Pyrolysis and Dioxin Production Characteristics of Mineralized Waste in Landfills

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Abstract

Compared with original municipal solid waste (MSW), mineralized waste (MW) has a lower moisture content, higher calorific value, and better energy utilization potential. However, due to the high chlorine content of MW and the presence of heavy metals, dioxin and other harmful substances are easily produced during pyrolysis. Therefore, this study investigated the effects of different external chlorine sources and pretreatment methods on the pyrolysis characteristics of MW and the formation of polychlorinated dibenzo-p-dioxins/polychloro dibenzofurans (PCDD/Fs) in pyrolysis fuel gas. This study also compared the heavy metal speciation in char formed during MW pyrolysis using in situ X-ray photoelectron spectroscopy. The results show that carbon and chlorine mainly exist in the form of C and organic chlorine and CuCl$_2$, respectively. Based on thermogravimetric analysis, MW pyrolysis is completed at 200–850°C. The char ignition loss rate is ~20%, and the maximum calorific value is 14,217 kJ kg$^{-1}$. The gaseous heavy metals in fuel gas is relatively stable, but the heavy metal concentration slightly decreases. Compared with other external chlorine sources (NaCl and PVC), CuCl$_2$ has the strongest catalytic effect to promote the gaseous PCDD/Fs formation during pyrolysis. During MW pyrolysis, the PCDD/F concentration is 49.13 ng m$^{-3}$. When the soil content of MW is high, the concentration of PCDD/Fs is low; it decreases from 10.46 to 7.21 ng m$^{-3}$. During the pyrolysis, the PCDD/F concentration of MW is higher than that of the original MSW. After the addition of 30% biomass, the PCDD/F content increases to 16.92 ng m$^{-3}$. The
experimental results of this study provide novel technical guidance for the resource
utilization of MW.

Keywords: mineralized waste, landfill, pyrolysis, dioxins, heavy metal, external
chlorine
Due to population growth, industrial development, and accelerated urbanization, the amount of domestic waste is increasing daily (Kazuva and Zhang, 2019). At present, common domestic waste treatment methods include landfill disposal, incineration, composting, and anaerobic digestion (Wang and Nakakubo, 2020; Zhan et al., 2020). Landfill disposal accounts for a large proportion of harmless waste treatment. However, construction standards have not been implemented at many older landfill sites, which has led to many problems (Powell et al., 2016). Therefore, there is a need for the resource utilization of landfill mineralized waste (MW). MW refers to harmless waste that is stored in landfills for a long time, which is also called stale waste and landfill waste. MW typically contains less than 10% organic matter and easily degradable substances that are completely or nearly degraded and is characterized by minimal amounts of leachate and landfill gas and peculiar smells (Wang et al., 2010; Kazuva and Zhang, 2019). The total global amount of MW has reached 2 billion tons, with China contributing at least 200 million tons. By the end of 2017, China operated 654 domestic waste sanitary landfills (harmless treatment plants). Compared with original municipal solid waste (MSW), MW has better permeability, looser structure (Youcai et al., 2002), higher proportion of combustible components, basic calorific value, and lower moisture content. After the transformation of waste into refuse-derived fuel (RDF), the calorific value can reach 10~20 MJ kg\(^{-1}\). RDF has notable energy utilization advantages during heat treatment and processes such as incineration and power
generation (Bridgwater, 2012; Chalermcharoenrat et al., 2015; Wolfsberger et al., 2015; Rotheut and Quicker, 2017). In this paper, MW refers to landfill waste with a depth of 6 m in 2016. Based on the analysis of the MW composition, the rubber and plastic content reaches up to 36.87%. Due to the short landfill period, the decomposition of organic matter is incomplete. The soil impurities in MW are removed by screening, resulting in a high proportion of combustible components and high calorific value. A similar calorific value was obtained in other studies (Cai et al., 2020).

