TECHNICAL NOTE

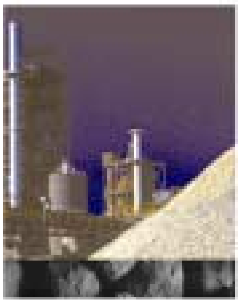
DIOXINS AND THE CEMENT INDUSTRY IN AUSTRALIA

Summary

Dioxin emissions have been measured from a range of Australian cement plants representing different operating processes, different fuel sources and different raw materials.

Results of repeated measurements over a decade show that levels of dioxin emissions from Australian cement manufacturing are consistently below stringent international standards both for cement kilns and for waste incineration plants. Further, dioxin emissions per unit of production compare favourably with levels reported in a number of other countries in Europe and North America. No significant difference in dioxin emissions due to use of waste-derived fuels was observed within plants.

Total dioxin emissions to air from the manufacture of all cement in Australia in a year are estimated to be in the order of 0.29-0.56 g I-TEQ/year, based on measurement of actual emissions. This places actual dioxin emissions from cement manufacture in Australia at the very lowest end of the range of 0.12-153 g I-TEQ/year for sources in Australia, as estimated in Environment Australia's 1998 report on dioxin emissions. This places cement manufacture as one of the lowest sources of industrial dioxin emissions in Australia. Furthermore, comparison with the estimated dioxin emissions from natural sources (bushfires and prescribed burning), places cement manufacturing as an insignificant contributor to overall dioxin emissions in Australia.



Introduction

"Dioxins" are a family of chemical compounds detectable in trace amounts throughout the environment. These compounds are the unintentional by-products of a range of industrial processes and of natural and man-made combustion processes.

Dioxins cause concerns because of their persistence in the environment and the potential of some dioxin compounds to cause adverse health effects.

In 1998, Environment Australia released a report entitled "Sources of Dioxins and Furans in Australia: Air Emissions". The report provided estimates of dioxin emissions to the air from both natural sources and man-made sources in Australia. In the report, dioxin emissions from the Australian cement industry were estimated on the basis of data from the US, UK and Germany, giving a range of emissions varying by three orders of magnitude.

CEMENT INDUSTRY FEDERATION

This Technical Note provides an overview of dioxins emissions from cement manufacturing in Australia, based on actual Australian data, and sets the performance of the Australian cement industry in an international context. Further background information on chemical terminology, exposures and potential health effects, and dioxin measurement techniques is contained in Appendix 1.

The Cement Manufacturing Process

In Australia, the primary cement product is called Portland cement. Portland cement is a fine powder consisting of a mixture of four basic materials: lime, silica, alumina and iron compounds. Raw materials can be fed into the kiln as a wet slurry or as a dry meal and are then heated to a very high temperature to induce chemical reactions that produce a fused material called clinker. The clinker is mixed with gypsum and ground into a fine powder to form the Portland cement.

The fuels most commonly used in Australia are coal and gas, which may be supplemented by waste-derived fuels such as tyres, waste oil, solvents and other similar materials. An oxygen-rich atmosphere, long residence time in the kiln, and high flame temperatures required in the process (>2000°C) provide optimum combustion conditions for these fuels.

Sources of Dioxins in Cement Manufacturing

In spite of the extensive literature available, many fundamental issues related to dioxin formation remain uncertain, or at least are the subject of considerable debate. There are two principal theories to explain the emission of dioxin into the environment from combustion processes: (1) formation from precursors, and (2) formation *de novo*.

It has been suggested that dioxin may form from precursor molecules, such as chlorinated aromatic hydrocarbons, which have a structural resemblance to dioxin. The precursors are products of incomplete combustion at high temperatures and later react further in the lower temperature region of the combustor. The formation of dioxin is believed to occur after the precursor has condensed and adsorbed onto the binding sites on the surface of particles.

Temperature in the range of 250-450°C has been identified as a necessary condition for dioxin formation to occur by this pathway, with either lower or higher temperatures inhibiting the process. These critical temperatures occur where the combustion gases have cooled in flue ducts, heat exchangers, air pollution control equipment or the stack. Thus, reducing the flue gas temperature below the critical level in the pollution control device, for example, has been shown to substantially limit dioxin formation in cement kilns.

Dioxins are also thought to be formed anew (*de novo*) in locations where combustion gases have cooled to critical temperatures. In these reactions, compounds which bear little resemblance to the molecular structure of dioxin combine and react in the cooler sections of the combustor. The presence of chlorine atoms is required for dioxin formation by this pathway.

