DIOXINS AND MERCURY IN A CEMENT PLANT: A CASE STUDY IN ANHUI PROVINCE, CHINA

Zhang LF[1], Yang X[1], Zhou R[1], Zhang YC[1], Huang J[1], Cao G[1], Mao YQ[1], Wang Y[1], Liu Y[1], Yu B[1], Lin J[2], Li XX[2]

[1]State Environmental Protection Key Laboratory of Dioxin Pollution Control, National Research Center for Environmental Analysis and Measurement, Beijing, China, 100029, lfzhang@cneac.com; [2]College of Resource Environment and Tourism, Capital Normal University, Beijing, China, 100048

Introduction

Cement is considered one of the most important building materials. China's cement output reached 2.38 billion tons in 2020[1], and ranked first in recent decades around the world. The proportion of rotary kilns with both a preheater and decomposition furnace in China's cement industry is now close to 100%. Generally, the raw material mixture composed of about 78% limestone, 20% sandstone, and 2%-3% correction materials (mainly iron powder) is milled in a raw mill and transported to raw meal silos. The raw meal is fed into the kiln system which comprises a tower of cyclone preheaters. The pre-calcined raw meal with fuel (mainly coal powder) are further calcined in rotary kiln at about 1450℃ forming clinker. The clinker together with gypsum and other additives, like mineral powder, coal fly-ash are further milled in a cement mill to form different cement products. Notably, kiln dust collected in kiln tail and head are reintroduced to raw meal and clinker, respectively.

Dioxins and mercury are pollutants of concern due to the toxicity, persistence, and bioaccumulation in the environment. Many studies had reported the dioxins and mercury emitting from cement plant, especially co-disposal solid waste. However, content of dioxins and mercury in powder samples, such as raw materials, kiln dusts, additives, and cement product during cement production remained unclear. Anhui is a big province of cement production, with the clinker production capacity takes the first place in China. In this study, powder samples together with stack gas were collected from a 5000 t/d cement plant in Anhui province. The primary aims of this study were: (1) to evaluate the contents of dioxins and mercury in powder samples and stack gas in a 5000 t/d cement plant; (2) to clarify the levels and profiles of dioxins in powder samples from different process stages of the cement plant; and (3) to preliminary estimate the elimination/emission factor of dioxins and mercury in cement plant. The study could provide essential knowledge on dioxins and mercury distribution during the whole process, and to develop possible strategies and techniques to control these pollutants from the cement industry.

Materials and methods

A measurement program was undertaken at a continuously operating pre-heater and pre-calciner cement kiln in Anhui province, China. Powder samples from multiple different process sites were collected, including iron powder (PS 1), coal powder (PS 2), raw meal (PS 3), cyclone dust (PS 4), clinker (PS 5), mineral powder (PS 6), gypsum (PS 7), coal fly-ash (PS 8), cement product (PS 9), kiln-tail fly-ash (PS 10), limestone (PS 11), sandstone (PS 12), and kiln-head fly-ash (PS 13). Because of general inhomogeneity, the powder samples were collected by fully mixed multipoint sampling. Stack gases (SG) were isokinetically sampled using an automatic isokinetic sampling method (Isostack Basic, TCR TECORA, Italy) and Ontario hydro method (C-5000, Environmental Supply Company, USA) for dioxins and mercury, respectively. Three consecutive stack gas samples were collected and analyzed for dioxins and mercury determination.

The collected powder samples and stack gas samples were analyzed according to HJ 77.3-2008 and HJ 77.2-2008[2] for dioxins determination. Briefly, samples (about 20 g for powder sample and 2.0 m^3 for stack gas) were Soxhlet extraction with toluene, and cleanup with multiple silica gel and active carbon columns. HRMS (DFS Thermo Fisher, USA) was used for dioxins sample analysis. The recoveries of $^{13}C_{12}$-labeled PCDD/F standards ranged from 60% to 130%. Concentrations of the congeners below the limit of detection were assigned concentration values equal to half of the respective limit of detection. Toxic equivalents (I-TEQ) were calculated using NATO/CCMS factors.