As reported, the contents of chlorine and heavy metal in MW are much higher than those of primary MSW. Furthermore, the concentration of polychlorinated dibenzo-p-dioxins/polychloro dibenzofurans (PCDD/Fs) produced during the incineration of MW may be higher than that of original MSW with the same quality due to the actions of chloride and metal catalysts. In recent years, new waste treatment methods have been established based on the development of pyrolysis technology, which involves heat treatment under an excess air coefficient below one. In contrast to waste incineration technology, waste pyrolysis and gasification would produce combustible gas, oil and char. Most importantly, the pollutant emissions such as NOX, CO, and PCDD/Fs could also be largely reduced (Bridgwater, 2012; Dong et al., 2015). Furthermore, this technology has many advantages, for instance energy saving, high resource recovery rate and low environmental pollution (Ferrara et al., 2014; Guan et al., 2015; Chen et al., 2016). Pyrolysis thus represents a potential solution to the global MW disposal problem; however, the pyrolysis mechanism of MW remains unclear.
In this study, the pyrolysis characteristics of MW were compared with those of MSW based on thermogravimetric analysis. Primary MW contains numerous soil impurities and biomass components, which have different effects on the pyrolysis process. Therefore, their pyrolysis characteristics must be analyzed. Organochlorine and inorganic chlorine differently affect the dioxin production during waste pyrolysis (Chen et al., 2020; Fujimori et al., 2020). Furthermore, NaCl and PVC (polyvinyl chloride) are the most common inorganic and organic chlorine sources, respectively. Therefore, the effects of pretreatment methods and chlorine sources (NaCl, PVC, and CuCl₂) on the PCDD/F formation during the pyrolysis of MW and MSW were analyzed. The emissions of heavy metals and other pollutants during pyrolysis were also studied. The results of this study may contribute to the development of novel methodologies for the disposal of MW.

2. Materials and Methods

2.1 Experimental materials

MW was collected from a landfill in Suzhou, China. Based on preliminary screening, MW was found to contain many impurities (mainly residues). The MW was placed in a drying oven at 105 °C for 10 h to remove the remaining water and then crushed into 3 mm particles to further separate the impurities in the fuel and determine its composition. The analyses were conducted according to the standards for the proximate analysis and chlorine determination of coal (GB/T212-2008) and (GB/T3558-1996). The physicochemical properties of MW were analyzed to determine whether it is suitable for energy utilization. The results are presented in Table 1. The results of the physicochemical properties analysis of mineralized waste used in this experiment are
shown in Table 2.

Table 1. Composition of mineralized waste.

<table>
<thead>
<tr>
<th>Components</th>
<th>Rubber and plastic</th>
<th>Textile</th>
<th>Herbs</th>
<th>Impurity soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>36.87%</td>
<td>2.18%</td>
<td>8.65%</td>
<td>52.3%</td>
</tr>
</tbody>
</table>

Table 2. Results of the analysis of the physicochemical properties of mineralized waste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (mass%)</th>
<th>Ultimate analysis (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-received basis</td>
<td>As-air-dried basis</td>
</tr>
<tr>
<td></td>
<td>M%</td>
<td>A%</td>
</tr>
<tr>
<td>Mineralized waste</td>
<td>43.19</td>
<td>22.47</td>
</tr>
<tr>
<td>MSW</td>
<td>21.62</td>
<td>35.51</td>
</tr>
</tbody>
</table>

