Emission Characteristics of Pollutants from Co-processing Aged Refuse in a Bench-scale Simulated Cement Kiln

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ABSTRACT

In this paper, a bench-scale simulated cement kiln was used to study the emission characteristics, as well as the main factors that influence them, of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), heavy metals, and hydrogen chloride (HCl) in flue gas generated by co-processing combustible components of aged refuse (CCAR). The main combustible components were plastics, textiles, and woods, and the calorific value of CCAR (> 2.5 × 10⁷ J kg⁻¹) was much higher than that of original municipal solid waste (OMSW). De novo synthesis was the dominant PCDD/F formation pathway during the co-processing of CCAR, and CCAR with higher chlorine and Cu content tended to generate more PCDD/Fs. The concentration of the PCDD/Fs produced by the pure raw meal used in this experiment was 3.25 ng m⁻³ (0.33 ng I-TEQ m⁻³), which increased to 3.87 (0.56), 6.27 (0.69), or 5.77 ng m⁻³ (0.72 ng I-TEQ m⁻³) when CCAR from different landfill periods was mixed in, with the more chlorinated substituted PCDD/F congeners, especially 1,2,3,4,6,7,8-HpCDF, exhibiting relatively high concentrations. However, the less chlorinated substituted PCDD/Fs, especially 2,3,7,8-PCDD and 2,3,4,7,8-PeCDF, contributed the major share of the I-TEQ value. Feeding CCAR through the raw meal inlet increased the formation of PCDD/Fs. Principal component analysis (PCA) was conducted to identify the similarities and differences between congener distributions among the various samples. Overall, the co-processing of CCAR increases the concentration of pollutants and requires more effective technologies for controlling emissions.

Keywords: Simulated cement kiln device; Aged refuse; PCDD/Fs; Heavy metals; Emission characteristics; PCA.

INTRODUCTION

Aged refuse that is bio-stabilized through years in the landfill (Xie et al., 2012) can also be called “stabilized waste” or “mineralized waste.” Substances such as kitchen waste, plants, and paper in the original municipal solid waste (OMSW) are basically decomposed into soil after long-term landfill, so the nature of the aged refuse is basically stable. Aged refuse can be divided into two categories according to the size of the particle: fine-grained (< 15 mm) and coarse-grained (> 15 mm). The main combustible components of coarse-grained aged refuse are substances that can be recycled and utilized, such as plastics, textiles, and woods (Zhao et al., 2001, 2002). Prechthai et al. (2008a) also found that coarse-grained aged refuse showed great potential for recycling as fuels and fine-grained aged refuse as compost. According to statistics, the total aged refuse in the world reached 2 billion tons, of which at least 200 million tons of aged refuse exist in China (Zhao et al., 2007). Typically, aged refuse consists of about 20-40 wt.% combustibles. This is often the case even when considering landfills located in completely different parts of the world (Prechthai et al., 2008b; Kaartinen et al., 2013; Krook et al., 2012). The capacity of the existing domestic landfills tends to be saturated, and the combustible components of aged refuse (CCAR) have a higher calorific value than the OMSW. Mining aged refuse from landfills and disposing of it properly can make room for landfilling more domestic waste. The key is how to achieve efficient and clean utilization of CCAR.

At present, researchers have already studied the disposal methods of aged refuse. In terms of fine-grained aged refuse, Hurst et al. (2005) believe it can be used as a covering material. Others found that fine-grained aged refuse can be used as an alternative low-cost treatment technology to physically adsorb pollutants from fishpond wastewater (Anijiofor et al., 2018). Liu et al. (2018) used fine-grained aged refuse as an efficient microbial agent, bio-stimulation agent, and soil conditioner. There is less research on coarse-grained aged refuse. Plasma gasification/vitrification technology was used to convert combustible
components into secondary fuels, but the energy consumption is too high to be used on a large scale. A mixture of waste plastic and waste lubricating oil with a mass ratio of 3:2 can be made into a fuel with a calorific value up to $2.9 \times 10^7 \text{ J kg}^{-1}$ by pyrolysis technology, but the viscosity may cause a malfunction of the incineration equipment (Wolfsberger et al., 2015). Esteban-Altabella et al. (2017) used a lysimeter to simulate how refuse from mechanical-biological treatment (MBT) plants evolved in a landfill and believed refuse landfills could be a reservoir of future fuel. The potential uses of CCAR are follows: for sale as fuel or as refuse-derived fuel (RDF), pyrolysis oil, gasification heat treatment, granulation, regenerating various plastics and rubber appliances, etc. Cement kiln co-processing as a method for disposing of solid waste has been used widely, so it may be feasible to co-dispose of CCAR in a cement kiln.

