Dioxin control in the co-processing of waste printed circuit board and copper concentrate with an Ausmelt furnace

Wei Li\textsuperscript{a}, Jia Sun\textsuperscript{b}, Deng-Feng Ma\textsuperscript{a}, Xian-Long Liu\textsuperscript{a}, Sheng Li\textsuperscript{a}, Jian-Ye Bei\textsuperscript{b}, Ming-Xiu Zhan\textsuperscript{b}, Xiao-Qing Lin\textsuperscript{c}, Tong Chen\textsuperscript{c}

\textsuperscript{a}Daye Nonferrous Metals Co., Ltd, Huangshi, 435005, Hubei Province, China
\textsuperscript{b}College of Metrology and Measurement Engineering, China Jiliang University, Hangzhou, 310018, Zhejiang Province, China
\textsuperscript{c}State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, 310027, Zhejiang Province, China

*Corresponding author: Tong Chen
E-mail address: chentong@zju.edu.cn

Abstract

In recent years, with the rapid growth of the amount of electronic equipment, the environmental pollution caused by waste printed circuit board (WPCB) has become increasingly serious. Co-processing of WPCB and copper concentrate is an economic and effective way to realize the resource utilization of WPCB. However, there are few reports on the inhibition of dioxin by high concentration of SO\textsubscript{2} generated from copper concentrate during co-processing. From the perspective of dioxin distribution, the effects of different co-processing ratios, SO\textsubscript{2} concentration and other factors were systematically studied. The actual environment of the Ausmelt furnace was simulated by using a laboratory tubular furnace, and the emission characteristics of dioxins were investigated. Compared with the disposal of WPCB alone, the total concentration and toxic equivalent quantity (TEQ) of dioxins decreased by 14.7-26.8% and 34.7-46.5%, respectively, with the change in the proportion used during co-processing. Additionally, with the increase in SO\textsubscript{2} concentration, the total concentration and TEQ value of dioxins decreased by 11.1-29.8% and 5.1-26.9%, respectively. Furthermore, the low-chlorinated dioxin congeners increased and high-chlorinated ones decreased. Most importantly, it was revealed that the dioxin formed during co-processing was suppressed by the deactivation of metal catalysts and the reduction of chlorine sources. These findings will facilitate the rational control of dioxin emissions with the co-processing of WPCB in an Ausmelt furnace.

Keywords: Dioxins, Co-processing, Waste printed circuit boards, Inhibition mechanism, SO\textsubscript{2}
1. INTRODUCTION

With the rapid development of the electronic industry and information industry, electronic products are being increasingly used in various fields, which will eventually lead to a sharp increase in waste electrical and electronic equipment production (Golmohammadzadeh et al., 2018). The printed circuit board has been applied in almost all electronic equipment (Duan et al., 2016; Jaunich et al., 2016). A shocking 53.6 million tons of electronic waste (e-waste) was generated globally in 2019, with a 21% increase in five years, and the amount is expected to be double by 2050 (Pariatamby and Victor, 2013; Cucchiella et al., 2016; Masud et al., 2019; Van Yken et al., 2021). Therefore, a large amount of waste printed circuit board (WPCB) would be generated from the modern electronic and electrical equipment.

WPCB is usually composed of plastics (mainly organic polymers containing halogen flame retardants), refractory oxides and various metal components (Awasthi et al., 2016; Wang et al., 2017a). WPCB also contains various heavy metals and halogen substances, which would not only cause serious pollution to soil, groundwater and the environment but also cause abnormal immune function, serious damage to the nervous system, circulatory system and kidneys, and even carcinogenesis (Sohaili et al., 2012; Hu et al., 2013; Sanyal et al., 2013; Tue et al., 2013; Yoshida et al., 2016). In the meanwhile, the WPCB recycling process will generate a large amount of waste liquid, slag, and exhaust gas. Furthermore, the disposal or incineration of WPCB in hazardous
waste landfills will lead to serious environmental impacts, such as the release of dioxins and other highly toxic substances (Ning et al., 2018).