2.2. Experimental system

As shown in Fig. 1, the co-pyrolysis experiments were performed in a continuous feed-type furnace (1 kg h⁻¹, 1 L min⁻¹), which consisted of heating and temperature control system, pyrolysis furnace chamber, a carrier gas supply and collection and condensation device. MW was pyrolyzed in the furnace chamber (600 °C) heated by electric heating modules. The top diaphragm was closed after the material entered the feeder to ensure a constant pyrolysis atmosphere. The pyrolysis gas and oil generated were introduced into the collection device. The pyrolysis chamber was equipped with two air intakes that were used to adjust the pyrolysis and gasification atmospheres. In this study, only N₂ was injected into the first air intake of the furnace to keep the inert atmosphere.
Different experimental conditions were applied to the MW, as shown in the Supplementary material. First, different external chlorine sources (1 wt.% Cl), including inorganic chlorine (NaCl), organic chlorine (PVC) and metal chloride (CuCl₂) were added to the MW to study the effect of chlorine content and state as well as the metal catalyst on the PCDD/F formation. Two pretreatment methods were applied, that is, feed after screening and direct feed (Group B) to find out the effect of soil on the pyrolysis product and pollutant. Second, the effect of biomass on the co-pyrolysis was studied by adding 30% biomass to the MW to increase the amount of combustible compound. The addition of biomass seems that it can improve the pyrolysis efficiency of MW and reduces the generation of PCDD/Fs. The results were compared with the pyrolysis of MSW. Each experiment was performed twice to ensure the data accuracy.

The sampling methods for fuel gas were mentioned in our previous study ((Cai et al., 2020).
<table>
<thead>
<tr>
<th>Group</th>
<th>Sample</th>
<th>Temperature (℃)</th>
<th>Chlorine source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mineralized waste</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Mineralized waste (with soil)</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Mineralized waste (with 30% biomass)</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Mineralized waste</td>
<td>600</td>
<td>NaCl</td>
</tr>
<tr>
<td>E</td>
<td>Mineralized waste</td>
<td>600</td>
<td>PVC</td>
</tr>
<tr>
<td>F</td>
<td>Mineralized waste</td>
<td>600</td>
<td>CuCl₂</td>
</tr>
<tr>
<td>G</td>
<td>MSW</td>
<td>600</td>
<td>-</td>
</tr>
</tbody>
</table>

### 2.3. Sample analysis

#### 2.3.1 Pretreatment and PCDD/F detection methods

The PCDD/F samples were pretreated according to USEPA method 1613, including extraction, concentration, and column passing. Prior to the Soxhlet extraction, the C\textsuperscript{13} Soxhlet standard (1613LCS) was added. The C\textsuperscript{13} purification standard (1613CUS) and C\textsuperscript{13} injection standard (1613ISS) were added before column passing and detection processes, respectively. The PCDD/F analysis of the pretreated samples followed the EPA method 1613. The identified and quantified methods for PCDD/Fs were reported in our previous study ((Cai et al., 2020).

#### 2.3.2 Analysis of the heavy metal speciation

The leaching toxicity were analyzed in accordance with the GB 16889-2008 landfill pollution control standard of the HJ/T300-2007 leaching procedure. The leaching sample was mixed with a liquid/solid ratio of 20:1 (mL g\textsuperscript{-1}) to adjust the pH of 2.64 ± 0.05, room temperature (23 ± 2 °C), and speed of 30 ± 2 revolutions min\textsuperscript{-1}, flipping approximately 18 ± 2 h. Finally, the heavy metal and chlorine concentration in the samples were detected using ICP–AES (ICAP6300) and high-temperature hydrolysis and ion chromatography (ICS-6000, Thermo, USA), respectively. During the
experiment, the gaseous heavy metals were absorbed by a mixture of hydrogen peroxide and nitric acid. According to USEPA3050 standard, it was determined by ICP-MS (thermoelectric science XLL) (Cai et al., 2020).

2.3.3 X-ray photoelectron spectrometer analysis of char

The elemental compositions on the surface of the pyrolysis char were determined using an X-ray photoelectron spectrometer (XPS; ESCALAB 250Xi; Thermo Fisher Scientific, USA) and Mg Kα ($h\nu = 1,253.6$ eV) radiation. The C 1s (285.0 eV) photoelectron peaks were used to calibrate the charge.