According to the research results, cement kiln solid waste co-processing technology requires a long residence time and high combustion temperature. Flue gas disturbance is beneficial to the complete incineration and decomposition of waste. An alkaline environment can inhibit formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) (Wang et al., 2012; Liu et al., 2015). Bypass venting systems can reduce the chlorine source required for PCDD/F formation (Sutou et al., 1999; Membranes, 2008). The cement kiln firing system and the exhaust gas treatment system have high adsorption (Choy et al., 2004), sedimentation, and dust collection characteristics, and the PCDD/Fs can be solidified in the clinker without causing re-diffusion of PCDD/Fs (Baidya et al., 2016).

With regard to the co-processing of CCAR in cement kilns, the pollution profiles and mechanisms, especially PCDD/Fs, have not yet been studied, although many field investigations of flue gas emission levels and profiles of PCDD/Fs in cement kilns have been done (van Loo, 2007; Conesa et al., 2011; Li et al., 2015; Liu et al., 2015; Zhan et al., 2016a). It is important to study these issues to ensure sustainable development of CCAR co-processing in cement kilns.

In this work, CCAR was sampled from different landfill periods, and the composition and basic characteristics were analyzed. A bench-scale simulated cement kiln device was used to study the emission characteristics and main influencing factors of PCDD/Fs, heavy metals, and hydrogen chloride in flue gas from co-processed CCAR.

**MATERIALS AND METHODS**

**Aged Refuse Source**

The aged refuse was sampled at the landfill of Tianziling Waste Treatment Plant in Hangzhou, Zhejiang Province, China. The designed use period of this landfill was 13 years, and it holds more than 9 million tons of solid waste from Hangzhou and surrounding municipal areas. After screening of aged refuse, samples of fine-grained refuse (grains $< 15 \text{ mm}$) and samples of coarse-grained refuse (grains $> 15 \text{ mm}$) were obtained. We studied mainly the combustible components (plastics, textiles, and woods) in coarse-grained aged refuse. The landfill time is about 11 (S1), 15 (S2), or 19 years (S3). The fractions of the three combustible components are shown in Fig. 1.

The plastics in S1 are mainly plastic bags and beverage bottles, and the textiles are mainly chemical fiber clothing and cushion trim. S2 plastics are mainly plastic bags, film, and toys; the textiles are mainly chemical fiber clothing and cotton clothing. S3 plastics are mainly plastic bags and agricultural film and rubber; the textiles are mainly cotton clothes. The wood in all three samples is mainly branches or wood blocks; leaves are rarely found.

It can be clearly seen from Fig. 1 that plastics are not easily degraded, so they account for the largest proportions, 60.5, 76.1, and 84.9%, and the proportion increases as the disposal time is extended. The proportion of textiles decreased sharply in older landfills, to 28.3, 9.6, and 5.5%, and the proportion of wood was 11.2, 14.3, and 9.6%, which was in the same range.