Less significant reaction pathways that have been proposed include gas-phase reactions, uncatalysed surface reactions and emission of residual dioxin from contaminated feedstock.

In summary, the scale of dioxin production in industrial combustion processes, such as those in the cement industry, is linked to type of furnace or kiln, operating conditions and the type and efficiency of the air pollution control devices. In general, it has been shown that dioxin emissions are limited by high temperatures and long residence time in the furnace or kiln, fast cooling of combustion products (by cooling flue gases) and use of dust collection equipment operating at low temperature. These conditions are those that are characteristic of the cement manufacturing process.

Emissions Limits and International Data

A survey of limits recommended or legislated in a number of other countries for dioxin emissions from cement kilns and waste incineration plants is shown in Table 1. Emission concentration results generally are normalised for oxygen concentration of the exhaust gas, usually to 7% or 11% O_2, to enable comparison of different process conditions. This is noted where that information is available. The Australian data reported in this Technical Note have been normalised to 11% O_2.

Jurisdiction	Limit Mechanism	Facility Type	Limit (ng/m^3)
Canada	CCME[1] Guideline	Cement kiln	0.5
EEC[2 a]	Regulation	Waste incineration plant	0.1
US[b]	Regulation - CAA[3]	Cement kiln	0.2

Table 1: Guidelines and regulations for dioxin emission to air.
Limits are expressed as ng I-TEQ dioxin per cubic metre of gas.
a normalised to 11% O_2
b normalised to 7% O_2, equivalent to 0.16 ng/m^3 at 11% O_2

[1] Canadian Council of Ministers of the Environment
[2] European Economic Community
[3] Clean Air Act

Data from Australian Cement Manufacturing

Data on dioxin emissions from Australian cement manufacturing have been gathered from plants using a range of process conditions, primary fuels and raw materials. Both wet and dry process plants are represented, as are plants using gas and using coal as primary fuel sources as well as some plants using waste-derived fuels. The emission data presented are based on single point measurements, include half limit of detection (LOD) values and are reported to 1989 NATO guidelines.

Concentration of Dioxin Emissions from Cement Plants

The measured concentrations of dioxins in stack gases are shown in Fig 1 and cover the range 0.001-0.07 ng I-TEQ/Nm^3 (55 data points). All measurements comply with stringent European limits for waste incinerators and with the US EPA Maximum Achievable Control Technology (MACT) standards for cement kilns.

Australian emissions data also compare favourably with emissions results reported for Canadian and for German cement plants. Emissions from cement manufacture in Canada have been reported as ranging from 0.008-0.65 ng I-TEQ/m^3. These results cover plants using conventional fuel, as well as plants using some proportion of waste-derived fuel. A German study of cement plants using standard fuels and waste-derived fuels reported emissions ranging from “the limit of detection” to 0.095 ng I-TEQ/m^3 for 160 data points (one result of 0.29 ng I-TEQ/m^3 was reported). In this German study, the type of fuel used did not affect dioxin emissions.

As with the German study, no difference in dioxin emissions was observed when waste-derived fuels were used in Australian plants.

