues in the cooler. Depositions from ambient air have shown concentrations up to 464, 517 and 14 800 pg TEQ/m^2 for rural, urban and contaminated air, respectively (Fiedler, 2003). A third possibility, which cannot be ruled out for the time being, is possible contamination during the preparation for analysis. Clinker is hard spheres which are difficult to crush and contamination during sample preparation in the laboratory is not unlikely.

Comparing the concentration levels of solid materials used in cement production (Table 4) with other known materials may provide a perspective (Jones and Sewart, 1997; Sinkkonen and Paasivirta, 1998; Rappe et al., 1999, 2000; Santillo et al., 2001). US EPA have estimated the mean PCDD/PCDF values for background urban and rural soils to be 13.4 and 4.1 ng I-TEQ/kg, respectively (Fiedler, 2003). Uncontaminated sediments within the EU

normally range from a few ng PCDD/PCDF TEQ/kg up to 50 ng TEQ/kg dry matters. Sediment cores from 11 lakes/reservoirs located in various geographic locations throughout the United States showed that the most recently deposited sediments had concentration levels ranging from 0.11 ng TEQ/kg to 15.6 ng TEQ/kg, with no known PCDD/PCDF sources nearby (Fiedler, 2003).

7. Conclusion

More than 2000 PCDD/PCDF cement kiln measurements have been evaluated in this study, representing most production technologies and waste feeding scenarios. The data generally indicates that most modern cement kilns today can meet an emission level of 0.1 ng I-TEQ/m^3 and that proper and responsible use of organic hazardous and other wastes to replace parts of the fossil fuel is not an important factor influencing the formation of PCDD/PCDFs. Many earlier emission factors and contribution estimates shows a tendency of exaggerating the influence of the use of hazardous waste on the emissions of PCDD/PCDFs.

Modern preheater/precalciner kilns generally seems to have lower emissions than older wet and long dry-process cement kilns without preheating, but the main influencing parameter stimulating formation of PCDD/PCDFs seems to be the availability of organics/precursors in the raw material and the temperature of the air pollution control device. Feeding of materials containing elevated concentrations of organics as part of raw-material-mix should therefore be avoided and the exhaust gases should be cooled quickly in wet and long dry cement kilns. The detailed understanding how PCDD/PCDFs are formed in cement production is not yet complete, but it seems that a combination of heterogeneous surface-catalyzed reactions and de novo synthesis in the preheater and the post-preheater zones are the most important.

PCDD/PCDFs could be identified and quantified in all raw materials, products and residues used and produced in the industry, but the concentrations were generally low, in the same magnitude as normal earth crust materials, soil and sediments.

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