3. Results and Discussion

3.1 Pyrolysis characteristics of mineralized waste

To determine the pyrolyzation characteristics of MW, thermogravimetry (TG) and derivative thermogravimetric (DTG) analyses were performed on each MW component. The results are shown in Fig. 2. The heating temperature increased from 25 to 850 °C at a rate of $10^\circ C \text{ min}^{-1}$, and TG and DTG curves were obtained after data analysis. Nitrogen was used as the carrier gas at a flow rate of 50 mL min$^{-1}$. Fig. 2a shows that the pyrolysis of MW consists of three reaction stages. The first peak occurs between 150 and 300 °C, mainly due to the dehydration and decomposition of short chain organic compounds and polymers (Li et al., 2010; Yu et al., 2013). At the second stage (300–500 °C), which is the main pyrolysis stage of MW. The second weight loss peak appears with a weight loss rate of approximately 37.3%. Flammable materials such as plastic and paper in MW decompose during this stage. At the third stage of 500–800 °C,
a slightly lower weight loss rate of 12.3% happened, which can be attributed to the pyrolysis of heavy molecular components.

Fig. 2b shows the TG/DTG curves of MW to which soil was added. The TG curve reaches the first weight loss peak with a weight loss rate of 5.1% between 100 and 300 °C. Between 300 and 500 °C, the second weight loss peak appears in the TG curve, representing the main pyrolysis stage of MW with a weight loss rate of ~21.3%. This rate decreases substantially when the temperature increases to ~500 °C. The weight loss curve becomes flat above 800 °C, and the pyrolysis ends. In this stage, the weight loss rate is ~12.1%.

Fig. 2c shows that the pyrolysis process of urban household waste consists of three stages. The trend of TG and DTG curves is similar to that of MW, but compared to MW, MSW has fewer non-pyrolysis components such as soil, thus having better pyrolysis efficiency.

Figs 2(a), 2(b) and 2(c) show that the pyrolysis characteristics of different raw materials significantly differ. Compared with MW containing soil, MW after soil separation has more combustible components and better pyrolysis rates. The components of MW and MSW after soil separation are similar, and the pyrolysis temperature range is relatively narrow (300–500 °C), leading to rapid pyrolysis at low temperatures. In this stage, mainly organic substances, such as rubber and plastics, are pyrolyzed. It mainly includes the primary and secondary pyrolysis reactions of pyrolysis products (Xu et al., 2018). Firstly, organic substances are pyrolyzed to produce small molecular olefins and...
cycloolefins. Subsequently, small organic molecules undergo a series of reactions with the pyrolysis temperature increase, leading to the formation of aromatic compounds (Kwon and Castald, 2008; Ding et al., 2015; Hao et al., 2017). During the whole pyrolysis process, in total, 30%~40% residues of MW and MSW are produced, which are mainly composed of carbon black, accelerator, and non-decomposable filler (Kyari et al., 2005). However, more detailed information regarding the products and the formation mechanism must be obtained by Py-GC/MS.

![TG and DTG curves](image-url)
Fig. 2. Thermal gravimetry (TG) and differential TG (DTG) curves of (a) mineralized waste, (b) mineralized waste with soil, and (c) municipal solid waste (MSW).

The pyrolysis characteristic index $p$ is a quantitative index, which can be used to measure the volatile release characteristics of waste. $P$ is directly proportional to the
maximum reaction rate and weight loss and inversely proportional to the initial pyrolysis temperature and thermal decomposition temperature range, which was in consistent with the previous studies (Wang et al., 2010; Zhao et al., 2011). The pyrolysis characteristic index \( P \) can be described as follows:

\[
P = \frac{(dm/dt)_{\text{max}} (dm/dt)_{\text{ave}}}{T_i (T_{\text{max}} - T_i)}
\]

where \( m \) is the sample mass, kg; \( t \) is the pyrolysis time, min; \( (dm/dt)_{\text{max}} \) is the maximum mass change rate during pyrolysis, % min\(^{-1}\); \( (dm/dt)_{\text{ave}} \) is the average change rate, kg min\(^{-1}\); \( m_\infty \) is the mass loss percentage at the end of pyrolysis, %; \( T_i \) is the initial pyrolysis temperature, °C; and \( T_{\text{max}} \) is the pyrolysis termination temperature, °C.

