

# CHARACTERIZATION OF CO-PROCESSING OF DDT IN A PREHEATER/PRECALCINER ROTARY CEMENT KILN SYSTEM

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## Abstract

Co-processing of DDT[2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane] by a modern preheater/precalciner rotary cement kiln system was characterized. The concentration of DDT and PCDD/PCDFs were measured in the exit gas of the main stack under normal baseline operation and when feeding DDT waste to the kiln inlet at a rate of 1 t/h during two days. DDT and PCDD/PCDFs were analyzed in samples of raw meal, clinker and cement kiln dust (CKD) and the destruction efficiency (DE) and the destruction and removal efficiency (DRE) for DDT were 99.99953% and 99.99998% respectively. The average PCDD/F concentration of flue gas was 0.014 ng-TEQ/Nm<sup>3</sup>, which was greatly lower than the national PCDD/Fs flue limit for China of 0.1 ng-TEQ/Nm<sup>3</sup>, further more, there is no significant change to the PCDD/Fs emission comparing with baseline. Under the co-processing of DDT condition, the PCDD/Fs emission factor for flue gas was 0.0396 μg/t. The concentration of DDT increased however slightly in the CKD and the potential of long term build up needs to be investigated further to ensure an environmentally sound destruction.

## 1. Introduction

Since 1970's, numerous studies and surveys have been carried out by many developed and developing countries to evaluate the performance of cement kiln co-processing on hazardous waste and its impact on cement quality and environment. The results of these studies demonstrated there are no difference in the emission or the product quality when waste materials are disposed by the most of modernized cement kiln system, especially, the PCDD/F flue gas concentration is generally greater below of the value of 0.1 ng-TEQ/Nm<sup>3</sup> (Stobiecki et al., 2003; Capmas, 2003; Conesa et al., 2006). With the economy fast growing, China is facing with increasing pressure come from hazardous waste management and dispose; cement kiln co-process can be one of the options for this issue. The trial application of cement kiln co-processing for hazardous waste is just beginning in China in the last 10 years. For POPs waste such as POPs pesticide (DDT, HCH and etc.), there are quite few studies on pollutant emission and disposal performance of cement kiln co-processing. In this study, the DDT wet-table powder was co-processed by a modernized dry process kiln with multi-stage preheater and precalciner, and the destruction performance and pollutants emission was studied, the PCDD/F emission factor was also calculated based on the case study.

## 2. Material and methods

### 2.1 DDT wet-table powder used in the test

The obsolete DDT Wet-table Powder (DWP) in this study gathering from some regional Centers of Disease Control (CDC) of China, which were originally prepared for mosquito prevention. The DWP appears in lighter yellow color powder, some of them taking forms of block, which is contained in 2 kg

per plastic bottle. The total concentration of DDT in weight is 10.63%, which is consist of 0.07% (pp'-DDE), 0.55%(pp'-DDD), 3.86%(op'-DDT), 6.16%(pp'-DDT).The remaining composition of the DWP were wetter agent and dispersant.

## 2.2 The dry process kiln with multi-stage preheater and precalciner, methodology and work condition

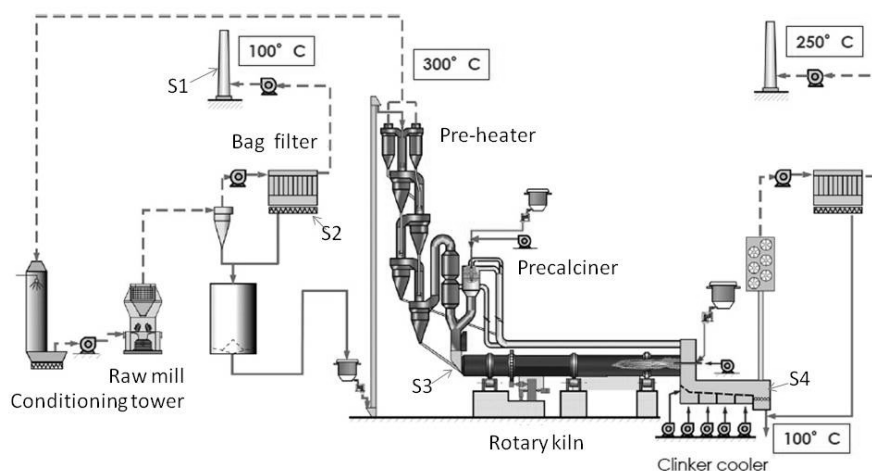


Fig. 1 The new dry process cement kiln system with suspension preheater and precalciner

The DWP contained in plastic bottle as whole were manually fed into waste loading point every span of 7 s, which is transported through conveyer belt into flu gas chamber at inlet of rotary kiln. The waste feed rate is roughly equivalent to 1 t/h, which excludes the weight of plastic bottle.

The flue gas was sampled at location of S1, the fly ash was sampled at the hopper of bag filter of S2, the raw meal was sampled at the raw meal homogenizing storage, the DWP was sampled at the waste loading point of S3 and clinker was sampled from the conveyer belt after the grater cooler going to the clinker storage of S4.

The baseline analysis of flue gas for PCDD/Fs and DDT were conducted one day before the DWP disposal test was fulfilled under the proper work condition.

The DWP disposal was continuously carried out within 13 h on the second day. The flue gas was sampled after the DWP was fed into kiln system for 1 h. The flue gas was sampled every 4h after the end of sampling work, and it was totally sampled 3 flue gas samples under the DWP disposal condition.

