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Pollution control technologies of dioxins in municipal solid waste incinerator

Hui Liu\textsuperscript{a}, Sifang Kong\textsuperscript{a}, Yangsheng Liu\textsuperscript{a, b, *}, Hui Zeng\textsuperscript{a, c}

\textsuperscript{a}Shenzhen Graduate School of Peking University, Shenzhen key laboratory of circular economy, Shenzhen 518055;
\textsuperscript{b}College of Environmental Science and Engineering, Peking University, Beijing 100871;
\textsuperscript{c}College of Environmental and Urban Science, Peking University, Beijing 100871

Abstract

Dioxins have been widely concerned for its high carcinogenicity and possibility of long-term influences on human body. One of the main sources of dioxins is the municipal solid waste incinerator. The control technologies of dioxins were reviewed in two aspects, namely PCDD/Fs control during incineration and removal of PCDD/Fs in exhaust gases and new development directions of control technologies of dioxins were previewed.

Keywords: dioxin; municipal solid waste; incineration; pollution control

1. Introduction

With the substantial increase in municipal waste production and the constant development of incineration technology, incineration has become one of the most important waste disposal technologies which is strived to develop by a lot of countries [1,2]. Municipal solid waste incineration produces a quantity of harmful substances such as acid gases, ash, heavy metals and chlorinated organics. In recent years, dioxin-like substances, which are persistent organic pollutants and have strong carcinogenicity, in the exhaust gases of incinerator, have aroused growing attention of the scholars [3].

Dioxins are a class of substance that structurally and chemically related to polyhalogenated aromatic hydrocarbons that mainly include polychlorinated dibenzo-p-dioxins (PCDDs or dioxins) and dibenzofurans (PCDFs or furans). They were firstly found in the fly ash samples by the Dutch and Swiss scientists in 1977 and 1978 [4,5]. In 1982, an explosion at ICMESA factory in Seveso, Italy, depositing...
these chemicals over an area of 2.8 km², until then, the problem of dioxins contamination began to cause attention to the public [6].

In this paper, the control technologies of dioxins were reviewed in two aspects, namely PCDD/Fs control during incineration and removal of PCDD/Fs in exhaust gases, and new development directions of control technologies were previewed.

2. Production and emission of dioxins in waste incineration

Dioxins are produced from the solid waste incinerator though two main mechanisms: formation from precursors and formation by de novo synthesis. Dioxins can be formed through the synthesis of a variety of precursors, such as chlorobenzene and chlorophenol. These precursors were produced through incomplete combustion, or heterogeneous catalytic reaction on the surface of fly ash. De novo synthesis uses macromolecule carbon and chlorine in fly ash to form dioxins at low temperature. However, the formation mechanisms of dioxins in the incineration process were so complicated that we have not come to the detailed reaction mechanism of this process [7].

At present, most countries have made an emission restriction on dioxin concentration in the off-gas of incineration plant, including the European Union and Japan which set the emission restriction at 0.1 ng-TEQ/m³ (TEQ is the toxic equivalent quantities where the most toxic congener TCDD is rated as 1.0 and the less toxic congeners as fractions of this). This is a safety and non-controversial standard in academic circle. Though the Chinese standard of GB 18485-2001 set the dioxin emission concentration at 1.0 ng-TEQ/m³, in fact some new incineration plants have begun to implement the emission restriction of 0.1 ng-TEQ/m³.

3. Pollution control technologies of dioxins

3.1. PCDD/Fs control during incineration

3.1.1. Improvement of combustion conditions

Different combustion conditions in incinerator, including the combustion temperature, residence time, disturbance between oxygen and garbage, preprocessing of garbage, fuel supplement and oxygen supply, will affect the amount of PCDD/Fs. The most important factors were known as "3T" which stands for temperature, residence time and turbulence. It is generally agreed that combustion temperatures of 850 °C and a gas residence time of 2 s or 1000 °C and a gas residence time of 1 s are necessary for total destruction. Creating turbulence in the combustion chamber is also needed to further mix air and fuel and the recommended turbulence Reynolds number is over 10,000 [3].

Besides the "3T" principle, a modern incineration plant also needs to meet the requirements of oxygen and garbage supply. Oxygen deficiency can lead to the incompletely burn of garbage; while oxygen excess can promote the formation of PCDD/F. In addition, considering the different components of the garbage, it is usually needed to pre-treatment of garbage, or to mix the garbage with fuel.

