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Evaluation of PCDD/Fs emissions during ceramic production: A laboratory study

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HIGHLIGHTS

- The first study on the dioxin emission investigation during ceramic production.
- Dioxin emission can be reduced remarkably at initial kiln temperature of 400 °C.
- Glaze coating may reduce the dioxin emission.

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ABSTRACT

Because of the ubiquity of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in kaolinitic clays, the ceramic industry is considered to be a potential source of PCDD/Fs. However, studies on the emission of PCDD/Fs from ceramic production are still very scarce. In this study, PCDD/Fs emissions during ceramic production were investigated in an electric laboratory batch kiln. The results showed that the PCDD/Fs were completely removed from the ceramic pieces after 30 min of firing at the peak temperature of 1200 °C. Nevertheless, on the mass and international toxic equivalent basis, 27.5% and 46.2% of the total PCDD/Fs amount in the raw clay were released into the atmosphere during firing, respectively. These PCDD/Fs were emitted into the air before the temperature was elevated to a level high enough for their destruction. Dechlorination reactions generated a broad distribution within the PCDD/Fs congeners including a variety of non-2,3,7,8-substituted ones. The emission of PCDD/Fs was decreased to 16.3 wt.% of the total PCDD/Fs amount in the raw clay, when the initial kiln temperature was enhanced to 600 °C. The emission of PCDD/Fs could be reduced significantly in the presence of a glaze coating on the ceramic test piece. These results indicated that ceramic production is an un-neglectable source of PCDD/Fs in the environment.

1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were detected for the first time in Tertiary ball clays of the Mississippi embayment in 1996 [1]. Since then, many studies confirmed that numerous Tertiary clays, specified as kaolin or ball clay, in North and South Americas, Europe, South Pacific, and Asia also contain PCDD/Fs [2].

Rappe and Anderson [3] found that the U.S. ball clays contained on average 1035 pg/g WHO-TEQ PCDD/Fs whereas the German kaolin exhibited a much lower content of 198 pg/g WHO-TEQ. Contrastly, kaolins from Georgia and North Carolina contained PCDD/Fs close to the limit of detection (LOD).

Abad et al. [4] analyzed two kaolin samples among other types of clay, and found that the PCDD/F contents of the kaolins were almost the same as those of German ball clays with values of 232 and 461 pg/g WHO-TEQ.

Schmitz et al. [5] collected and analyzed Tertiary primary non-sedimentary kaolin and sedimentary kaolinitic clays in Europe. The results showed that the PCDD concentrations were in the range of 3–91 pg/g, 711–45,935 pg/g, and 13,513–1,191,120 pg/g, in primary kaolin, secondary kaolinitic clay, and lignitic clays, respectively.

Horii et al. [2] investigated the distributions and characteristics of PCDD/Fs in kaolin clays collected from ten countries. The results demonstrated that PCDD/Fs were ubiquitous in all kaolins analyzed, at total concentrations ranging from 1.2 pg/g (Brazil) to 520,000 pg/g (the U.S.).

Despite intensive studies on the occurrence of PCDD/Fs in Tertiary clays, no study has been conducted on the fate and evolution of PCDD/Fs during ceramic manufacturing. Ferrario and Byrne [6] found that the final fired ceramic products were free of PCDD/Fs. However, it was not known whether some of the disappeared PCDD/Fs had volatilized and evaporated into the atmosphere before the temperature was elevated to a level high enough for their destruction.

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Table 1
Chemical and mineralogical composition of the clay mixture.

Chemical composition (wt.%)	SiO_2	59.2
	Al_2O_3	27.6
	Fe_2O_3	1.21
	CaO	2.04
	MgO	0.52
	Na_2O	1.58
	K_2O	1.86
	TiO_2	0.34
	L.O.I. (1000 °C)	4.28
Mineralogical composition (wt.%)	Illite	10
	Kaolinite	35
	Chlorite	4
	Quartz	18
	Albite	26
	Microcline	3
	Hematite	2
	Calcite	0.8
$\sum$PCDDs content (pg/g)		217.74
$\sum$PCDFs content (pg/g)		0.26
$\sum$I-TEQ (pg/g)		1.25

Considering the large scale of ceramic manufacturing in the world, there is an urgent need for studying the fate of PCDD/Fs in clay materials during ceramic production. This study was performed in an electric laboratory batch kiln to examine the emission phenomenon of PCDD/Fs during the firing of ceramic tile body. The results may be useful for understanding the extent of dioxin release into the environment and the contribution of PCDD/Fs from the ceramic industry to the environment.

2. Materials and methods

2.1. Materials

One typical raw kaolinitic clay used in manufacturing the main types of tile bodies made in the Chinese ceramic tile industry was selected. Table 1 presents the relevant characteristics of the clay compositions.

