SOUR II

PCDD/F-Emissions from German Cement Clinker Kilns

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1. Introduction

Portland cement clinker is manufactured by burning a homogenized raw material mix of defined composition to sintering in industrial rotary kilns of various designs. As in any high temperature process PCDD/F formation can occur in the flue gas downstream from the burning zone especially in the air pollution control device. For more than 10 years now PCDD/F emissions from cement clinker kilns have been examined extensively. Up to now the Research Institute of the German Cement Industry, Düsseldorf, (Forschungsinstitut der Zementindustrie) has performed more than 150 single PCDD/F emission measurements at German cement clinker kilns which are now comprehensively presented for the first time.

2. Cement manufacturing process

Portland cement is produced by intergrinding Portland cement clinker and calcium sulfate. Portland composite cements may also include granulated blast furnace slag, natural pozzolanas, siliceous fly ash, burnt shale or lime stone as major constituents. The cement clinker is burnt in rotary kilns using a raw material mixture of lime stone and clay. If an essential chemical component needed in the cement raw mixture is not present in the required amount, corrective ingredients providing e.g. quartz or iron oxide are used as additives. The preheated, ground and homogenized raw material is fed to the rotary kiln in which it is sintered to form clinker at material temperatures of 1 450 °C. In order to provide these temperatures high calorific fuels are used at the main burner at the kiln outlet yielding gas temperatures of about 2 000 °C. The clinker is finally cooled in the clinker cooler. The recovered heat is mainly used as preheated combustion air (secondary air).

The raw material components are interground and prepared for kiln feed as a slurry (wet kiln), as pellets (Lepol kiln) or raw meal (suspension preheater kiln). In Germany only suspension preheater kilns (about 50 kilns, 80 % of national clinker capacity) and Lepol kilns (about 25 kilns, 20 % of national clinker capacity) are operated.

Figure 1 and figure 2 schematically show the suspension preheater kiln and the Lepol kiln, respectively. In the suspension preheater kiln (figure 1) the raw meal is fed to the top of the preheater. The heat from the kiln gas is transferred to the raw material. Gas/solid separation takes place in cyclones which provide that the raw meal is transported down to the kiln by gravity. The kiln gas exits the preheater tower. Its remaining heat is used to dry the raw material when being ground in the raw mill. For times when the raw mill is not operated the gas is cooled-down by water injection in a conditioning tower in order to provide optimized dedusting conditions in the electrostatic precipitator (ESP). Recent suspension preheater kilns provide a secondary firing where extended precalcination of the lime stone takes place. Temperatures are determined by the calcining reaction to less than 850 °C allowing also low calorific fuels to be used.

In Lepol kilns (figure 2) the raw material is pelletized and preheated in a grate preheater. Gas temperatures levels for both kiln types are also given in figure 1 und 2.

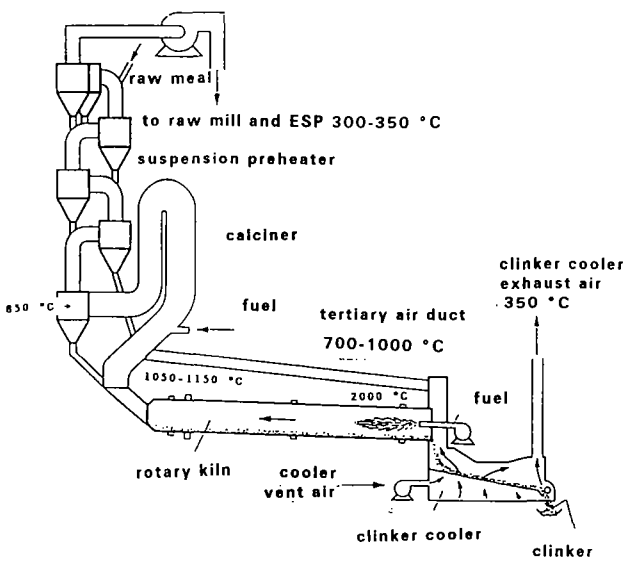

Figure 1: Suspension preheater kiln with precalciner. Typical gas temperatures as indicated.