3.1.2. Control of the temperature-time profile of flue gases

The de novo synthesis mechanism which is an important mechanism for dioxin formation during incineration happens in the post-combustion region of incinerator. A series of studies of Fangmark et al. [8,9] have shown that combustion temperature and residence time of the post-combustion region is the most important parameters affecting the formation of chlorinated aromatic compounds.
Therefore, in order to reduce the formation of PCDD/Fs, it is needed to reduce the residence time of the exhaust gases in the post-combustion region, or make the temperature of exhaust gases in the post-combustion quickly decrease to below 260 °C. A key parameter to achieve rapid cooling may be the average exhaust gases cooling rate or quenching rate. Different quenching rates will produce different levels of PCDD/F and congener distribution [10]. In a waste heat boiler, in order to achieve a PCDD/F level of 1 ng-TE/Nm³ at boiler outlet, a cooling rate in the range of 500–1000 °C/s is probably necessary [11]. However, in practice such a high cooling rate is difficult to achieve as the volume of flue gases is large.

3.1.3. Separation of fly ashes

It is generally accepted that low-temperature surface catalytic reaction mechanism is the main formation mechanism of PCDD/F in the post-combustion zones. The occurrence of this mechanism needs the active sites of solid surfaces, such as fly ash. Therefore, in theory, if we can capture or separate the fly ash particles before the exhaust gases enter the combustion region, the generation of PCDD/F will be effectively reduced.

Fängmark et al. [9,12] used the cyclone separation method to separate the fly ash particles in the exhaust gases in a laboratory-scale fluidized bed reactor. However, results showed that the yield of chlorinated aromatics was not changed. Fängmark suggested that this is because the particle size of fly ash also influence of generation of PCDD/F. General dust removal method only separate large particles of fly ash, while the small particles of fly ash is the major contributor in the formation of chlorinated aromatic hydrocarbons.

The formation mechanism of dioxins in the actual incineration process is so complex that it may conceal the effect of fly ash separation; therefore, rare studies are concentrating in the method of fly ash separation in recent years.

3.1.4. Injection of inorganic additives

Adding inhibitors or blockers to inhibit the generation of dioxins in incineration process is a mainly dioxin control method which is widely studied by lots of researches. Generally, inorganic inhibitors include sulfur compounds, basic compounds and ammonia. Ammonia commonly used in the joint removal of NOx and PCDD/F through the catalytic reaction.

Since the chlorine level in the exhaust gases is an important factor affecting the formation of PCDD/Fs, alkaline compounds which have the ability of absorbing HCl can reduce the level of PCDD/Fs. Ca-based inhibitors which have been widely studied have shown the ability to absorb HCl and other acid gases [13]. However, these experiments concentrated in the absorption of acidic gases in the post-combustion process, which means HCl was existed in the exhaust gases and led to the corrosion of the device and reproduction of PCDD/Fs. If we can get rid of HCl in the high temperature region, the formation of PCDD/Fs will be significantly reduced. However, studies have shown that Ca-based inhibitors have a very low efficiency of removal of acid gases in the high temperature zone [14]. Tsuyumoto et al. [15, 16] proposed a kind of new inhibitor-sodium silicate foam which can used for the adsorption of HCl and suppression of dioxin generation and its effect is much better than that of Ca-based inhibitors. However, whether HCl concentration is the control factor of dioxin concentration is unclear, and some studies show that even though adding alkaline inhibitors can reduce the HCl concentration, the concentration of PCDD/F may be elevated [17].

Sulfur compounds (eg. Na₂S, SO₂, SO₃, Na₂S₂O₃, etc.), which are the most commonly used inorganic inhibitors, can effectively inhibit the formation of dioxins [18]. The research of U.S. Environmental
Protection Agency [19] showed that SO\textsubscript{2} can be an effective inhibitor which can reduce the regeneration of dioxins (mainly PCDFs) and its main mechanism is that SO\textsubscript{2} can inhibit the catalysis of CuCl\textsubscript{2}. However, some study showed that the addition of sulfur compounds will result in the increase of dioxin concentration [20].