At present, the disposal processes for WPCB mainly include mechanical and physical (Nekouei et al., 2018; Park et al., 2019), hydrometallurgy (Li et al., 2018; Tatariants et al., 2018), biological (Abdelbasir et al., 2018) and pyrometallurgical treatment methods (Wang et al., 2017b; Abu-Elyazeed et al., 2021; Themelis, 2023), while controlling the emission of dioxins has always been a difficult problem. Related studies have shown that the dioxins generated by WPCB co-processed in Ausmelt furnace could be effectively decomposed, due to the high smelting temperature (1200-1350°C) of copper concentrate. In addition, copper concentrate contains abundant sulfur, which can inhibit the formation of dioxins (Chen et al., 2014; Zhan et al., 2016a).

That sulfur acts as an effective inhibitor for dioxin formation has been proved in some laboratory studies. The transformation of chlorine atoms to hydrogen chloride in the homogeneous gas phase has been suggested as the inhibition mechanism (Hunsinger et al., 2007). Because chlorine formed by the Deacon reaction is essential for the de novo synthesis pathway of dioxins. Most importantly, sulfur may sulfonate phenolic precursors to generate bibenzothianthracene or bibenzothiophene sulfide, which could block the formation pathway of dioxin precursors (Chen et al., 2015; Lin et al., 2015a; Lin et al., 2015b; Zhan et al., 2016b).

In this study, the emission characteristics of dioxins, heavy metals and other pollutants in flue gas and residue were studied during the co-processing of WPCB and
copper concentrate. Comprehensive characterization, including scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), was applied to analyze the elemental distribution. The purpose of this work was to (I) explore the emission characteristics of dioxin formation and heavy metals during the co-processing of WPCB and copper concentrate, (II) explore the effect on the inhibition of dioxins by \( \text{SO}_2 \) at high temperatures, and (III) reveal the inhibition mechanism of sulfur based on dioxin formation.

2. MATERIALS AND METHODS

2.1 Experimental Material

The main experimental raw materials including WPCB, copper concentrate, coal powder, slag, spray water and sediment, were all provided by Daye Nonferrous Metals Co., Ltd.. The actual smelting materials are shown in Table 1. To ensure the accuracy of the experiment, the pulverized coal was prepared by combining pulverized coal and ready-made pulverized coal to reduce the influence of origin or composition on the experimental results. The copper concentrate were divided as high-sulfur and low-sulfur copper concentrate. The mixing ratio of coal and copper content used in the experiment strictly follows the on-site material ratio, as shown in Table 1.

The industrial analysis of WPCB particles which were smaller than 0.3 mm was carried out, and the analysis results are shown in Table S1. The results showed that the volatiles in WPCB accounted for 29.46 wt.% and might consist of organic compounds.
such as brominated flame retardants (BFRs). The ash content was 68.62 wt.% and mainly composed of copper metal and glass fiber reinforcement materials.

As shown in Table S2, Cu was the element with the highest content in the WPCB raw materials. Cu is the most important metal element for the normal operation of circuit boards, and it comes from the copper foil in the substrate. It is also the main metal element targeted for recycling at present. The analysis indicates that the glass fiber reinforcement material in the circuit board substrate contains Al, Si, Ca, and Mg, with varying concentration levels. The Br content was also high, possibly due to the existence of BFRs, which makes it necessary to consider the influence of pollutants such as bromo-benzene, bromo-phenol and PBDD/Fs generated during the WPCB disposal process.