![Fig. 1. Fraction of combustibles in the CCAR samples.](image-url)
The Bench-scale Simulated Cement Kiln Device

In the new dry-process cement production system, the cement clinker is produced in three main stages: (1) the high temperature incineration stage, (2) the precalcer burner and cyclone preheater stage (850–250°C), and (3) the post-preheater stage (Karstensen, 2008). On the one hand, many scholars have verified that the second stage is the main area for pollutant formation (Phair, 2006; Pardo et al., 2011; Schneider et al., 2011; Van Thuong et al., 2014). On the other hand, the main components of CCAR are plastics, textiles, and woods; the content of heavy metals and chlorine are relatively high; and co-processing of CCAR may affect the normal operation of the cement kiln and increase PCDD/F emissions. So, a bench-scale simulated cement kiln device (Fig. 2) was designed and manufactured to simulate the precalcer burner and cyclone preheater stages and to study the formation of pollutants, especially PCDD/Fs, in the flue gas. The overall height of the device is ~1.8 m, the height of the precalcer burner is ~0.7 m, and the total height of the 5-stage cyclone preheater is 0.7 m. It is equipped with a temperature controller to control the temperature in the precalcer burner and keep it above 850°C. There are two automatic screw feeders that can achieve continuous feed, which will be used to study the effects of adding CCAR from different locations on the formation of pollutants, especially PCDD/Fs. The device has a total of 6 sampling holes for collecting flue gas from each stage of the cyclone and the precalcer burners. A raw meal bucket and an ash bucket are used to collect raw meal and ash.

Experimental Design

The experimental conditions are presented in Table 1. The experiments for each group were carried out twice to ensure the accuracy and stability of the results. The temperature of the precalcer burner was controlled at 850°C and for the first stage of the cyclone separator (C1) was ~320°C, as measured by a thermocouple during the experiment.

Experiments in Groups A, B, C, D, and E were conducted to learn the possible factors that influence pollutant formation from different CCAR and different adding positions. Experiments in Group A can be regarded as controls. Group B, C, and D be used to investigate the role of different CCAR in pollution formation. Groups C and E are conducted to determine the influence of adding CCAR in different positions (Automatic Feeder 1 and 2) on pollution formation.

Fig. 2. Simulated cement kiln device.
Table 1. Experimental conditions.

| Groups | Reactants | Automatic Feeders | Quantity (g (10 min)⁻¹) | Flue gas (L min⁻¹) | Time (min) |
|--------|-----------|-------------------|------------------------|-------------------|-----------|
| A      | Raw meal  | 1                 | 20                     | 1                 | 30        |
| B      | 5%S1 + Raw meal | 1                 | 20                     | 1                 | 30        |
| C      | 5%S2 + Raw meal | 1                 | 20                     | 1                 | 30        |
| D      | 5%S3 + Raw meal | 1                 | 20                     | 1                 | 30        |
| E      | Raw meal/S2 1/2 | 19/1              | 1                      |                   | 30        |

Heavy metals in the flue gas were absorbed by a solution of 5% nitric acid and 10% hydrogen peroxide, and HCl was absorbed by a 0.1 mol L⁻¹ sodium hydroxide solution. PCDD/Fs were collected by an XAD-II resin and toluene solution, and the toluene solution was placed in an ice bath. The device’s total inlet flow rate was 20 L min⁻¹.

Analysis Procedures

According to U.S. EPA Method 1613 (EPA, 1994) for purifying PCDD/F samples, identification and quantification of PCDD/Fs were accomplished by high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on a 6890 Series gas chromatograph (Agilent, USA) coupled with a JMS-800D mass spectrometer (JEOL, Japan). A DB-5ms capillary column (I.D.: 60 m × 0.25 mm; film thickness: 0.25 µm) was used to separate the PCDD/F congeners. The mean recoveries of the standards for PCDD/Fs ranged from 30–135%, which were within the acceptable range of 25–150%. The toxic equivalencies (I-TEQs) were calculated using the NATO/CCMS factors.

RESULTS AND DISCUSSION

Calorific Value, Proximate Analysis, and Ultimate Analysis of CCAR

The samples were pulverized and subjected to calorific value measurement, proximate analysis, and ultimate analysis. The results are shown in Tables 2–3. It can be seen that the plastics in the CCAR have a high calorific value, all above 3.0 × 10⁷ J kg⁻¹, and the calorific values of textiles and woods are lower, but also above 1.5 × 10⁷ J kg⁻¹. The total calorific values of S1, S2, and S3 were calculated to be 2.7, 3.2, and 3.0 × 10⁷ J kg⁻¹, respectively; the total ash was 19.48, 13.94, and 17.17%, respectively; and the total Vad% were 74.27, 79.14, and 75.67%, respectively. Therefore, the value of thermal transformation of CCAR is high.