3.1.5. Injection of organic additives

Generally, organic inhibitors can react with catalysts forming complex substances at low temperature, which can inhibit the formation of precursor and the de novo synthesis. Although the inhibition mechanism of organic inhibitors is not yet clear, it is generally believed that there is interaction between the catalyst and the inhibitor. Organic inhibitors which are commonly used include 2-aminoethanol, triethanolamine, urea, ethylene glycol, etc. Dickson et al. [21] tested a dozen of catalytic inhibitors and the results showed that the most effective inhibitors are 2-aminoethanol and triethanolamine which all belong to the polyfunctional amine. This is because these amine inhibitors can react with Cu\textsuperscript{2+}, which has the highest catalytic activity during the formation of PCDD/Fs and form complexes [21].

In recent years, some researchers proposed that injection of methane in the burning zone or the post-combustion zone could effectively inhibit the formation of dioxins [22,23]. This is because the addition of methane led to a significant increase in the concentration of free radicals, thus promoting the oxidation of dioxins.

3.2. Removal of PCDD/Fs in exhaust gases

3.2.1. Scrubber coupled with bag filter or electrostatic precipitator

Scrubbers combined with bag filters or electrostatic precipitators have a better effect on PCDD/F removal than the effects when they used alone [24]. For example, Kim et al [25] achieved 90-92% removal efficiency of dioxin with a combined gas cleaning system which contains a heat sink, a scrubber and a wet electrostatic precipitator, and at the same time effectively removed NO\textsubscript{x}, SO\textsubscript{x}, HCl and dust.

In recent years, researchers have found that the wet scrubber may lead to an increase in the amount of PCDD/Fs, making it become a potential source of pollution [26,27]. The main reason is that PCDD/Fs will be adsorbed and desorbed between the exhaust gases and the plastic filler in the scrubber, which known as "memory effect". Adding activated carbon powder in the wet scrubber [28] or improving the structure of the wet scrubber [29] can minimize the memory effect. Recently, Li et al [30] found that the bag filter also has a memory effect on PCDD/F. In order to reduce this effect, it is needed to avoid the unstable combustion conditions, and to replace the aging filter periodically.

3.2.2. Activated carbon adsorption

The process of activated carbon adsorption involves two steps: firstly, the activated carbon is injected into the exhaust stream to remove PCDD/Fs; subsequently, an electrostatic precipitator or fabric filter placed downstream is used to remove activated carbon particles and residual dust. According to the different method of adding activated carbon, the process of activated carbon adsorption can be divided into three different types: entrained flow, moving-bed and fixed-bed processes. Since the efficiency of activated carbon adsorption are generally high, this technology has been widely used in the incineration plant and research is more concentrated in studying the adsorption phenomena and characteristics of activated carbon adsorption in recent years [31–33].
Activated carbon adsorption is a convenient and simple technology, but there are still some problems. First of all, activated carbon needs to be injected into cooled exhaust gases to prevent the de novo synthesis [34]. Secondly, this process consumes a large amount of activated carbon, thus increasing the cost of the incineration plant. To solve this problem, a system combining an adsorber and a regenerator [35] or a double-bag filter system [36] can be used.

3.2.3. Catalytic filter and the combined dioxin and NOx destruction

The catalytic oxidation technology which can directly destroy PCDD/Fs is proven to be an effective technology and it can reduce the concentration of PCDD/Fs in the exhaust gases to below 0.1 ng TEQ/Nm³. Hagenmaier and his colleagues proved that the catalysts for selective catalytic reduction (SCR) of NOx, such as TiO₂-V₂O₅/WO₃, can also be used for oxidating PCDD/Fs and these two processes have the same reaction temperature [37,38].

The reactor used for the removal of PCDD/Fs separately is the catalytic filter. The most commonly used catalytic filter is called REMEDIA™ D/F catalytic filter system which is manufactured by W. L. Gore & Associates Ltd. [39]. A large number of research results showed that, this catalytic system can achieve a PCDD/F destruction rate of over 98%, and the activity of the catalysts in it will not reduced in three years [40,41]. The combined dioxin and NOx destruction can be achieved by the injection of ammonia, and this technology has gained successful application in the incineration plant. For example, Goemans et al. [42] reported that the united removal device in urban waste incineration plant in Ghent, Belgium effectively remove 99% of dioxins and 90% of NOx.