Table 1 Actual material ratios of the Ausmelt furnace

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass (t d⁻¹)</th>
<th>Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-sulfur ore</td>
<td>2770</td>
<td>57.03</td>
</tr>
<tr>
<td>Low-sulfur ore</td>
<td>1895</td>
<td>39.02</td>
</tr>
<tr>
<td>Pulverized coal</td>
<td>37</td>
<td>0.76</td>
</tr>
<tr>
<td>Lump coal</td>
<td>35</td>
<td>0.72</td>
</tr>
<tr>
<td>Circuit board</td>
<td>120</td>
<td>2.47</td>
</tr>
</tbody>
</table>

2.2 Experimental Design

Fig. 1 is a diagram of the tubular furnace used for the experimental study of dioxin control via WPCB co-processing with an Ausmelt furnace. The total length of the horizontal tubular furnace is 1.2 m, the heating rate is 5 °C min⁻¹, and the maximum temperature can reach 1400°C. The diameter of the quartz inner tube is 88 mm, and that of the outer tube is 100 mm. When conducting smelting experiments, first, the heating program of the high-temperature tubular furnace was begun. When the furnace reached
the required smelting temperature, the corundum boat containing the above samples was pushed into the constant-temperature zone in the middle of the furnace tube.

According to the experimental conditions, different proportions of gases were used to create the injection atmosphere. The pressure of the oxygen cylinder, nitrogen cylinder and SO2 cylinder was reduced through a pressure reducing valve, and then a flow meter and control valve were used to adjust the gas proportions. Then, a four-way valve was used for premixing to form a uniform gas mixture. After the end of the experiment, the corundum boat was removed. After it cooled to room temperature, the calcined sample was mixed evenly and stored. The rear end of the tube furnace tube is connected with the gas-phase absorber corresponding to the measured item. The operating temperature for this experiment is set at 1200°C, the mass of the reaction material is set at 10 g, and the atmosphere flow rate is set at 400 ml min⁻¹. The specific experimental conditions are shown in Table 2.

<table>
<thead>
<tr>
<th>Group</th>
<th>Reactants</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>WPCB</td>
<td>70% O₂/30% N₂</td>
</tr>
<tr>
<td>A-2</td>
<td>98.5% Copper concentrate + 1.5% pulverized coal</td>
<td>70% O₂/30% N₂</td>
</tr>
<tr>
<td>B-1</td>
<td>2.5% WPCB + 96% copper concentrate + 1.5% pulverized coal</td>
<td>70% O₂/30% N₂</td>
</tr>
<tr>
<td>B-2</td>
<td>10% WPCB + 88.5% copper concentrate + 1.5% pulverized coal</td>
<td>70% O₂/30% N₂</td>
</tr>
<tr>
<td>C-1</td>
<td>WPCB</td>
<td>60% O₂/39.9% N₂/0.1% SO₂</td>
</tr>
<tr>
<td>C-2</td>
<td>WPCB</td>
<td>60% O₂/38% N₂/2% SO₂</td>
</tr>
</tbody>
</table>
2.3 Experimental Analysis Methods

2.3.1 Dioxins detection method

In this study, the process used to pretreat samples for dioxin analysis was performed using USEPA METHOD 1613 (Office, 1994). The method was used to detect the concentration of dioxin in samples by isotope dilution combined with high-resolution chromatography/high-resolution mass spectrometry (HRGC/HRMS). This experiment uses a 7890 Series gas chromatograph (Agilent, USA) coupled with a JMS-800D mass spectrometer (JEOL, Japan), as the high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). The part in the particulate phase was collected in the filter and the other part of the sample in the gaseous phase was collected by XAD-II resin. The processing and analysis of dioxin was based on our previous research (Zhan et al., 2019). The capillary column used was DB-5ms (60 m × 0.25 mm I.D., 0.25 µm film thickness). Details of the cleanup procedure and the analysis method of dioxins can be found by the research that of Yan et al. (2010).
2.3.2 Conventional pollutants detection in flue gas

Conventional pollutants in flue gas (SO$_2$, NO$_x$, CO, HCl, etc.) were detected online using a Fourier transform infrared spectroscopy (FTIR) flue gas analysis instrument Gasmet (Dx4000, Finland), and the test results were hourly mean values.

2.3.3 Heavy metal detection

The heavy metal content was detected according to USEPA Method 29 (Myers et al., 2002). The solid samples, including the mixture of bottom slag and fly ash, were removed from the fused corundum boat after incineration and cooling. The gas-phase samples were absorbed by an absorption solution consisting of 5% HNO$_3$, 10% H$_2$O$_2$ and deionized water. The digestion solution was prepared through processes such as grinding, digestion and heating. Both the solid sample digestion solution and gas-phase heavy metal absorption solution were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, X series II; Thermo Fisher Scientific Inc.) to determine the concentration of heavy metals.