The pyrolysis characteristics of stale and domestic waste are shown in Table 4.

**Table 4. Basic pyrolysis parameters.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Maximum reaction rate temperature (°C)</th>
<th>( P ) (107%·°C − 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Termination</td>
<td>First peak</td>
</tr>
<tr>
<td>MW</td>
<td>225</td>
<td>821</td>
<td>321</td>
</tr>
<tr>
<td>MW (soild)</td>
<td>195</td>
<td>832</td>
<td>344</td>
</tr>
<tr>
<td>MSW</td>
<td>201</td>
<td>819</td>
<td>352</td>
</tr>
</tbody>
</table>

\( P \), pyrolysis characteristic index; MSW, municipal solid waste; MW, mineralized waste

Based on the thermal analysis curve of the sample, the reaction kinetic parameters can be calculated with derivative and integral methods.

Based on the mass action theorem, the reaction rate was expressed as follows:

\[
\frac{da}{dt} = kf(a)
\]
where $k$ is the reaction rate constant; $w_0$ is the initial mass of the sample; $w_\infty$ is the mass when the mass of the sample stable; and $w_\tau$ is the instantaneous mass of the sample.

The correlation between the reaction temperature $T$ and $k$ can be expressed with the Arrhenius equation:

$$k = A \exp \left( -\frac{E}{RT} \right)$$  \hspace{1cm} (4)

The pre-exponential factor and apparent activation energy can be calculated with the Coats–Redfern integral method, and Eq. (2) is transformed into Eq. (5):

$$\ln \left( \frac{G(\alpha)}{T^2} \right) = \ln \left( \frac{AE}{\beta E} \right) - \frac{E}{RT}$$  \hspace{1cm} (5)

where $\alpha$ is the reaction conversion percentage; $\beta$ is the heating rate (10 K min$^{-1}$); $R$ is the gas constant; $T$ is the temperature; °C; $A$ is the pre-exponential factor; and $E$ is the activation energy, kJ mol$^{-1}$.

Based on the kinetic model function of the solid-phase reaction with random nucleation in similar studies, that is $G(\alpha) = -\ln(1-\alpha)$, the equation can be transformed into

$$\ln \left( \frac{-\ln(1-\alpha)}{T^2} \right) = \ln \left( \frac{AE}{\beta E} \right) - \frac{E}{RT}$$  \hspace{1cm} (6)

The kinetic fitting equation and reaction kinetic parameters of the pyrolysis process of stale and domestic waste are shown in Table 5.

**Table 5. Reaction kinetic parameters.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature(°C)</th>
<th>Fitting equation</th>
<th>Correlation coefficient</th>
<th>Activation energy (kJ mol$^{-1}$)</th>
<th>Preexponential factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>225-389</td>
<td>$Y = -1273.7X - 15.3$</td>
<td>0.9868</td>
<td>10.6</td>
<td>5.6E7</td>
</tr>
<tr>
<td></td>
<td>390-622</td>
<td>$Y = -1773.9X - 16.4$</td>
<td>0.9823</td>
<td>14.7</td>
<td>2.3E8</td>
</tr>
<tr>
<td></td>
<td>623-821</td>
<td>$Y = -1910.6X - 16.6$</td>
<td>0.9993</td>
<td>15.9</td>
<td>3.1E8</td>
</tr>
</tbody>
</table>
Table 5 shows that the correlation coefficient of the fitting equation ranges from 0.9688 to 0.9993, the activation energy varies between 5 and 16 kJ mol\(^{-1}\), and the activation energy required for the pyrolysis is low.

### 3.2 Analysis of pyrolysis products

The compositions of pyrolytic carbon were qualitatively analyzed and compared based on each peak identified in the full scanning spectrum. Despite screening the combustible components of MW, the pyrolysis products are predominantly char, and the outputs of pyrolysis oil and pyrolysis gas are smaller due to the smaller concentrations of organic components. Pyrolytic carbon mainly originates from carbon black, which is added during rubber production. In addition, secondary reactions (aromatization and condensation) during pyrolysis also produce small amounts of char-like substances on the carbon black surface (Roy et al., 1999).

