



# A review on the formation and remediations of polychlorinated dibenzo *p*-dioxins and dibenzo-furans (PCDD/Fs) during thermal processes with a focus on MSW process

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## Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) are notorious pollutants classified as persistent organic pollutants (POPs), which even at trace levels can bio-accumulate in the environment and have negative effects on organisms. Due to their adverse health effects, countries around the globe have introduced stringent emission standards to reduce the formation of PCDD/Fs. Using data in the literature over the past two decades (2001 to 2023), this review discussed the PCDD/F emissions from incineration facilities, E-waste recycling, iron sintering, secondary metal smelting plants, and crematories. But the review only focused on pollutants and remediation strategies from the incineration processes. There are two heterogeneous mechanism pathways that lead to the formation of PCDD/Fs, firstly, the De novo phase, using macromolecules of carbon or polycyclic aromatic hydrocarbons to begin the synthesis, and secondly, the condensation reaction beginning with the rearrangement of the molecular structure of the precursor compound. On the remediation strategies, adsorption injections were the most preferred method; however, recent studies reported other strategies such as catalytic filtration systems, an electron beam system, and good combustion practices. This review concluded that a lot has been done to manage and prevent PCDD/F formation efficiently to the level which no longer poses a hazard to human health and the environment.

**Keywords** PCDD/Fs · Emissions · Remediations · Incineration · Carbon injections · Catalytic filtration · Electron beam

## Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) are notorious pollutants classified as persistent organic pollutants (POPs), which even at trace levels can bio-accumulate in the environment and have negative effects on organisms (Li et al. 2021). These pollutants are mainly generated from anthropogenic activities as by-product of many industrial and combustion processes such as manufacture of pesticides and herbicides, chlorine bleaching of paper, e-waste dismantling activities, metal smelting processes, and waste incineration (Lemieux et al. 2004; Li

et al. 2007; Lonati et al. 2007; Chen et al. 2015; Honda et al. 2021). There are 17 congeners (7 PCDDs and 10 PCDFs) of the 210 compounds that pose great concerns because of their lateral position of the chlorine atom, which gives acute toxic properties (Hoogenboom et al. 2015; Li et al. 2016). According to Ssebugere et al. (2019), the congeners of toxic concern include 1,2,3,7,8-PeCDD; 2,3,7,8-TCDD; 2,3,4,7,8-PeCDF; 1,2,3,6,7,8-HxCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; OCDD; 2,3,7,8-TCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,7,8-PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-2,3,4,7,8-PeCDF; 1,2,3,7,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,7,8,9-HpCDF; and OCDF.

PCDD/Fs have raised public health concerns due to their potential carcinogenic properties and possible health implications (Chen et al. 2006; IARC 2012; Zhou et al. 2017). PCDD/Fs alter fundamental cell growth and differentiation, which may negatively influence reproduction, development, and immunity; cause chloracne; and lead to cancer (Chan and Wong 2013; Yu et al. 2018; Marquès and Domingo 2019). According to Steenland et al. (2004) and Chan and Wong (2013), reports from the World Health Organization

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(WHO) indicate that PCDD/Fs increased the risk of breast cancer. In 2012, the International Agency for Research on Cancer (IARC) of the WHO classified 2,3,7,8-TCDD as a group 1 carcinogen “known human carcinogen” (IARC 2012). Due to the potential toxicity of PCDD/Fs and their frequent presence at different environmental matrix, human biomonitoring of PCDD/Fs has been an important issue to assess the risks of these chemicals on human health. The concentrations of PCDD/Fs have been determined in tissues such as kidney, liver, lung, pancreas, and adipose tissue, but most biomonitoring studies have been conducted using blood and breast milk (Marquès and Domingo 2019).

PCDD/Fs yield in thermal process such as municipal solid waste (MSW) incineration process is the balance or superposition of formation and destruction through heterogeneous and homogeneous pathways (Altarawneh et al. 2009; Hell et al. 2009; Lin et al. 2014). Structurally related precursors at a temperature of between 400 and 800°C in the gaseous phase form part of homogeneous pathways (Khachatryan et al. 2003; Karademir and Korucu 2013; Cao et al. 2018). The most important and direct precursors include monocyclic aromatic compounds such as chlorinated phenols and chlorobenzenes with quinolines recently receiving attention as possible precursor compounds (Altarawneh et al. 2009). Heterogeneous pathway involves two routes with the first pathway called *de novo* synthesis. This route proceeds first by the burning of carbonaceous material with simultaneous oxidation and chlorination at temperature between 200 and 400°C in the presence of oxygen (Wang et al. 2007). The second route involves transition-metal catalytic assisted coupling of precursors also in the temperature of between 200 and 400°C (Altarawneh et al. 2009; Vermeulen and Caneghem 2014; Cheruiyot et al. 2016; Cardellicchio 2020).