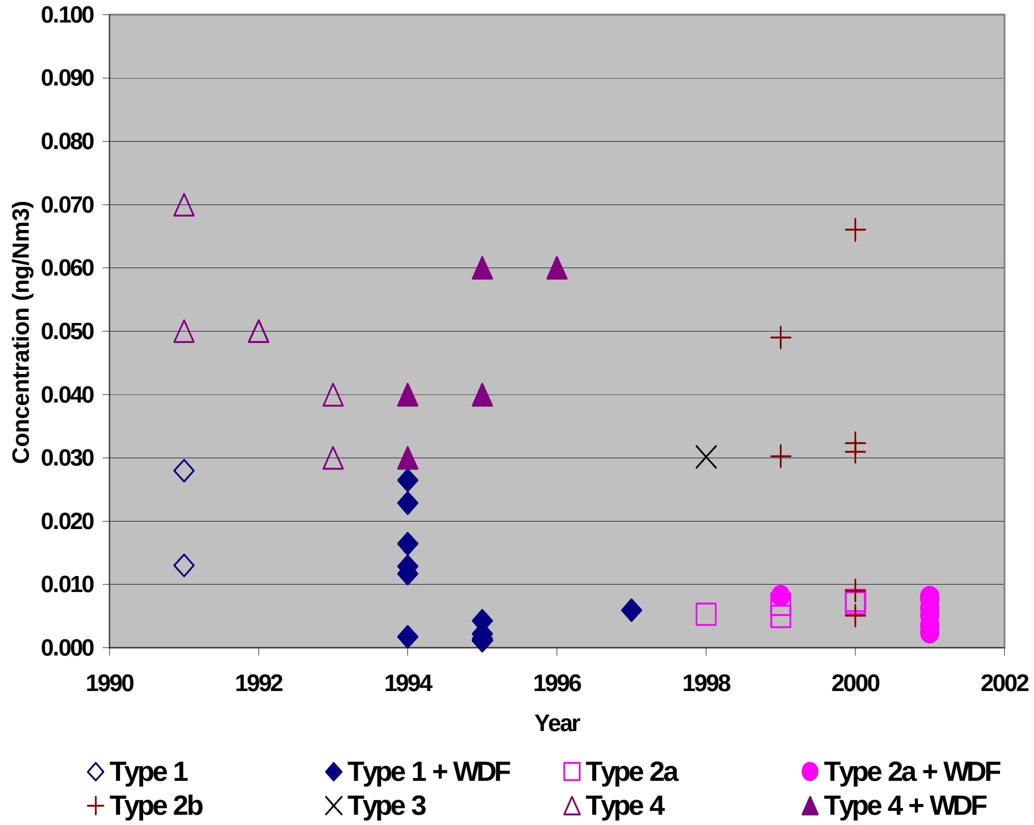


Figure 1: Concentration of dioxin emissions from Australian cement plants, 1991-2001.

Results are expressed as ng I-TEQ dioxin per cubic metre of gas, dry and corrected for 11% O_2.

Facilities using waste-derived fuels are indicated by "+ WDF". The type of production facility is described as following: type of process, primary fuel, pollution control device.

Type 1 – wet, gas, electrostatic precipitator (ESP)
Type 2a – dry, coal, bag filters
Type 2b – dry, coal, ESP
Type 3 – wet, coal, ESP
Type 4 – dry, gas, ESP

<u>Dioxin Emissions per Unit of Clinker Production</u>

Dioxin emissions per tonne of clinker produced in these Australian plants are shown in Figure 2 and cover the range 0.004-0.27 µg I-TEQ/t clinker (42 data points). This data set contains less data points than the data presented in Figure 1 due to the insufficient operating information contained in earlier (1991-1995) test reports. These emission rates from Australian cement manufacture compare very favourably with those reported from the US, UK, and Germany (see Figure 2 and Table 2) and, notably, Australian results are well below the upper bound of the data reported from other countries.

In the Australian data, there appears to be no difference in dioxin emissions when waste-derived fuels are used. One of the deficiencies of the overseas data is the lack of studies that enable within-plant comparison of the effects of fuel type on dioxin emissions. The US EPA has acknowledged the variability in dioxin emissions caused by process conditions and method of pollution control.