Chlorine Content of CCAR

The chlorine content of each CCAR and the OMSW is shown in Table 4. The plastics’ chlorine content is the highest, the woods’ chlorine content is the lowest, and the chlorine content increases as the disposal time is extended. The total chlorine content of S1, S2, and S3 was calculated to be 1.08, 1.52, and 4.12 wt.%, respectively. Some researchers analyzed the chlorine content of municipal solid waste (MSW) in Shanghai during the period of 2007–2016, which ranged from 0.14 to 0.4 wt.%, with an average of 0.27 wt% (Zhou et al., 2014). Others analyzed the chlorine content of MSW in Kaohsiung in 1998, 2005, and 2010, which was 0.42, 0.37, and 0.13 wt.%, and the average value was 0.31 wt% (Huang et al., 2011). The chlorine content of CCAR was much higher than that of OMSW. This was similar to the findings by others (Rotheut and Quicker, 2017).

CCAR Combustion and Volatile Matter Release Characteristics

CCAR was subjected to thermogravimetric experiments. The experimental results are shown in Figs. 3–5. It can be seen in Figs. 3–5 that the ignition temperatures of the three samples are 365, 395, and 400°C, which increases with the landfill age. The maximum combustion rates are 7.5, 11.5, and 7.7 wt.% min⁻¹, and the mean combustion rates are 1.28, 1.44, and 1.00 wt.% min⁻¹, which are similar to pulverized coal (1.00–1.40 wt.% min⁻¹) and lower than biomass (1.5–1.6 wt.% min⁻¹) (Ávila et al., 2017; Mureddu et al., 2018). It can be seen that the longer landfill age corresponds to higher combustion rates. A different behavior has been observed for Sample 3 (S3). The reason may be the effect of ash content on combustion rate because different ash content can affect heat transfer (S3 contains more rubber than S1 and S2, which leaves much more residue after decomposing). Further analysis of the volatile release characteristics in combination with the

Table 2. Calorific value and proximate analysis of CCAR (Air-dried basis).

| No. | Mₐd % | Aₐd % | Vₐd % | Fₑₐd % | Calorific value (× 10⁶ J kg⁻¹) |
|-----|-------|-------|-------|--------|-----------------------------|
| Plastics | 1 | 1.57 | 21.58 | 74.10 | 2.75 | 32.33 |
| 2 | 1.32 | 14.18 | 81.76 | 2.74 | 35.55 |
| 3 | 1.22 | 16.52 | 78.18 | 4.08 | 32.18 |
| Textiles | 1 | 1.43 | 16.80 | 69.82 | 11.95 | 19.39 |
| 2 | 2.22 | 18.35 | 74.21 | 5.22 | 28.18 |
| 3 | 2.29 | 23.31 | 64.21 | 10.19 | 21.69 |
| Woods | 1 | 5.89 | 14.92 | 67.72 | 11.47 | 17.11 |
| 2 | 7.69 | 9.74 | 68.54 | 14.03 | 16.72 |
| 3 | 6.01 | 19.39 | 60.01 | 14.59 | 15.54 |
Table 3. Ultimate analysis of CCAR (Air-dried basis).

| No. | C_{ad} % | H_{ad} % | N_{ad} % | S_{ad} % | O_{ad} % |
|-----|----------|----------|----------|----------|----------|
| Plastics | | | | | |
| 1 | 64.11 | 7.18 | 0.58 | 0.9 | 4.08 |
| 2 | 70.71 | 7.89 | 0.5 | 0.64 | 4.76 |
| 3 | 52.4 | 5.76 | 0.44 | 0.71 | 22.95 |
| Textiles | | | | | |
| 1 | 47.04 | 3.59 | 0.87 | 0.9 | 29.37 |
| 2 | 62.3 | 6.45 | 3.8 | 0.86 | 6.02 |
| 3 | 49.89 | 4.78 | 10.47 | 0.59 | 8.67 |
| Woods | | | | | |
| 1 | 41.28 | 3.38 | 0.62 | 0.29 | 33.62 |
| 2 | 43.29 | 3.47 | 0.48 | 0.53 | 34.8 |
| 3 | 37.59 | 3.09 | 0.61 | 0.32 | 32.99 |