The comprehensive review on the formation of PCDD/Fs in combustion processes has been reported (Stanmore 2004). In the report, the operational conditions such as temperature, gaseous content, solid species, and residence time were analyzed and reported (Stanmore 2004). A review by Kulkarni et al. (2008) reported on the sources and remediation of PCDD/Fs. The report discussed the thermal sources of PCDD/Fs and the remediation of the surrounding environment (Kulkarni et al. 2008). Treatment of both flue gas and fly ash has also been thoroughly discussed. A study on the mechanisms for the formation, chlorination, dechlorination, and destruction of PCDD/Fs has been reviewed (Altarawneh et al. 2009). Mechanisms including modelling formation of PCDD/Fs in both gaseous and heterogeneous pathways have been proposed which include the formation, chlorination, dechlorination, and destruction of PCDDs and PCDFs (Altarawneh et al. 2009). Ssebugere et al. (2019) study reported that while some of the PCDD/F sources from hotspot areas have been

established, little has been done to solve the issues related to reduction and establish public health implications of PCDD/Fs.

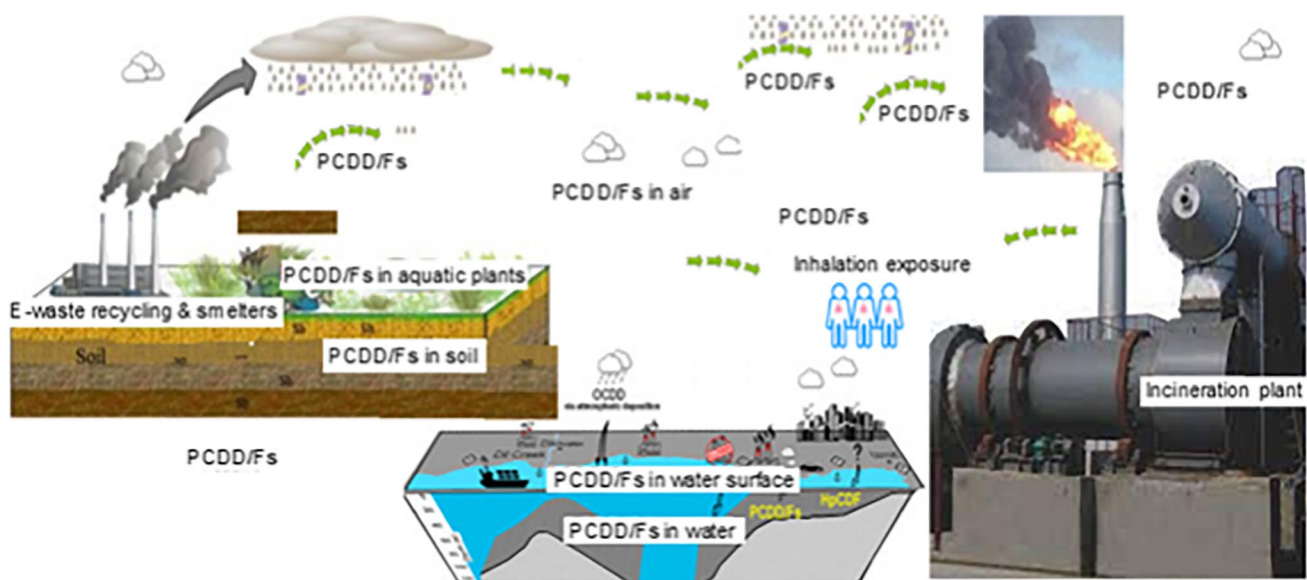
With the tremendous increase in municipal waste manufacturing and the regular improvement of incineration technology, incineration has emerged as one of the most important waste disposal technologies (Ying et al. 2023). However, municipality solid waste incineration processes still produce extent harmful gaseous emissions that are harmful to humans and the environment, that have aroused a developing interest among scholars (Han et al. 2016; Tang et al. 2022). This review will discuss the latest strategies implemented in recent years for the remediation of PCDD/Fs during incineration. Among the strategies, the use of ceramic filters, activated carbon embedded with metal catalyst such as vanadium oxide-tungsten oxide or titanium oxide, and surface-functionalized activated carbon are discussed with the aim of identifying strategies to minimize the emission of PCDD/Fs in the environment. With emission standards around the globe becoming more stringent (i.e., 0.1 ng WHO<sub>2005</sub> TEQ. m<sup>-3</sup>), this review will improve the awareness on the emissions and remediation strategies of PCDD/Fs that are unintentionally produced during incineration processes.