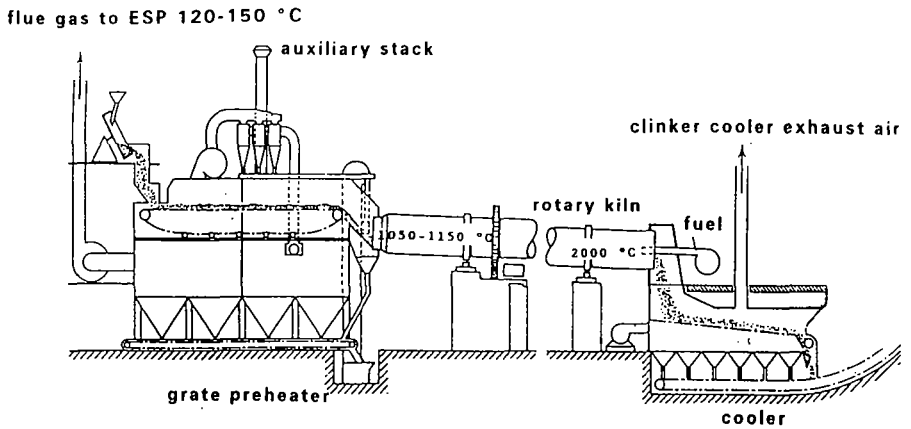

Figure 2: Lepol kiln. Typical gas temperatures as indicated.

Cement kilns use air pollution control devices for dedusting the kiln's exit gas. All German cement kilns use ESP. The daily averaged dust concentration of the cleaned gas is at least less than 50 mg/m^3 (dry and normal condition). Gas temperatures in the ESP typically range from 95 to 205 °C (suspension preheater kiln) and 120 to 150 °C (Lepol kilns).

3. Emission measurements

All PCDD/F emission measurements reported here were performed by using the filter/cooler sampling method according to Guide Line VDI [1]. Sampling ports were always downstream from the ESP where the flue gas had been dedusted. Sampling time was about 6 hours; a total of 20-25 m^3 flue gas was extracted from the stack gas. During sampling the respective kiln was in a representative mode of operation, i.e. the raw feed was at least 70 % of kiln capacity. Secondary fuels such as used oil, bleaching earth, used car tyres or waste-derived fuels were used in some kilns. In some cases secondary raw material substitutes like e.g. fly ash, or old sand were used as corrective ingriedients.

The results from the PCDD/F emission measurements here reported have all been converted to an oxygen concentration in the flue gas of 11 vol.-%. The results are depicted in figure 3. The I-TEQ concentrations have been calculated according to NATO/CCMS taking congenere concentrations below detection limit as 0.

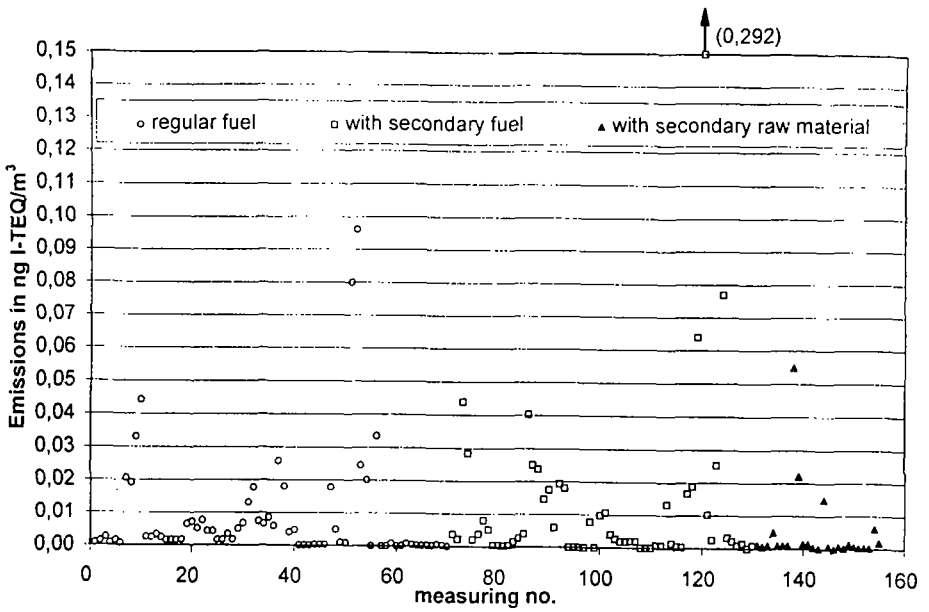

Figure 3: Dioxin emissions of cement kilns (values referred to 11 vol.-% O_2, normal, dry condition)

Since the operating temperatures of air pollution control devices are known to affect PCDD/F formation the reported data are depicted in figure 4 with respect to stack temperatures at the sampling port. This temperature also corresponds to the flue gas temperature at the ESP since heat losses along the gas ducts could be neglected.