Table 4. Chlorine contents of CCAR and OMSW (wt.%).

| | Plastics | Textiles | Woods | Total chlorine contents |
|---|----------|----------|-------|------------------------|
| S1 | 1.36 | 0.71 | 0.54 | 1.08 |
| S2 | 1.77 | 0.93 | 0.61 | 1.52 |
| S3 | 4.6 | 1.43 | 1.4 | 4.12 |
| Typical Chinese cities | / | / | / | 0.64 |
| Kaohsiung | / | / | / | 0.31 |

Fig. 3. CCAR S1 (a) TG/DTG curve and (b) DSC/DDSC curve.
DSC/DDSC curve shows that the three samples began to weigh less at 100–150°C, corresponding to a small endothermic peak in the DCS curve, which may be the loss of free water; the maximum weight loss peak appeared at ~500°C. Two endothermic peaks and one exothermic peak appeared in the corresponding DCS curve. It can be inferred that in the nitrogen atmosphere, HCl, Cl₂, H₂S, and C₆H₆ were mainly released at this temperature by further pyrolysis of macromolecular organic matter, which is inferred to be pyrolysis of plastics in CCAR. Between 650 and 700°C, there is a small weight loss peak, mainly caused by the pyrolysis of coke. When the temperature was further increased to 800°C, the thermogravimetric curves of samples were basically level, and the residue ratio was < 25%.

**CCAR Heavy Metals**

The sorted plastics, textiles, and woods were pulverized separately and mixed according to the proportions, and then 0.1 g of each mixed sample (S1, S2, and S3) was subjected to microwave digestion to measure the heavy metal content; the results are shown in Table 5.

As shown in Table 5, the heavy metal content in CCAR is significantly higher than in OMSW. The OMSW 1 and 2 values are from other research (Jin et al., 2018) and also increase gradually with landfill age, which is similar to the results of another investigation (Zhao et al., 2007). The content is significantly higher than the Chinese national standard for heavy metals in the raw materials of the kiln (GB 30760-2014). According to the maximum allowable heavy metal content, it can be calculated that the amount of CCAR in the raw meal preparation system cannot exceed 15%. Otherwise, the raw meal entering the kiln will not meet the kiln standard, and the pollutant emissions are likely to exceed the standard and may affect the quality of the cement. For example, when the amount of CCAR is 15%, the cadmium and chromium content reaches 0.94 (< 1) and 97.4 (< 98) mg kg⁻¹, respectively. The iron (Fe) and copper (Cu) content is > 1% and > 250 mg kg⁻¹, respectively. During the thermal transformation process, certain forms of these heavy metals (mainly CuCl₂, FeCl₃, and other chlorine-containing metal compounds) have a strong influence on the formation of PCDD/Fs.

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**Fig. 4.** CCAR S2 (a) TG/DTG curve and (b) DSC/DDSC curve.
The Analysis of Heavy Metals and HCl in C1 Flue Gas

The results are shown in Table 6. It can be seen that the content of the volatile heavy metal Hg and the semi-volatile heavy metals As, Pb, and Cd in C1 flue gas is low. Except for Group B, the two types of heavy metal concentrations before and after co-processing of CCAR are in the same range. The concentrations of low-volatility heavy metals, such as Cr, Cu, and Sn, were high and increased (from 1.62 mg m$^{-3}$ to 1.99, 5.76, and 6.42 mg m$^{-3}$ for B, C, and D, respectively) significantly after co-processing of CCAR because there are heavy metals, especially Cr and Cu, in CCAR, which is consistent with the results reported by researchers who investigated cement kiln co-processing of waste tires (Conesa et al., 2016). In addition, most of the low-volatility heavy metals, such as Cr and Cu, will be solidified in the cement clinker, and the change in