2.2. Laboratory kiln

The emission experiments were performed in an electric batch kiln. The kiln has a length of about 120 cm with an inner diameter of about 25 cm. The kaolinitic clay was made into rectangular test pieces (moisture content 18 wt.%), 10 cm in length and width, and 1 cm thick. The mean dry bulk density of these pieces was 2.05 g/cm^3. To simulate industrial conditions, the laboratory thermal treatment was carried out in air atmosphere at a flow rate of 5 L/min in the kiln. The pieces were subjected to the standard thermal cycles, with total firing times (cold to cold) of 70 min, heating rate 40 °C/min, and peak firing temperature of 1200 °C (residence time 25 min).

2.3. Sampling

The gas sample was withdrawn through the outlet in the kiln, using an automatic isokinetic sampling system (Clean Air Instrumentation, France) according to USEPA Method 23. The sampling train consisted of a heated probe liner, filter box equipped with a glass fiber filter and a water-cooled XAD-2 adsorbent trap. Before sampling, the XAD-2 was spiked with a known quantity of USEPA Method 23 surrogate standard solution, containing five surrogate $^{13}C_{12}$-PCDD/Fs ($^{37}Cl_4$-PCDD/Fs) target compounds (Wellington Laboratories, Ontario, Canada). The samples were tightly wrapped individually with aluminum foil (to prevent pollution and loss), sealed in labeled resealable bags. Once the sampling has been completed, the samples were immediately refrigerated at 4 °C.

2.4. Sample preparation

The raw clay and tiles were ground into fine particles using a superfine pulverizer (CAX, Shanghai Yuanhua Machinery Co., Ltd., China). Analysis of PCDD/Fs was carried out based on USEPA Method 23 and 1668A modifications. In brief, the particles and XAD-2 were spiked with a known amount of $^{13}C_{12}$-PCDD/Fs internal standards (Wellington Laboratories, Ontario, Canada). The samples were extracted using toluene for 24 h in a Soxhlet apparatus, and the extracts were concentrated on a rotary evaporator. The extracts were then sequentially purified using acidic silica-gel columns (44 wt.% sulfuric acid-impregnated silica gel) and 10 wt.% silver nitrate-impregnated silica gel [2,7]. The analyte was fractionated using an active carbon column (50 wt.% active carbon-blended silica gel and 50 wt.% active carbon dispersed silica gel). The column was eluted with toluene after a passage of hexane. The toluene fraction that contained PCDD/Fs was concentrated to almost dryness by rotary evaporator under nitrogen, and $^{13}C_{12}$-labeled PCDD/Fs standards were added into the corresponding fractions to calculate the recoveries.

2.5. Chemical and mineralogical analysis

Element compositions such as Si, Al, Fe, K, Ti and Mg were determined in clays using energy dispersive X-ray spectroscopy (Horiba Co., Kyoto, Japan) equipped with scanning electron microscope (Hitachi High-Technologies Co., Tokyo, Japan).

The qualitative mineral content of the clay sample was determined via X-ray diffraction using random powdered samples and <2 μm fraction prepared as oriented clay films.

2.6. PCDD/Fs analysis

Concentrations of PCDD/Fs were determined with high resolution gas chromatography (HRGC) (Agilent 6890N)/high resolution mass spectrometer (HRMS) (JEOL JMS-800D) using a fused silica capillary column DB-5 (60 m × 0.25 mm × 0.25 μm). The inlet temperature of GC was 250 °C; sampling mode was splitless sampling; sample size was 1.5 μL; the column temperature was set to 130 °C for the first 1 min, increased 15 °C/min to a temperature of 180 °C, then increased 3 °C/min to 310 °C and maintained at 310 °C for 5 min. The MS was operated with a resolution >10,000 under SIM mode. Ion source temperature was set as 300 °C. The temperature of GC–MS interface was set to 300 °C. Ionization current was 500 A; electron impact source voltage was 38 eV; ion acceleration voltage was 10 kV; mass correction mode was lock mass mode.

2.7. Quality assurance

Field and laboratory blanks were routinely monitored and in most cases were under the LOD (0.01 pg/g). The mean recoveries of surrogate standards ranged from 79% to 104%, which are within the acceptable 70–130% range set by the USEPA Method 23. The samples were extracted with a blank, which consisted of a Soxhlet thimble containing anhydrous sodium sulfate. The international toxic equivalent (I-TEQ) was calculated using the international toxic equivalence factor [8]. In the case of values below the LOD, I-TEQ was calculated by using half of the LOD.

In order to obtain comparable results for the heat-treated pieces, a correction was made taking into account the loss on ignition at the firing stage. Then the corrected values were used to calculate