2.4 Quality Control

The experimental research on dioxin control via the co-processing of WPCB was conducted in an Ausmelt furnace. The research objects, trace dioxins, are easily affected by other factors in the experimental process of generation and inhibition. In order to improve the reliability and accuracy of research data, the laboratory was organized and cleaned before the experiment. The instruments and equipment used in the experiment were carefully inspected. During the experiment, the experimental conditions and data
were carefully recorded, as well as the phenomena observed during the experiment to ensure the traceability of the experimental data. The recovery of labeled dioxins in each sample was all within the limits.

3. RESULTS AND DISCUSSION

3.1 Emission Characteristics of Dioxins

Fig. 2 shows the emission and toxic equivalent quantity (TEQ) concentrations of dioxins during co-processing of WPCB at high temperature. When disposing of discarded circuit boards separately, the concentrations of dioxins in the gas and solid phase were 1.819 ng m$^{-3}$ and 4.031 ng kg$^{-1}$, respectively. The corresponding TEQ values were 0.149 ng I-TEQ m$^{-3}$ and 0.262 ng I-TEQ kg$^{-1}$, respectively. When copper concentrate and pulverized coal were disposed, the concentrations of dioxins in the gas and solid phases were 3.492 ng m$^{-3}$ and 1.678 ng kg$^{-1}$, respectively. The TEQ values were 0.187 ng I-TEQ m$^{-3}$ and 0.090 ng I-TEQ kg$^{-1}$, respectively. When WPCB was co-disposed of with copper concentrate, the content of dioxins in the solid phase decreased with increasing proportion of copper concentrate. The content and TEQ of dioxins with 88.5% copper concentrate were 3.174 ng kg$^{-1}$ and 0.217 ng I-TEQ kg$^{-1}$, respectively. Furthermore, the inhibition rates of the dioxin content and TEQ value were 21.3% and 17.2%, respectively. When the copper concentrate proportion increased to 96%, the content and TEQ of dioxins were 2.883 ng kg$^{-1}$ and 0.181 ng I-TEQ kg$^{-1}$, respectively. The inhibition rates of the dioxin content and TEQ value were 28.5% and 37.2%,
respectively. The concentration ranges of dioxins in the solid and gas phases were consistent with the current emission status of other solid waste incinerators (Han et al., 2017; Zhan et al., 2018). The inhibition rates of the dioxin content and TEQ value became 28.5% and 30.9%, respectively. The results showed that co-processing with copper concentrate could inhibit the formation of dioxins in the solid phase, and the inhibition rates increased with the increasing proportion of copper concentrate. In the gas phase, an opposite trend was found for the dioxin formation. Under the conditions of adding circuit boards at a ratio of 2.5%, the concentrations of dioxins and TEQ values were 2.503 ng m$^{-3}$ and 0.134 ng I-TEQ m$^{-3}$, respectively. When the co-processing ratio increased to 10%, the concentrations of dioxins and TEQ value were 2.234 ng m$^{-3}$ and 0.123 ng I-TEQ m$^{-3}$. The low dioxin generated in the flue gas might be because the experimental temperature was high (1200℃), the calorific value of the WPCB material was high, and the combustion reaction was intense and sufficient. In addition, the concentration of dioxin in the flue gas under the condition of pure copper concentrate was higher. With the increase in the proportion of WPCB for co-processing, the concentration of dioxin gradually decreased, indicating that the addition of WPCB makes the combustion more intense and the reaction more complete.
Fig. 2 Total concentration and toxic equivalent concentration of dioxins in the solid (a) and gas phases (b)