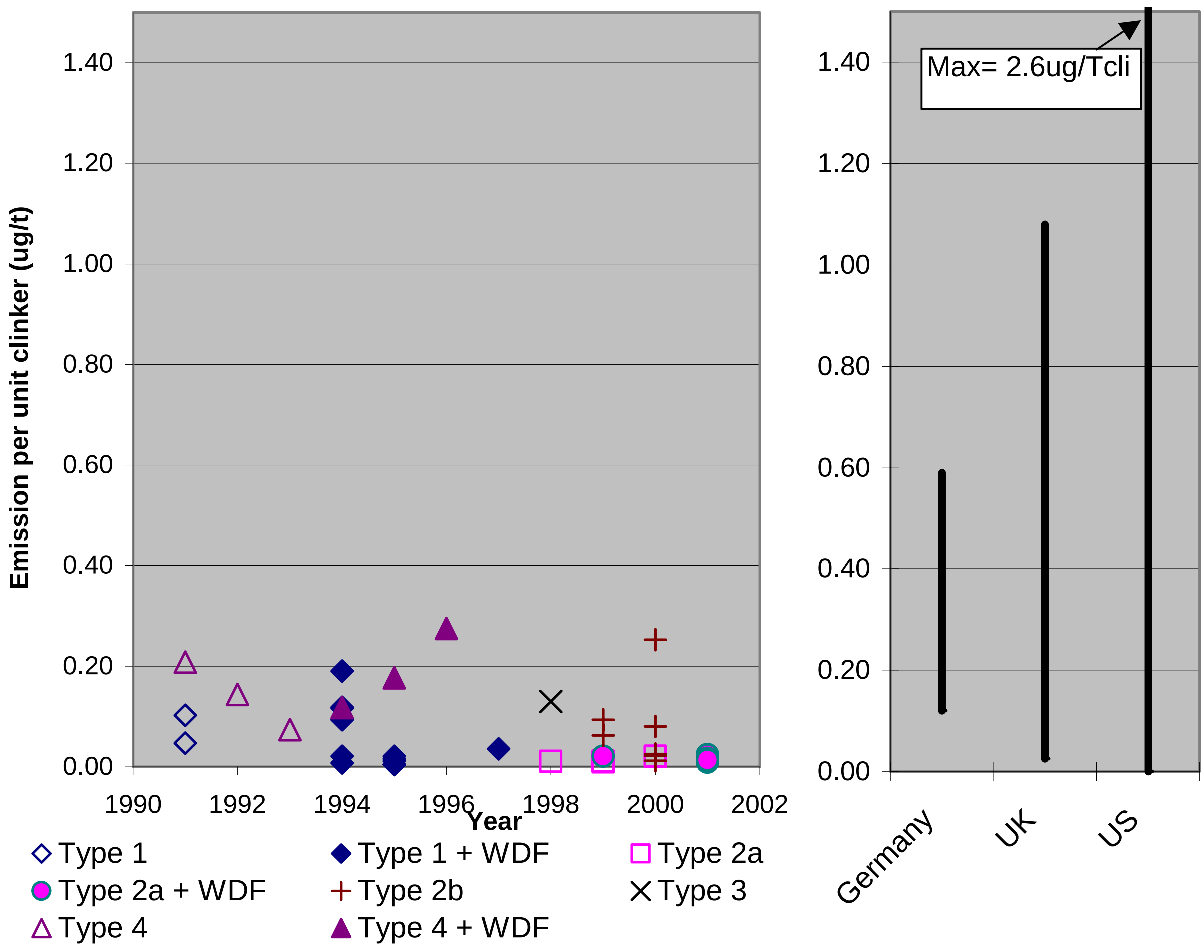


Figure 2: Dioxin emissions per unit of clinker production at Australian cement plants, 1991-2001.

Results are expresses as µg I-TEQ dioxin per tonne of clinker produced.
Facilities using waste-derived fuels are indicated by "+ WDF". The type of production facility is described as following: type of process, primary fuel, pollution control device.

Type 1 – wet, gas, electrostatic precipitator (ESP)
Type 2a – dry, coal, bag filters
Type 2b – dry, coal, ESP
Type 3 – wet, coal, ESP
Type 4 – dry, gas, ESP

Data on dioxin emissions from cement manufacturing that have been presented in international studies and inventories are presented in Table 2.

Country	Reference	Fuel Type	Emissions (μg/t clinker)
Germany	HMIP 1995[1]	Standard fuel	0.12-0.59
UK	HMIP 1995	Standard fuel	0.025-1.04
UK	HMIP 1995	Waste-derived fuel used	0.025-1.08
US[a]	US EPA 1998[2]	Standard fuel	0-2.6

Table 2: Dioxin emissions from cement manufacture

a US EPA notes that these data have a "low" confidence rating because only 6% of plants using standard fuel have been tested

Annual Cement Industry Emissions in Australia

Based on the measured dioxin emissions and the production rates of the various plants, it is expected that total dioxin emissions from cement manufacture in Australia are in the range 0.29-0.56 g I-TEQ/year. Actual dioxin emissions from all the cement manufactured in Australia for an entire year is at the very lowest end of the range 0.12-153 g I-TEQ/year estimated in Environment Australia's 1998 report on dioxin emissions. This places cement manufacture as one of the lowest sources of man made dioxin emissions in Australia. Comparison of dioxin emissions from Australian cement manufacture with the estimated dioxin emissions from natural sources of bushfires and prescribed burning (72-1700 g I-TEQ/year) places cement manufacture as an insignificant contributor to overall dioxin emissions in Australia.

[1] Her Majesty's Inspectorate of Pollution (HMIP), (1995), *'A Review of Dioxin Emissions in the UK'*, Report No. DOE/HMIP/RR/95/004, Department of the Environment.

[2] US-EPA, (1998): www/usepa.com

Appendix 1: Background information

Chemical Terminology

The dioxin family of compounds falls into two major categories, the polychlorinated dibenzo-p-dioxins (PCDD) and the polychlorinated dibenzofurans (PCDF). For purposes of discussion in this paper, these groups will be collectively referred to as dioxins. There are 75 individual PCDD compounds and 135 PCDF compounds, which are classified into groups depending on the number of chlorine atoms in the molecule. The position and the number of chlorine atoms influence the chemical and potentially harmful properties of the individual compounds.