### Table 5. Heavy metal content of CCAR and OMSW (mg kg$^{-1}$).

|      | S1      | S2      | S3      | OMSW 1  | OMSW 2  | Standard |
|------|---------|---------|---------|---------|---------|----------|
| Al   | 22,739.2| 21,746  | 25,983.9| /       | /       | /        |
| As   | 51.4    | 49.5    | 53.4    | 0.05–43.7| 0.03–42.2| 28       |
| Cd   | 6.3     | 6.1     | 6.3     | 0.09–146.7| 1.86–169.2| 1        |
| Cr   | 638.2   | 613.3   | 649.1   | 6.8–302.5| 4.57–302.5| 98       |
| Cu   | 245.9   | 260.7   | 284     | 3.7–133.8| 6.05–145.9| 65       |
| Fe   | 13,860.3| 15,083  | 16,861.8| /       | /       | /        |
| Pb   | 232.3   | 170.7   | 220.5   | 0.09–146.7| 1.9–169.2| 67       |
| Se   | 3.7     | 4.6     | 3.8     | /       | /       | /        |
| Zn   | 612     | 686     | 671.8   | 3.86–274.5| 2.9–617.2| 361      |

Fig. 5. CCAR S3 (a) TG/DTG curve and (b) DSC/DDSC curve.
concentration of these heavy metals will affect the cement compressive strength (Krobthong et al., 2012). HCl is mainly derived from the combustion of PVC substances and inorganic chlorides present in CCAR. In the case of full combustion, the chlorine in the PVC can be completely converted into HCl. The release of HCl is increased in the presence of moisture and sulfur, and ~50–60% of NaCl is converted to HCl (Kanters et al., 1996). The reactions are shown in Eqs. (1) and (2).

\[
\begin{align*}
\text{C}_n\text{H}_m\text{Cl}_p + \text{pO}_2 & \rightarrow \text{XCO}_2 + \text{YCO}^\uparrow + \text{ZH}_2\text{O}^\uparrow + \text{WHCl}^\uparrow \quad (1) \\
2\text{NaCl}(g) + \text{SO}_2(g) + 0.5\text{O}_2 + \text{H}_2\text{O}(g) & \rightarrow \text{NaSO}_4(g) + \text{HCl}(g) \quad (2)
\end{align*}
\]

Except for Group A and Group E, the emissions of HCl are higher than the limit of 10 mg m\(^{-3}\) specified in the Chinese national standard (GB 30485-2013). Because the main CCAR components are plastics, textiles, and woods, the content of Cl is high, and the flue gas at C1 has not passed through the air pollution control device. In addition, the existence of a large amount of Cl will cause much harm. First of all, the existence of HCl, O\(_2\), and precursors at a certain temperature (250–600°C) will lead to synthesis of PCDD/Fs. It is well known that CuCl\(_2\) is an important metal catalyst for de novo synthesis (Huang and Buekens, 1995; Mubeen et al., 2017; Lin et al., 2018). S1 (11 years), S2 (15 years), and S3 (19 years) have different compositions of combustible components due to different landfill ages, and the heavy metal concentration (especially Cu and Fe) and chlorine content are also different, which is the main reason for the difference in PCDD/Fs produced in Group B, Group C, and Group D. The overall trend is that CCAR with more chlorine and Cu is likely to generate more PCDD/Fs when co-processing.

Comparing the data of Groups C and E, it can be seen that CCAR has different impacts on the formation of PCDD/Fs when input from different feed inlets. The addition of CCAR at the raw meal preparation system produces more PCDD/Fs than addition at the precalciner burner. The PCDD/F concentrations when the CCAR is input from the raw meal preparation system and the precalciner burner are 7.91 and 7.41 ng m\(^{-3}\), respectively, with corresponding TEQ values of 0.69 and 0.55 ng I-TEQ m\(^{-3}\), respectively. The reason may be that the temperature at the precalciner burner is 850–900°C, so the CCAR is more likely to be burned completely and fewer PCDD/Fs are formed. It is also confirmed that the main formation area of PCDD/Fs in the cement kiln is the cyclone preheater at the temperature range 250–500°C, which verifies previous work of other researchers who believe that this area is the major area for PCDD/F formation (Xhrouet et al., 2001; Liu et al., 2015; Li et al., 2016).