Fig. 3 shows the distribution of gas-phase and solid-phase dioxin isomers under different conditions. It was found that compared with A-1, the emission levels of dioxins on other conditions were significantly reduced, indicating that co-processing with copper concentrate or the injection of SO₂ had good inhibition effects on the dioxin formation. It was found that 2,3,7,8-TCDF, OCDF, OCDD, 1,2,3,4,6,7,8-HPCDD, and 1,2,3,4,6,7,8-HPCDF were the main contributors to dioxin emissions, accounting for
more than 90% to the total dioxin emission concentration (Fig. 3a). When the SO$_2$ was injected, the content of 2,3,7,8-TCDF significantly increased, and the distribution of other homologous compounds decreased except for OCDF. The change in distribution may be due to that the sulfur compounds could block the formation of highly chlorinated dioxins to some extent. In the solid phase (Fig. 3b), OCDD, OCDF, 1,2,3,4,7,8,9-HPCDF, and 1,2,3,4,6,7,8-HPCDD were the main contributors to dioxin emissions, accounting for more than 80%. After co-processing and SO$_2$ injection, the overall distribution trend was that the content of high-chlorinated homologs decreased, while the content of low-chlorinated homologs increased, indicating that the addition of sulfur compounds would inhibit the conversion of low-chlorinated to high-chlorinated homologs.
Fig. 3 Concentration distribution of dioxin isomers in the gas (a) and solid (b) phase

3.2 Emission Characteristics of Heavy Metal

The heavy metal contents in the solid phase and gas phase under experimental conditions 1-4 are shown in Tables S3 and S4. The heavy metal emission amount from pure WPCB before co-processing was much higher than that from pure copper concentrate smelting (Table S4). The concentration of Ni/Zn/Pb exceeded the emission level from copper concentrate smelting by more than two orders of magnitude, and other heavy metal concentrations also exceeded the copper concentrate smelting emissions. The emission level of heavy metals in the gas phase decreased significantly under co-processing conditions, and the emission levels of all heavy metals were lower than those without co-processing of WPCB, among which Zn decreased the most, from 58.591 to 0.108 mg m\(^{-3}\) after co-processing with a decrease of 99.8%. The main reason is that a large amount of Zn in the circuit board might migrate from the solid phase to the gas phase, while the Zn concentration in the solid phase is relatively high under...
several experimental conditions of co-processing. It is possible that co-processing has a good solidification effect on Zn by affecting its gas-solid phase migration. In addition, the reduction efficiency of Cr, Ba, Co, Ni and Pb reached more than 90%. By comparing B-1 and B-2, it was found that the increase amount of copper concentrate could reduce the emission levels of Se, Ba, As and Pb, while it would increase the overall emission level of heavy metals. Furthermore, the emission concentration of Cu increased from 0.341 to 1.552 mg m$^{-3}$. The possible reason is that an increase of copper concentrate addition could increase the concentration of Cu in the reaction materials, leading to an increase in the Cu concentration in the gas phase. With the increasing proportion of WPCB in B-2, the Ba, As, and Pb concentrations increased considerably. WPCB was the main source of these three heavy metal elements because the concentration was higher in A-1. In addition, Ni did not exhibit the same trend probably due to its migration occurred. In general, the emission level of heavy metals in the gas phase reached 92.56 mg m$^{-3}$ before co-processing. However, it dropped to 0.68–2 mg m$^{-3}$ after co-processing with a decrease of more than 97.8%. Therefore, co-processing has a good inhibitory effect on the emission of heavy metals in the gas phase.

Before co-processing, the solid phase heavy metal emissions (Table S3) in A-1 were mainly Zn, Ba, Ni, Sr, and Cu, with a total emission level of 164,652 mg kg$^{-1}$. The solid phase heavy metal emissions in A-2 were mainly Ba, Cu, Zn, and Pb, with a total emission level of 42,051 mg kg$^{-1}$. The solid phase heavy metal emissions in A-1 are higher than those in A-2, possibly due to a large amount of heavy metal impurities in
the WPCB, and the content of Cu comes from copper foil in the substrate (Arshadi and Mousavi, 2014; Silvas et al., 2015). The Cu content in several co-processing experimental conditions is much lower than that of waste circuit boards, and the Cu element content directly affects the generation of dioxins in the previous stage. At high temperatures, Cu, Zn, and Pb usually evaporate in the form of chlorides, and when the flue gas reaches the lower temperature area, it condenses and enriches in fly ash. The Pearson correlation coefficients between Cl content in fly ash and Cu, Zn, and Pb are 0.96, 0.74, and 0.61, respectively. The chloride of Cu is the most effective catalyst for dioxin formation. The contents of Cu and Zn are positively correlated with the content of dioxins (Lin et al., 2006). Furthermore, the chloride of Pb (PbCl₂) can promote the generation of chlorinated aromatic hydrocarbons and produce synergistic effects with other metal catalysts such as CuCl₂ and FeCl₂.