The calorific value and ignition loss of pyrolytic char are provided in the supplementary material. When MW is pyrolyzed, the lowest ignition loss rate of char of 11.2% is observed in Group B because this group contains more incombustible soil impurities. Therefore, the calorific value of char is low (3,696 kJ kg\(^{-1}\)). The highest ignition loss rate of 28.2% is obtained in group C because of the addition of biomass. After adding an external chlorine source, the ignition loss rate of char is ~23%, which is similar to
that without chlorine. Compared with MSW, MW char has a higher calorific value and is more suitable for resource reuse.

Fig. 3a shows the distributions of several elements in the char. The main C peak of the char is observed at 284.8 eV, indicating that carbon mainly exists in the form of C. The peak binding energy of 287–288 eV corresponds to O-bearing groups such as C-O, C=O, and O-C=O (Yang et al., 2009; Edwards et al., 2011). Furthermore, the peak corresponding to the C=O group appears at 293 eV in the MW char spectrum, indicating a high carbon oxidation level of MW char. The distribution of chlorine in the char is shown in Fig. 3b. Most of chlorine were presented as organic chlorine (~200 eV) and inorganic chlorine (~199 eV and 201.1 eV; mainly Cl). Fig. 3c shows the Cu 2p spectrum of char, in which the main peak occurs at 932.2 eV. A vibration satellite peak can also be observed at 939.9 eV. Based on the existence of satellite peaks and their binding energy, Cu$^{2+}$ exists on the surface of char. These results show that the strong resynthesis ability of PCDD/Fs in MW char may be related to the presence of Cu$^{2+}$ (Sun et al., 2016).

The concentrations of Cu and Fe which are the main heavy metals catalyzing the PCDD/F formation are high in pyrolytic char. The heavy metal residues are stable and typically incorporated in minerals. Therefore, Fe and Cu in char would migrate under reducing conditions. In a reducing atmosphere, Cu$^{2+}$ and Fe$^{3+}$ can be reduced to dense Cu$_2$O and Fe$_3$O$_4$, respectively, resulting in a decrease in the catalytic activity of heavy metals (Jin et al., 2014; Huang et al., 2020; Zhang et al., 2021). It can be speculated
that metal catalysts in MW promote the PCDD/F formation, resulting in a higher PCDD/F generation capacity of MW char compared with that of MSW char. The higher level of reduced Fe species, enhanced carbon oxidation and chlorination; and strong interaction between Cu and Fe contributed most to the PCDD/F synthesis in the char (Ashok and Kawi, 2014).
Fig. 3. *In situ* X-ray photoelectron spectrometer (XPS) peaks of (a) C 2p, (b) Cl 2p, and (c) Cu 2p.

3.3 Heavy metals emission

Heavy metals mainly exist in mineral salt, hydroxide, sulfide and oxide forms in MW (Jin et al., 2016; Liu et al., 2018; Kurashima et al., 2019; Bogusz and Oleszczuk, 2020). During pyrolysis, the mineral salts and hydroxides would generally converted into sulfides or oxides with high thermal stability (Praspaliauskas et al., 2018). When the amount of heavy metals catalysts were enough for the catalytic reaction, further increases in the heavy metal content have minor effect on the reaction rate and will not further increase the concentrations of PCDD/Fs or their precursors (Blumenstock et al., 2000).