3.2.4. Process of electron beam radiation

Electron beam radiation process is a new technology for destruction of dioxin. Paur et al. [43] firstly proved the feasibility of using electron beam to degrade gaseous PCDD/Fs. Hirota et al. [44] reported that the combination of electron beam radiation and hydrated lime can remove HCl, SO2, NOx and chlorine compounds in exhaust gases. Fengler [45] found that the electron beam can broke down the toxic chlorine compounds into on-toxic organic acids such as formic acid, acetic acid and chloroacetic acid with fairly low energy consumption.

Electron beam radiation can handle large volumes of exhaust gases, especially when the temperature of the gas is relatively low [46]. At the same time, this process has no secondary pollution and the energy consumption is moderate, therefore, has a bright prospect.

3.2.5. Other technologies

Plasma technology which has recently been proven to be a novel technology for the treatment of fly ash and exhaust gases in the incineration plant [47,48], may produce some negative by-products during the treatment process. One possible solution is the combination of plasma and catalysis. Compared with the SCR system, not only the operation temperature of the combined system can be significantly reduced, but also a lot of active particles which produced from plasma can eliminate dioxins.

Due to the high investment and maintenance costs of SCR system, incineration plants in many countries prefer the SNCR system. Since the SNCR system needs high temperature (higher than 1123 K), NOx and PCDD/F removal efficiency is not high, so we need to find a new reducing agent or additive to reduce the reaction temperature of SNCR process [49].

4. Conclusion
Inhibiting the formation of dioxins in the combustion process which can greatly reduce the investment of terminal treatment equipment is a more economical and environmental friendly method to reduce dioxins. The most commonly used technology, "3T" principle, can reduce the formation of dioxins to some extent, but cannot prevent the generation of PCDD/Fs in the post-combustion region. Therefore, PCDD/Fs produced in the post-combustion region needs to get more attention. At present, the remaining problems of dioxins removal in the post-combustion region are as follows:

- Since the volume of the off-gas is quite large in the actual incineration plants, it is difficult to achieve rapid cooling in the post-combustion region;
- The mechanism of fly ash separation is unclear and the actual effect has not been confirmed in the industry;
- The mechanism of inhibitors is unclear; the actual effect has not been confirmed in the industry; and secondary pollution may be produced during this process.

One of the most promising control technologies in the post-combustion region is the technology of inhibitors. Future experiments are needed to find more inhibitors and test their relationship with the level of PCDD/Fs. Currently, the key factor which limits the development of dioxin control technologies is that the formation mechanism of dioxins in the process of incineration is unclear and the dioxin pollution control technologies rely on the understanding of the formation mechanism. Therefore, it is needed to further study the formation mechanism of dioxins in the process of incineration to provide theoretical guidance for the development of control technologies.

Well-developed technologies for removal of PCDD/Fs in exhaust gases can reduce the level of PCDD/Fs to some extent, but they all have some disadvantages. The most commonly used terminal treatment method is the combination of a semi-dry scrubber and a bag filter with the injection of activated carbon, and it can often be used in conjunction with the "3T" technology to control the level of PCDD/Fs to below the limit value. However, activated carbon technology only transfers the dioxins from gaseous to solid, and the consumption of activated carbon increase the cost of the incineration plant. Catalysis can completely destroy PCDD/Fs and can simultaneously remove NOx. Compared with the activated carbon technology, the method of catalytic filter also has some limitations. For example, granular activated carbon can remove mercury in exhausted gases, while catalytic filter cannot. In addition, even at low temperature, activated carbon can also effectively remove PCDD/Fs, but catalysts are almost ineffective when the temperature is less than 160 °C. Electron beam radiation, plasma and SNCR are novel process for destruction of dioxins and needs for more research.

The existing control technologies are mostly single treatment technologies for dioxin. Heavy metals in the waste incineration (such as mercury, lead, cadmium, chromium, copper, zinc, nickel, etc.) are also important pollutants [50]. However, there is little study concerning about the joint control of dioxins and heavy metals and the development of related technologies. The only joint removal technology is the injection of activated carbon or alkaline sorbent [51]. Further study of the joint removal technology for dioxin and heavy metals is expected, for example, finding suitable catalytic/oxidizing/complexing agents to eliminate heavy metals and dioxin contamination simultaneously.

In short, the development of dioxin control during incineration, further clarifying the formation mechanism of dioxins and the development of joint removal technology for dioxin and heavy metals is the future development trend of dioxin pollution control technologies.

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Reference