After co-processing, the emission levels of the four heavy metal elements Se, Ba, Ni, and Sr decreased significantly, while the emission levels of the four heavy metal elements Pb, Cr, As, and Co showed a significant upward trend. In addition, the other heavy metal elements fluctuated within a certain range. Compared with B-1 and B-2, the content of Ni, As, and Pb reduced with the increase of the copper concentrate addition. The results also showed that the other heavy metal pollutants fluctuated within a certain range, indicating that the effect of copper concentrate addition on solid heavy metal pollutants was not significant. The total heavy metal emission levels of A-2, B-1, and B-2 were similar, and the Cu element was decreased compared to A-1. This might be due to the fact that copper concentrate smelting is the main source for solid heavy metal pollutants in the co-processing process. The heavy metal content in waste circuit boards is relatively insufficient, indicating a significant correlation between solid heavy metal pollutant emissions and copper concentrate. Overall, the emission level of heavy
metals in solid has slightly decreased after co-processing.

3.3 Inhibition of dioxins by SO₂

Fig. 4 shows the inhibitory effect of SO₂ on dioxins generated in the co-processing WPCB at high temperature. By comparing C-1 and C-2, it can be found that the concentration of SO₂ has an obvious inhibitory effect on the formation of dioxins. When 0.1% SO₂ was added, the dioxin concentrations in the gas and solid phases were 3.012 ng m⁻³ and 3.561 ng kg⁻¹, respectively. Furthermore, the TEQs values were 0.198 ng I-TEQ m⁻³ and 0.402 ng I-TEQ kg⁻¹, respectively. When the concentration of SO₂ increased to 2%, the dioxin concentration decreased to 2.497 ng m⁻³ and 2.580 ng kg⁻¹, and the TEQ values decreased to 0.138 ng I-TEQ m⁻³ and 0.338 ng I-TEQ kg⁻¹, respectively. The results showing a good inhibitory effect of SO₂ on the dioxin formation, which was more obvious in the solid phase dioxins with a decrease of 36%.

In contrast, in the gas phase, the inhibition effect of dioxins was not obtained. Previous studies have also confirmed that SO₂ has a good inhibitory effect on dioxins (Hajizadeh et al., 2012; Chen et al., 2015). Although the concentration of dioxins decreased with increasing concentration of SO₂, the overall concentration was still high, which might be attributed to the “memory effect” (Ma et al., 2020). The “memory effect” has been also found in full-scale rotary kiln incinerators, which would increase the concentration of dioxins in the gas and particle phases (Peng et al., 2023). That is, when the concentration of dioxins in the flue gas decreases, the precursors of dioxins and the residual carbon containing Cu or Fe catalyst can form and precipitate dioxins, thus
weakening the inhibitory effect of sulfur.

In summary, the experimental results show that SO$_2$ has a good inhibitory effect on the formation of dioxins. SO$_2$ can significantly inhibit the formation of dioxins and reduce the TEQ concentration.