### Congener Distributions of PCDD/Fs

The congener profile of PCDD/Fs helps determine their sources and helps us speculate about their potential formation mechanisms (Zhao et al., 2017). The congener profiles of the seventeen toxic 2,3,7,8-substituted PCDD/Fs in Groups A–E are shown in Fig. 6. Groups A and E mainly consisted of highly chlorinated congeners, and OCDD and OCDF were also the main congeners. Congeners with lower chlorine content were mainly absent in Groups B–D, indicating that de novo synthesis was the dominant PCDD/F formation pathway for the cement kiln (Zhan et al., 2016a). The ratio of PCDFs/PCDDs increased from 1.7 (Group A) to 1.98 (Group B), 3.83 (Group C), and 3.45 (Group D) after co-processing of CCAR, indicating that co-processing of CCAR in a cement kiln further promotes the de novo synthesis of PCDD/Fs. It is well known that CuCl\(_2\) is an important metal catalyst for de novo synthesis (Huang and Buekens, 1995; Mubeen et al., 2017; Lin et al., 2018). S1 (11 years), S2 (15 years), and S3 (19 years) have different compositions of combustible components due to different landfill ages, and the heavy metal concentration (especially Cu and Fe) and chlorine content are also different, which is the main reason for the difference in PCDD/Fs produced in Group B, Group C, and Group D. The overall trend is that CCAR with more chlorine and Cu is likely to generate more PCDD/Fs when co-processing.

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### Table 6. Concentrations of heavy metals and HCl in C1 flue gas (mg m\(^{-3}\)).

|   | As + Pb + Cd | Cr + Cu + Sn + Mn + Ni + Be | Hg | HCl |
|---|-------------|---------------------------|----|-----|
| A | 0.17        | 1.62                      | 0.010 | 6.81 |
| B | 0.38        | 1.99                      | 0.040 | 11.31 |
| C | 0.15        | 5.76                      | 0.009 | 11.10 |
| D | 0.17        | 6.42                      | 0.016 | 12.58 |
| E | 0.19        | 3.21                      | 0.007 | 7.36  |
Table 7. Concentration and distribution of seventeen 2,3,7,8-substituted PCDD/Fs in groups.

|        | A    | B    | C    | D    | E    | Unit     |
|--------|------|------|------|------|------|----------|
| PCDDs  | 1.91 | 1.95 | 1.64 | 1.67 | 3.59 | ng m⁻³   |
| PCDFs  | 3.25 | 3.87 | 6.27 | 5.77 | 3.82 | ng m⁻³   |
| PCDD/Fs| 5.16 | 5.82 | 7.91 | 7.44 | 7.41 | ng m⁻³   |
| PCDF/PCDD | 1.70 | 1.98 | 3.83 | 3.45 | 1.07 | /        |
| Cl-PCDD| 7.39 | 6.72 | 6.34 | 6.47 | 7.53 | /        |
| Cl-PCDF| 6.71 | 6.34 | 6.43 | 6.41 | 6.38 | /        |
| Cl-PCDD/Fs | 6.97 | 6.47 | 6.41 | 6.42 | 6.94 | /        |
| I-TEQ  | 0.33 | 0.56 | 0.69 | 0.72 | 0.55 | ng I-TEQ m⁻³ |

Fig. 6. Congener distribution of seventeen 2,3,7,8-substituted PCDD/Fs in Groups A–E: (a) PCDD/F concentration distribution and (b) PCDD/F TEQ values distribution.
1,2,3,4,6,7,8-HpCDF were the leading congeners, with the fractions of 55.1 and 59.5%, respectively. Similar results were also found in previous studies on the emission concentrations and emission factors of PCDD/Fs from cement kilns in China (Zou et al., 2018). The distribution of other congeners was uniform. This indicates that the addition of CCAR at the precalciner burner has little effect on the distribution of PCDD/F congeners. In Group B, 1,2,3,4,6,7,8-HpCDF, OCDD, 1,2,3,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,7,8,9-HpCDF were the five most abundant congeners, with the total fraction of 59.3%. The main PCDD/Fs produced in Groups C and D were PCDFs. Group C was dominated by two highly chlorinated PCDF isomers, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8,9-HpCDF, and the sum of the two was 39.8%. The distribution of other PCDF isomers was uniform. The fraction of OCDF in Group D reached 18.8%, and the distribution of other PCDF congeners was uniform.