Mercury in powder samples (about 100 mg) were determined using the adsorptive atomic spectrometry with cold vapor generation method (Pyro-915+, Lumex Instruments, Russia). Mercury in stack gas samples (about 1.5 m^3) were determined using acid digestion methods and atomic fluorescence spectrometer (AFS-9800, Beijing Haiguang Instruments, China). Each powder sample was determined three times for mercury analysis. The detection limit for mercury in powder samples and stack gas were below 0.2 μg/kg and 0.001 μg/m^3.

Results and discussion

Dioxins in the cement plant

The dioxins contents in powder samples ranged from 0.48 to 25 ng TEQ/kg. The dioxins contents in most of the powder samples were below 10 ng TEQ/kg. The highest dioxins content was observed in PS1, indicating iron powder is one of the most dioxins contaminated raw material. The dioxins produced in fly-ash from kiln-tail (PS

10) and kiln-head (PS 13) were 9.5 and 1.2 ng TEQ/kg, respectively. PS13 was mainly composed of particles from clinker. Therefore, the amount of dioxins generation in kiln-head was very little, comparing the content in PS13 and PS 5. Dioxins content in cement product (PS 9) was 0.51 ng TEQ/kg. The average concentration of stack gas was 0.0094 ng TEQ/m^3, which is far below the maximum acceptable emission concentration of dioxins (0.1 ng TEQ/m^3) on co-processing of solid wastes in cement kiln (GB 30485-2013)[3]. This value is consistent with the reported results from a 5000 t/d cement plant in Hubei, China[4].

Table 1. Dioxins and mercury content in samples from the cement plant

Abbreviation	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7
Dioxins content (ng TEQ/kg)	25	0.48	1.3	0.51	0.49	2.0	0.49
Hg content ± standard deviation (μg/kg)	823±8.2	229±19	1060±8.2	35.4±1.6	ND	231±21	1.5±1.7
Abbreviation	PS 8	PS 9	PS 10	PS 11	PS 12	PS 13	SG
Dioxins content (ng TEQ/kg)	0.48	0.51	9.5±3.5	0.48	1.6	1.2±0.9	0.0094± 0.0018 (ng TEQ/m^3)
Hg content ± standard deviation (μg/kg)	395±7.5	64.6±3.7	4790±710	2.1±1.0	28.0±0.4	1.3±0.9	66.0±92.8 (μg/m^3)

The homolog profile of PCDD/Fs can be used to demonstrate the distribution of homologs with different degrees of chlorination. As shown in Figure 1, OctaCDD, heptaCDD/Fs and tetraCDF were obviously higher than those of other homologs in most of the samples, with detection rates were 79%, 64%, and 64%, respectively. It was interesting that octaCDD was dominant in PS 2 (coal powder), PS 11 (limestone), and PS 12 (sandstone), indicating similar formation mechanism. The homolog profiles of PS10 and PS13 were different, indicating longer thermal process in kiln-tail are inclined to form lower chlorinated furans.