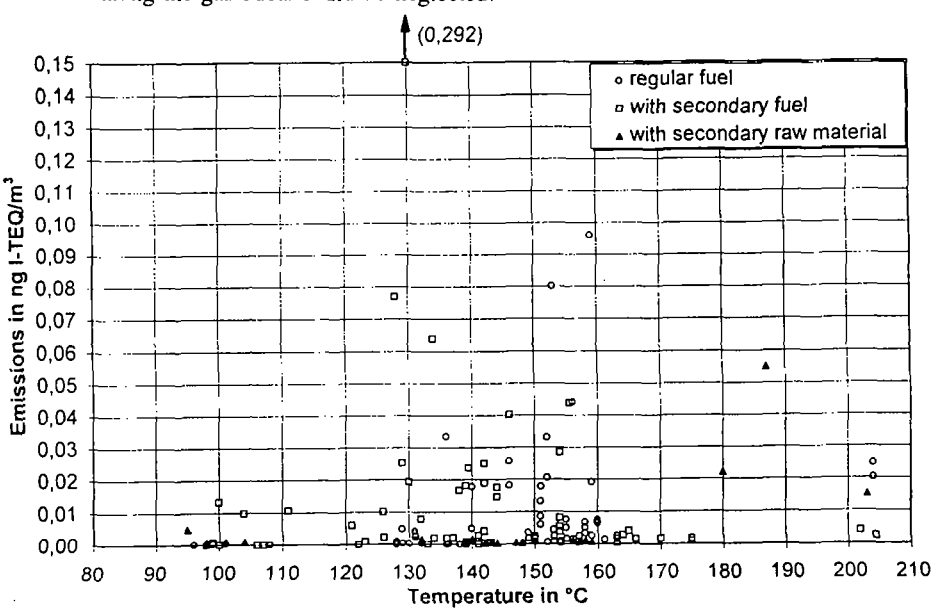

Figure 4: Dioxin emissions of cement kilns versus stack gas temperature (values referred to 11 vol.-% O_2, normal, dry condition)

4. Discussions and conclusion

The reported concentrations refer to PCDD/F emissions measured at 16 different kilns. All measurements were carried out by the Forschungsinstitut since 1989 until present. They are reported without any made selections. Therefore, these data can be assumed to represent the PCDD/F emissions from the cement clinker kilns investigated. The average concentration amounts to about 0.02 ngTE/m^3. No significant difference is indicated from the type of fuel being burnt. For the reported measurements the ESP temperatures were from about 95 to 205 °C. At this temperature range there is no indication that temperature correlates with the PCDD/F concentration in stack. Detailed examinations have also shown that the oxygen content as well as the dust concentration in stack do not correlate with the reported emission concentrations. For these circumstances it seems that from an operator's point of view the PCDD/F emission concentrations cannot be influenced.

The reported data indicate that the examined cement kilns can mostly comply with an emission concentration of 0.1 ngTE/m^3 given as limit value in the German and European legislation for industrial processes burning waste or hazardous waste, respectively.

However, the fluctuations of the various emission data also show that a reduced emission limit value of less than 0.1 ng TE/m^3 will be hard to be complied with; especially when an external variability of about 0.025 ng TE/m^3 is taken into account as measurement uncertainty as pointed out in the new European Standard prEN 1948-3 [2].

It is known from the literature that investigations carried out in the US have revealed some cases with higher concentrations of PCDD/F than those found in Germany as presented in this report [3].

There appears however to be agreement that the formation of PCDD/F in cement kilns is not influenced by co-firing of alternative fuels and furthermore that dioxin/furans are formed in/after the preheater and the air pollution control device where chlorine and hydrocarbons from the raw materials are available in sufficient quantities.

This may explain, why in specific cases, the combination of certain kiln systems with unfavourable raw materials, can generate PCDD/F-concentrations in excess of 0.1 ng TE/m^3 as reported from the US cement industry.

5. References

[1] VDI 3499, P. 2, Draft: Emission measurement. Determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) Filter/condenser method. March 1993 (German)
Beuth-Verlag, Berlin-Köln.

[2] Stationary source emission - Determination of the mass concentration of PCDDs/PCDFs - Part 3: Indentification and quantification; European standard prEN 1948-3: 1995

[3] Schreiber, J. Evens, J.J.: Dioxin emission results from recent testing at cement kilns. Organohalogen Compounds 20, 373 (1994)