## 2.3 Sampling and analytical method

The sampling of the exit gas was conducted in compliance with China's national standards [12,13]. Sampling of DDT in exit gas was conducted according to the USEPA Method TO-4A and China's national standard HJ 77.2-2008 and GBZ/T 160.77—2004 [14,15]. The sampling of solid samples was conducted in accordance with China's national method of HJ/T20-1998 and HJ 77.3-2008 [16,17]. Solid samples were homogenised and reduced to the weight of 500 g, sealed in reagent bottles and kept in dark storage place. DDT powder was sampled every 30 min in a reagent bottle and wrapped with thick plastic bag on site. PCDD/PCDF was analyzed in solid and gas samples in accordance with the Chinese National standard of HJ77-2 and standard of HJ77-3.

DDT was analyzed in solid and gas samples in accordance with the Chinese national standard of GB

5085.3-2007 18, 19]. The DDT powder was extracted by hexane, then diluted and Soxhlet extracted, cleaned by concentrated sulphuric acid and acidified silica-column, and finally quantified by internal standard method GC-ECD.

### 3. Results and Discussion

The concentration of DDT and PCDD/PCDF in exit gas with and without treatment of DDT powder. The DDT concentration without DDT was 18.38 ng/Nm<sup>3</sup>; under DDT treatment the concentration doubled in the first and the second sample, while the third sample fell back to below the concentration of the baseline; the average concentration was 35.19 ng/Nm<sup>3</sup>.

The concentration of PCDD/PCDF without DDT was 0.012 ng-TEQ/Nm<sup>3</sup> and the average concentration when feeding DDT was 0.014 ng-TEQ/Nm<sup>3</sup>. A recent survey showed that the average PCDD/PCDF concentration from 110 cement kiln in Europe was 0.016 ng I-TEQ/m<sup>3</sup><sup>[1]</sup>.

The concentration of DDT and PCDD/PCDF in raw meal, clinker and CKD during DDT treatment. The DDT concentration in clinker was 0.0682 ng/g and 7.78 ng/g in CKD; no DDT was detected in the raw meal. As the CKD are continuously fed back to the process, this might indicate a build up of DDT in the clinker and CKD and needs to be investigated further over longer periods.

The concentration of PCDD/PCDF in raw meal is slightly higher than clinker, but this might be due to an analytical error. The concentration of PCDD/PCDF in CKD seems to be significantly higher than in raw meal and clinker and needs to be investigated further over longer periods.

An international survey found that the average PCDD/PCDF concentration of 11 raw meal samples, 57 clinker samples and 90 CKD samples was 1.4 ng I-TEQ/kg, 1.24 ng I-TEQ/kg, and 6.7 ng I-TEQ/kg respectively<sup>[2]</sup>, indicating that the PCDD/PCDF concentrations found in this project is of the same magnitude.

The introduction of 1 t/h DDT powder with content of 10.63% amounts to 106.3 kg DDT/h; the throughput of raw meal is 400 t/h with a DDT concentration below the detection limit; the clinker production was 227.6 t/h with a DDT concentration of 0.0682 ng/g; the volume of exit gas was 644,000 Nm<sup>3</sup>/h with a DDT concentration of 30 ng/m<sup>3</sup>; the output of CKD was 60 t/h with a DDT concentration of 7.78 ng/g. The DE and the DRE of the DDT was calculated to be 99.99953% and 99.99982% respectively; the DDT identified in the exit gas, clinker and CKD constituted 3.8%, 3.1% and 93.1% of the total DDT output respectively.

The PCDD/PCDF emission factor for exit gas, clinker and CKD was calculated to be 0.04 µg I-TEQ/t, 0.22 µg I-TEQ/t and 1.24 µg I-TEQ/t respectively. The average emission factor for exit gas from new modern dry suspension preheater rotary cement kiln provided by the UNEP Toolkit is 0.05 µg I-TEQ/t<sup>[4]</sup>.

Cement kilns usually have limited tolerance for chlorine and the total input needs to be controlled carefully to avoid process clogging and impacts on the product quality<sup>[5]</sup>. The chlorine input from the DDT was calculated to constitute 53 kg/h, or 0.013 % of the total throughput from other input materials.

The temperature of the kiln inlet (where the DDT was fed) was measured to be 1095 °C. The concentration of all other emissions to air was in compliance with China's Emission standard of air pollutants for cement industry. The coal feed to the precalciner went down from 22.2 t/h to 19.5 t/h during the DDT feed, maybe indicating a fuel saving potential but this needs to be verified through more comprehensive investigations.

#### 4. Conclusion

The concentration of DDT and PCDD/PCDFs were measured in the exit gas of the main stack of a modern preheater/precalciner cement kiln in the Hubei Province when feeding DDT waste to the kiln inlet at a rate of 1 t/h. DDT and PCDD/PCDFs were also analyzed in raw meal, clinker and cement kiln dust and the destruction efficiency and the destruction and removal efficiency for DDT were 99.99953% and 99.99998% respectively.

There were no significant difference in PCDD/PCDF concentration of the exit gas under normal baseline operation or when feeding DDT waste. The emission factor for PCDD/PCDF was comparable with international levels and the concentration of all air pollutants in the exit gas were in compliance with Chinese emission limit values.

The concentration of DDT increased slightly in cement kiln dust during the one day testing and the potential of long term build up needs to be investigated further.

#### Acknowledge

Huaxin(Wuxue) Waste Material Disposal Company is highly acknowledged for the cooperation in the test burns. Tsinghua University is highly acknowledged for the support of PCDD/Fs and DDT sampling and analysis.

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