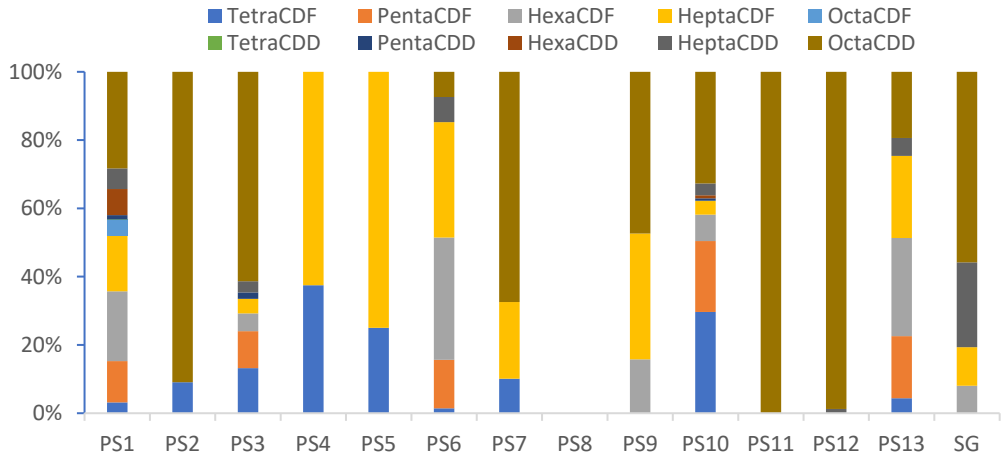

Figure 1. Homolog profiles of PCDD/Fs in samples from the cement plant

The congener profiles of PCDD/Fs can provide useful information for identifying their sources in the environment or speculation regarding their potential formation mechanisms. Figure 2 depicts the congener profiles of 2,3,7,8-PCDD/Fs in powder samples and stack gas from the cement plant. OctaCDD and 1,2,3,4,6,7,8-heptaCDF were observed to be the main congeners in the samples. Formation of PCDD/Fs in cement kiln may occurs in the cyclone preheater zone and the post-preheater zone[5]. The former zone at the upper end of the kiln where the raw meal is added, the gas temperatures typically range from approximately 850-340℃ and can have a retention time up to 25s. This zone constitutes the cooler, the mill dryer and the air pollution control device, with gas temperatures typically in the range from approximately 340-50℃ from the top of the preheater to the exit stack outlet. In fact, PS10 and PS13 were produced after high temperature calcination. OctaCDD, 1,2,3,4,6,7,8-heptaCDD, 1,2,3,4,6,7,8-heptaCDF, and 2,3,7,8-tetraCDF were inclined to form in stack gas after high temperature of municipal solid waste incinerator (n=62, unpublished data). Generally, the gas temperature and residence time in a kiln system was much higher and longer than those in a solid waste incinerator[6]. Furthermore, the extent of temperature drop was larger for kiln-head than kiln-tail, leading to high lower-chlorinated PCDFs formation in PS10 than PS13.

It was assumed that the raw meal and clinker yield ratio is 1.7, which means 1.7 tons of raw meal will be used to produce 1 ton of clinker. For a 5000 t/d cement plant, the amount of raw meal was about 8500 ton per day. The usage of iron powder was about 170 ton per day based on the 2% correction materials in raw mill. As shown in Table 1, dioxins content in iron powder was 25 ng TEQ/kg. About 4.25 mg TEQ dioxins were destructed per day. The estimated elimination factor was 0.85 µg TEQ/t clinker. The total amount of eliminated dioxins was about 1 g TEQ per year in this cement plant. Thus, cement plants can be used as organic pollutants destruction facility under proper operation. In short, the current pollution control facilities of cement plant meet the national and industrial dioxins control requirements.

