Formation and release of POP's in the Cement Industry

Kåre Helge Karstensen[1]

[1]SINTEF, Oslo

Executive summary

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

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

The objective of this study is to compile data on POP's emissions from the cement industry, to share state of the art knowledge about PCDD/F formation mechanisms in cement production possesses and how it is possible to control PCDD/F

emissions from cement kilns by utilising primary measures, i.e. integrated process optimisation. This report is providing the most comprehensive data set available, collected from public literature, scientific databases and individual company measurements.

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

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

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

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

The data presented and discussed in this report shows that:

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

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

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

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

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

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