![Fig. 4 Gas- and solid-phase dioxins and toxic equivalent concentrations](image)

### 3.4 Inhibition Mechanism

By comparing the inhibitory effect of dioxins in flue gas and solid residue, it was found that the inhibitory effect of sulfur on dioxins in solid residue was stronger than that in flue gas, which was consistent with the research results conducted by Chen (Chen et al., 2014). This phenomenon may be attributed to three reasons. First, it is possible that flue gas dioxins are mainly gas-phase dioxins which are generated through high-temperature homogeneous synthesis rather than low-temperature heterogeneous catalysis, leading to a limited inhibition effect. Furthermore, the sulfur reacts with the metal catalyst on the solid residue surface and the chlorine source in the flue gas to block the catalytic reaction on the solid residue surface, thus blocking the formation of dioxins on the solid residue surface. In addition, sulfur forms a metal complex with the metal catalyst and covers the solid residue surface, inhibiting the formation of dioxins.
on the solid residue surface. SEM results showed (Fig. 5) that many particles were
attached to the surface of solid residue after co-processing, indicating that a series of
reactions occurred on the surface of solid residue. Sulfur or SO₂ would react with metal
catalysts to form sulfate, which condensed on the surface of solid residue when the flue
gas temperature decreased. On the one hand, the addition of sulfur reduces the catalytic
dioxin-generating effect of the metal catalyst by reacting with the metal catalyst; on the
other hand, the complexes generated by the two groups cover the surface of the solid
residue, reducing the availability of dioxin-generating sites. Moreover, the changes in
the composition of the residue surface were also analyzed (Fig. 6). The S/Cl ratio of
solid residue doubled after co-processing. The increase in sulfur content in the solid
residue confirmed the formation of sulfate on the solid residue surface. Considering the
distribution of dioxin homologs, the chlorination of the solid residue surface was
inhibited. Based on the above results, this study suggested that both co-processing and
SO₂ injection could inhibit the formation of dioxins, while the deactivation of the metal
catalyst and reduction of the chlorine source were the main mechanisms inhibiting the
formation of dioxins.
4. CONCLUSIONS

By exploring the dioxin emission characteristics in the co-processing of waste printed circuit board and copper concentrate with an Ausmelt furnace, some conclusions were obtained:

1. The total concentrations and TEQ values of dioxins formed from the WPCB incineration decreased by 14.7% and 34.7% with the addition of 88.5 wt.%
copper concentrate. The total concentration and the TEQ value of dioxin decreased by 26.8% and 46.5% when the addition of copper concentrate increased to 96 wt.%. The ratio of low chlorine dioxin homologs increased when the WPCB was co-processed with copper concentrate, indicating that the addition of sulfur could not only affect the formation amount of dioxins but also the formation pathways.

(2) The co-processing condition showed a good inhibitory effect on the emission level of gaseous heavy metals, and the total concentration of gaseous heavy metals decreased by over 97.6% after co-processing. The inhibitory effect of co-processing on the emission level of heavy metals in solid phase is relatively average, with a slight decrease in the emission level compared to the experimental conditions before co-processing.

(3) The total concentration and TEQ value of dioxins formed from the WPCB incineration decreased by 11.1% and 5.1% with the addition of 0.1 vol.% SO₂. The total concentration and the TEQ value of dioxin decreased by 29.8% and 26.9% when the addition of SO₂ increased to 2 vol.%. This also exhibited inhibitory effects on the isomers with higher emissions. A "memory effect" was also observed in the gas phase. In this study, deactivation of the metal catalyst and reduction of the chlorine source were the main mechanisms inhibiting dioxin formation.

The generation of dioxins and their impact on the environment could be largely
reduced by controlling the particle size of circuit boards at the source, adding alkaline inhibitors during the process, adsorption of tail end activated carbon, or rapid cooling of flue gas.

Statements & Declarations

Ethical approval
Not applicable.

Consent to participate
Not applicable.

Consent to publish
Not applicable.

Authors contributions
Wei Li carried out experiment and wrote manuscript. Jia Sun researched literature. Jian-Ye Bei, Deng-Feng Ma, Xian-Long Liu, Sheng Li checked the manuscript. Ming-Xiu Zhan, Xiao-Qing Lin, Tong Chen edited and reviewed. All authors read and approved the final manuscript.

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Competing interests
We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of.

**Availability of data and materials**

Present study data are available with corresponding author and are available on reasonable request.

**REFERENCE**