As shown in the Table 6, the heavy metals in the fuel gas are relatively stable under different conditions. During pyrolysis, all heavy metal concentrations, except for those of Cu and Fe, minimally change after the addition of different chlorides. After adding...
CuCl₂, the Cu and Fe concentrations increase to 0.2866 and 0.4441 mg L⁻¹, respectively. This may be due to CuCl₂ acting as a catalyst of the pyrolysis reaction, thereby increasing the heavy metal concentration of the fuel gas. In groups A and B, the concentration of pyrolysis heavy metals in MW minimally changes after screening and is lower than that of MSW. However, due to the heavy metals such as Cu and Fe contained in the soil, the content of Cu and Fe increased to a certain extent. After adding biomass for the co-pyrolysis, the heavy metal concentrations exhibit only minimal changes, except for the Fe concentration, which slightly increases. Other studies also revealed that the content of heavy metals in pyrolytic gas was relatively stable (Czajczyńska et al., 2017). Therefore, the chlorine source and pretreatment method have negligible effects on the heavy metal concentrations in the pyrolysis fuel gas of MW and do not increase the heavy metal emissions. The heavy metal concentration was similar with that of the co-pyrolysis of MSW and industrial solid waste (Ma et al., 2021). However, char may absorb more heavy metals; therefore, the heavy metal content of char must be closely monitored.

Table 6. Heavy metal in fuel gas for groups A–G.

<table>
<thead>
<tr>
<th>Group</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0009</td>
<td>0.0008</td>
<td>0.0123</td>
<td>0.0196</td>
<td>0.3478</td>
<td>0.0038</td>
<td>0.0032</td>
<td>0.332</td>
</tr>
<tr>
<td>B</td>
<td>0.0008</td>
<td>0.0011</td>
<td>0.0031</td>
<td>0.1515</td>
<td>0.6027</td>
<td>0.0300</td>
<td>0.4654</td>
<td>0.0807</td>
</tr>
<tr>
<td>C</td>
<td>0.0009</td>
<td>0.0007</td>
<td>0.0017</td>
<td>0.0659</td>
<td>0.3645</td>
<td>0.0145</td>
<td>0.2774</td>
<td>0.0639</td>
</tr>
<tr>
<td>D</td>
<td>0.0003</td>
<td>0.0011</td>
<td>0.0020</td>
<td>0.0540</td>
<td>0.3021</td>
<td>0.0035</td>
<td>0.2346</td>
<td>0.0468</td>
</tr>
<tr>
<td>E</td>
<td>0.0005</td>
<td>0.0008</td>
<td>0.0004</td>
<td>0.0475</td>
<td>0.2891</td>
<td>0.0198</td>
<td>0.2172</td>
<td>0.0421</td>
</tr>
</tbody>
</table>
3.4 Effects of chlorine sources and pretreatment methods on PCDD/Fs

As shown in Fig. 4, the concentration of PCDD/Fs in fuel gas slightly decreases from 1.42 to 0.80 ng m\(^{-3}\) when NaCl was added in the reactant. The concentration of PCDD/Fs in fuel gas increased from 1.42 to 1.69 ng m\(^{-3}\) after adding PVC. Furthermore, the concentration of PCDD/Fs in fuel gas significantly increased to 6.40 ng m\(^{-3}\) after adding CuCl\(_2\). The above-mentioned results showed that a notable effect on the formation of PCDD/Fs during MW pyrolysis was observed with the adding of the external chlorine source. The concentration of PCDD/Fs in the MW decreased from 10.46 to 7.21 ng m\(^{-3}\) since the content of unselected soil with the low PCDD/F concentration was low. After the addition of 30% biomass, the PCDD/F content increases to 16.92 ng m\(^{-3}\). Biomass pyrolysis will produce biochar which was in rich of carbon and further enhance the formation of PCDD/Fs. The emission of PCDD/Fs was even found to be enhanced on pyrolytic conditions (Garrido et al., 2017). For instance, Maasikmets et al. (2016) studied pollutant emissions from the residential combustion of wood with MSW and obtained high emissions of PCDD/Fs and hexachlorobenzenes (HCBs).