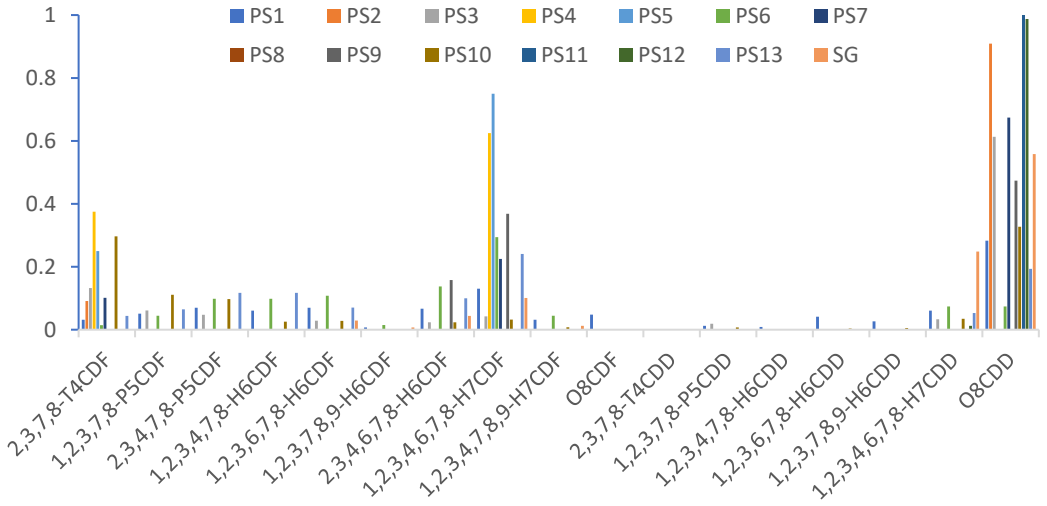

Figure 2. Congener profiles of 2,3,7,8-PCDD/Fs in samples from the cement plant

Mercury in the cement plant

The mercury content in powder samples ranged from ND to 4790 µg/kg. The highest mercury content was observed in PS10, indicating most of the mercury is condensed in the fly-ash from the kiln-tail. As shown in Table 1, mercury content ranked second to third were raw meal (PS 3, 1060 µg/kg) and iron powder (PS 1, 823 µg/kg). High mercury in PS 3 was partially due to the input from PS1 as raw material, but the most important was the recycled fly-ash from PS10. Recirculation of the kiln dust to the kiln will cause release of the captured mercury[4]. Unfortunately, current pollution control measures of cement plants have little effect on reducing atmospheric mercury during the production of clinker[7]. According to Table 1, the average concentration of stack gas was 66.0 µg/m^3. This value exceeds the mercury emission limit (50 µg/m^3) prescribed in the emission standard of air pollutants for cement industry of China (GB 4915-2013)[8]. It should be note that mercury concentrations in the stack gas samples had a high value of standard deviation, indicating the strong fluctuation of mercury emission in the stack gas of cement plant.

The major species emitted into the atmosphere from the cement plant was elementary mercury (Hg^0), accounting for 50% to 99% of the total mercury in stack gas. However, oxidized mercury (Hg^{2+}) dominating the stack gas in some individual cases. The exhaust gases from the preheater/precalciner were used to dry the raw meal, which may absorb a lot of oxidized mercury. The exhaust gases were routed directly to the main filter when the raw mill is shut off. Significant fluctuations in mercury emissions and high Hg concentration (316 µg/m^3, with more Hg^{2+}) have been observed due to shut-off of raw mill[9]. Further study is needed to clarify the mercury content and species fluctuation during this special case.

The standard dry flue gas volume emitted in kiln-tail was 360 thousand cubic meter per hour. It was assumed that about 570 g atmospheric mercury emission per day. The estimated emission factor of atmospheric mercury was 0.114 g/t clinker, which is similar with recent research result (0.091 g/t clinker) from 60 cement production lines in 23 provinces in China[7]. The total emitted amount of atmospheric mercury was about 170 kg per year from this cement plant. Hence, more pollution control measures on mercury in cement plants are needs in the future.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2016YFC0208104). We thank Pan Aijun, Chen Zhi, and A Bu for sample and operation information collection.

References

1. *National Bureau of Statistics*, China, (2021).
2. *National Environmental Protection Standard*, China, (2008).
3. *National Standard for pollution control on co-processing of solid wastes in cement kiln*, China, (2013).
4. Li Y, Chen T, Zhang J, et al. (2015) *Waste Management*. 36: 130-135.
5. Karstensen KH (2008) *Chemospehre*. 70: 543-560.
6. Zheng Y, Jensen AD (2012) *Progress in Energy and Combustion Science*. 38: 599-629.
7. Cui J, He J, Xiao Y, et al. (2021) *Atmospheric Environment*. 246: 118133.
8. *National emission standard of air pollutants for cement industry*, China, (2013).
9. Won JH, Lee TG (2012) *Atmospheric Environment*. 62: 265-271.