The major contributions to the total TEQ were usually from 2,3,7,8-TCDD and 2,3,4,7,8-PeCDF, accounting for 68.0, 49.7, 44.3, 40.3, and 57.5% for Groups A, B, C, D, and E respectively, which was similar to the findings by others (Abad et al., 2004; Rivera-Austrui et al., 2014), but this is different from the distribution of PCDD/F TEQ values in the flue gas (the 2,3,7,8-PCDF toxic equivalency contribution is the largest, accounting for 60–68%) when Conesa et al. (2016) studied cement kiln co-processing of solid recovered fuel (SRF) and waste tires. This may be due to the different physical and chemical characteristics, dosage, and feeding position of the waste. And this is also different from the distribution of PCDD/F TEQ values in the flue gas when other researchers studied the emissions factors of PCDD/Fs from the stack flue gas of an MSWI (Hsieh et al., 2018; Zhan et al., 2018). This may be due to the different characteristics between CCAR and OMSW.

The CCAR of B, C, and D in this study was added in the raw meal preparation system, and the dosage was 5%, while in another study, the waste as substitute fuel was added at the rotary kiln, and the replacement ratio was as high as 40% (Conesa et al., 2008).

**Principle Component Analysis**

Principal component analysis (PCA) was used to learn the similarities and differences of congener distributions among various samples (Fig. 7). The matrix is used to statistically investigate the signatures representing ten PCDD/F homologue groups of all five samples. Before statistical analysis, no data transformation was performed. Factor 1 and Factor 2 separate all samples into two clusters (A and B), which separately explains 65.5 and 22.1% of the total variance. PCA shows that homologue profiles of Group E are closer to those of Group A, and homologue profiles of Groups B, C, and D are similar. In general, results of clustering obtained from PCA are in accordance with the former discussion. This further verified that the CCAR is completely burned in the precalciner burner, which has little effect on the distribution of congeners (E is compared with A), but that is added at the raw meal preparation system would significantly influence the distribution of congeners (B, C, and D are compared with A).

**CONCLUSION**

The CCAR samples selected for co-processing in this study were sourced from 11-, 15-, and 19-year-old landfills and possessed calorific values as high as 2.7, 3.2, and 3.0 × 10⁷ J kg⁻¹, respectively. However, the samples also contained high amounts of chlorine (> 1 wt.%) and heavy metals, especially Cu (> 250 mg kg⁻¹); hence, the potential risks posed by co-processing CCAR must be carefully evaluated.
After the samples were co-processed using a simulated cement kiln, the concentrations of heavy metals in the flue gas rose, particularly for low-volatility heavy metals, such as Cr, Cu, and Sn, which significantly increased (from 1.62 to 1.99, 5.76, and 6.42 mg m⁻³, respectively). PCDD/Fs are primarily produced via de novo synthesis, and co-processing further aggravated this process. The highly chlorinated congeners significantly contributed to the PCDD/F concentrations, whereas the less chlorinated congeners significantly contributed to the TEQ values. The amount of generated PCDD/Fs also increased with the landfill age. Furthermore, we determined that the PCDD/Fs mainly generated PCDD/Fs also increased with the landfill age. Thus, verifying similar conclusions reached by other researchers for real-world cement manufacturing systems.

PCA also confirmed that the CCAR was fully combusted when input from the precalciner burner and therefore did not significantly affect the distribution of the PCDD/F congeners. By contrast, when the CCAR was fed from the raw meal inlet, the amount of generated PCDD/Fs increased; thus, the raw meal feeding system should not be used for CCAR.

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