The compound 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin) is considered to be the most harmful member of the dioxin family and those compounds which have at least four chlorine atoms substituted at the 2, 3, 7, and 8 positions are considered to have “dioxin-like” effects. Of the 210 dioxin compounds, only 17 are substituted in these positions and are considered potentially harmful to humans.

These dioxin-like compounds are found in complex mixtures. For risk assessment purposes, procedures to describe the cumulative harmful effects of these mixtures as a single result have been developed. Thus, the generally accepted method of reporting dioxin results is in terms of an international toxic equivalent quantity (I-TEQ).

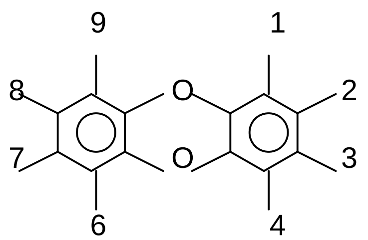
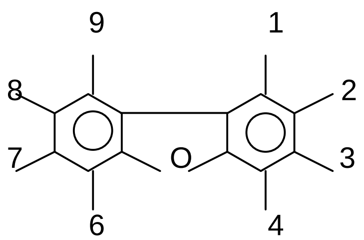
Common Name	**Dioxin**	**Furan**
Chemical Name	Polychlorinated dibenzo-p-dioxin	Polychlorinated dibenzofuran
Abbreviation	PCDD	PCDF
Chemical Formula		

Figure 1: Dioxin Terminology

Exposures and Health Effects

Dioxins are ubiquitous in soil, sediments and air. These compounds are the unintentional by-products of a range of natural and man-made combustion processes. The relative amounts of dioxin compounds produced depend on the type of production or combustion process and vary widely.

Dioxins are poorly soluble in water, are not very volatile and adsorb strongly to particles and surfaces. The most harmful compounds are stable in the environment and accumulate in the fatty tissues of animals and humans.

Exposure to dioxin in sufficient doses is associated with a number of ailments and illnesses, such as an increased risk of severe skin lesions, altered liver function and lipid metabolism, depression of the immune system, and endocrine and nervous system abnormalities. It can also cause cancers of the liver and other organs in animals.

In 1997, the International Agency for Research on Cancer (IARC) classified the most harmful form of dioxin as carcinogenic to humans. All other forms of dioxins were classified as non-carcinogenic to humans.

More than 90% of the daily intake of dioxins results from eating food, primarily, meat, dairy products and fish.

Dioxin Measurement Techniques

Measurement of PCDDs and PCDFs presents a number of challenges. Firstly, these compounds are usually present at extremely low levels in environmental samples, therefore very sensitive and careful methods of sampling and analysis are required. Additionally, because of the different toxicities of the dioxin compounds, the individual levels of the 17 “dioxin-like” compounds must be determined, to enable proper risk assessment. The remaining 193 dioxin compounds can seriously interfere with the determination of the concentrations of the forms of dioxin of the most interest.

Contamination of samples can also present serious problems. Potential sources of contamination include sampling technique and experience and care of sampling personnel, equipment and containers, solvents and reagents, glassware and other samples.

The analysis of dioxins in environmental and biological samples generally proceeds in five stages, each of which must be carefully controlled and optimised to ensure reliable data. These five stages are: (1) sampling, (2) extraction, (3) clean-up, (4) separation and (5) quantification.

To measure emissions to air from cement manufacturing, a 5 m^3 representative sample of stack gases is collected. Dioxins can be attached to dust particles or be in the vapour phase. Particles are collected on a glass fibre filter and the vapour phase is condensed on a cooled resin trap, with sampling occurring over a period of one to five hours, depending on air flow from the source.

At the laboratory, the collected samples undergo extensive chemical extraction, clean-up and separation procedures to remove other compounds which might interfere with the analysis. Quantification of the dioxin compounds occurs by mass spectrometer. A number of specialist studies on dioxin emissions from cement kilns indicate that there is an inherent profile for dioxin emissions from the cement manufacturing process, which provides a distinctive identification characteristic of the test sample. A review of potentially contaminated testing results can be undertaken by qualified specialists based on the characteristic profile of the emission source.

Due to the complexity of the procedures and the sensitive instruments required for analysis, the cost of a dioxin sampling and analysis run in Australia is between $5,000 and $6,000 per sample.

Also, because of the care required in preparation of sampling equipment, sampling, storage and transport of samples and laboratory analysis, there are numerous opportunities for samples to become contaminated. The extremely low level of detection required for the analysis for these elements means that only one small mistake in any part of the sampling and analysis process can result in erroneously high results being reported.