In summary, the inorganic chlorine source has minor effects on PCDD/F formation. Conversely, the PCDD/F formation would be significantly promoted by the addition of an organic chlorine source. The concentration of PCDD/Fs is ~1.2 times that without a chlorine source because chlorinated organic compounds and benzene aromatic
compounds are generated after heating and decomposing of PVC, which can promote the PCDD/F formation (Soudais et al., 2007; Aljoumaa and Ajji, 2017; Bahari et al., 2017). The concentration of PCDD/Fs in group B is 0.96 ng m$^{-3}$, that is, lower than that of group A. The results show that component interaction during MW pyrolysis minimally affects the concentration of PCDD/Fs in fuel gas. In addition, the inorganic salts on the surface of MW can be dissolved by washing with water, which also explains why inorganic chlorine minimally affects the PCDD/F formation in fuel gas during the pyrolysis of MW.
Fig. 4. Concentration of PCDD/Fs in fuel gas during the pyrolysis of mineralized waste.

As can be seen in Fig. 5, the PCDD/Fs in fuel gas of group A are predominantly PCDFs, among which the 2,3,7,8-TCDF content is the highest, accounting for 20.4%, which has the highest toxicity sharing. This indicates that the de novo synthesis reaction is the major method for PCDD/F formation (Huang and Buekens, 1995). The pyrolysis reaction parameters, including the reactant, temperature, atmosphere, would also affect the distribution of PCDD/F homologue. The chlorination pathway of DD/F could not be the major formation pathway of PCDDs, but it partly contributed to the formation of PCDFs (Shibata et al., 2003; Rao et al., 2021). In Group B, PCDD/Fs are still the main polychlorinated difurans in fuel gas, but the content of polychlorinated difluorides is 6% lower than that in Group A. This is mainly because Group B contains more soil and does not participate in the formation of dioxins. After adding 30% biomass, PCDDs are dominant, and the addition of biomass will not affect the formation of PCDD. De novo synthesis is still dominant. The two main congeners of the PCDFs are 1,2,3,4,6,7,8-HpCDF and OCDF, with OCDD accounting for most of the PCDD/F congeners. Although 2,3,4,7,8-PeCDF is not the main congener, its toxic equivalent factor reaches 0.5. Thus, it contributes the most to the total TEQ. Our results also indicate a strong correlation between the concentration of 2,3,4,7,8-PeCDF and TEQ of PCDD/Fs with a correlation coefficient of 0.945 (Hatanaka et al., 2001). After adding NaCl, PVC, and CuCl₂, the PCDD/Fs are still dominated by PCDFs, indicating that de novo synthesis might be the dominant method for PCDD/F formation. The proportion of 2,3,7,8-TCDF
slightly decreases, whereas the proportion of 1,2,3,4,6,7,8-HpCDF slightly increases. Some researcher also reported that the fractions of OCDD and HpCDFs were relatively larger within PCDDs and PCDFs, respectively (Sørmo et al., 2024).

4. Conclusions

(1) The thermogravimetric experiments showed that MW and MSW pyrolyze at 300–800 °C and 200–800 °C, respectively. Compared with the original MSW, MW exhibited a higher weight loss rate of ~70% at 800 °C.

(2) The results of speciation analysis and in situ XPS of heavy metals indicated high content of reducible metals in MW char. The PCDD/F synthesis ability of MW char was higher than that of MSW char, which might be due to the chlorination of carbon, enhanced oxidation and the interaction between copper and iron.

(3) Among the different chlorine sources, CuCl₂ had the strongest catalytic effect on the gaseous PCDD/F formation during MW incineration. Among the two
pretreatments, the interaction between MW components had an insignificant effect on
the concentration of PCDD/Fs in the fuel gas. In addition, the distributions of 17
PCDD/F isomers were substantially affected by the addition of external chlorine
sources.

CRediT authorship contribution statement

Jianying Fu: Conceptualization, Data curation, Formal analysis, Writing – original
draft. Hancheng Ma: Data curation, Writing – review & editing. Mingxiu Zhan:
Investigation, Writing – review & editing. Wentao Jiao: Investigation, Writing –
review & editing. Xu Xu: Investigation, Writing – review & editing. Xiaodong Li:
Writing – review & editing, Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal
relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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