## Methodology

The search for scientific literature used in the review was obtained from online databases of ScienceDirect, Web of Science, and Scopus covering studies published from 2001 to 2023 using the following keywords and their combinations: PCDDs, or PCDFs, or environment, or POPs, or thermal process, or incineration processes. A total of 4015 articles were found online with the search “polychlorinated dibenzo dioxins and dibenzo furans.” The data was considered when it met the following criteria: (1) the data was published in English; (2) data was published in a scientific journal; and (3) it referred to the formation and remediation of PCDD/Fs during incineration processes. Of the 4015 articles found, 142 articles fitted the criteria above with earlier published data from the developed world (i.e., USA, Canada, and western Europe) and recently more published data from China.

## Emission of PCDD/Fs associated with MSW incineration process

Major emission sources of PCDD/Fs in the environment include metal smelting, e-waste recycling, solid waste incineration, metallurgical facilities and smelting, and crematories (Chen et al. 2006; Tejima et al. 2007; Mari and Domingo 2010; Cheruiyot et al. 2016). Small concentrations



**Fig. 1** PCDD/F emissions from MSW, e-waste recycling, and metal smelters distributed to different pathways (air, soil, water, surface water, and aquatic plants)

of these pollutants are present as contaminants in products such as sodium pentachlorophenol pesticide (Chun et al. 2015). Khairy et al. (2016) and Wu et al. (2018) expressed that nearly all combustion and thermal industrial processes involving chlorine and carbon at the temperatures from 200 to 400°C and between 500 and 800°C are major sources of PCDD/Fs in the environment. Khairy et al. (2016) stated that the following processes such as waste incinerators; coal, oil, and wood combustion; vehicle traffic; combustion in most of metallurgical processes, especially sintering; low thermal processes; accident fires; and chemical production were found to be generating PCDD/F emissions. These compounds are characterized by being persistent in the environment and can bio-accumulate in adipose tissues of living organisms, biomagnified in food chains, and travel long distances to air, water, soil, and sediments (Ssebugere et al. 2019) (Fig. 1).

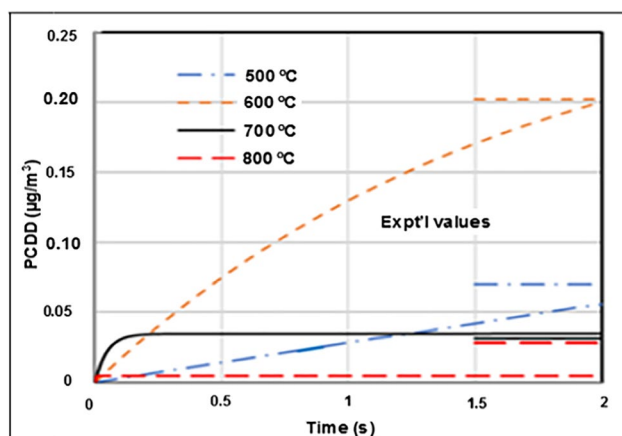
### MSW incineration facilities as PCDD/F emission source

According to Wang et al. (2019), studies of PCDD/F formation mechanisms in incineration especially under various feeding compositions are still at its infancy, despite having several studies reporting on emission levels (Wang et al. 2015; Cao et al. 2019; Pham et al. 2019; Trinh et al. 2019; Wang et al. 2019; Klima et al. 2020). However, Safavi et al. (2021) conveyed that there are two heterogeneous mechanism pathways that lead to the formation of PCDD/Fs, firstly, the De novo phase, using macromolecules of carbon or polycyclic aromatic hydrocarbons to begin the synthesis,

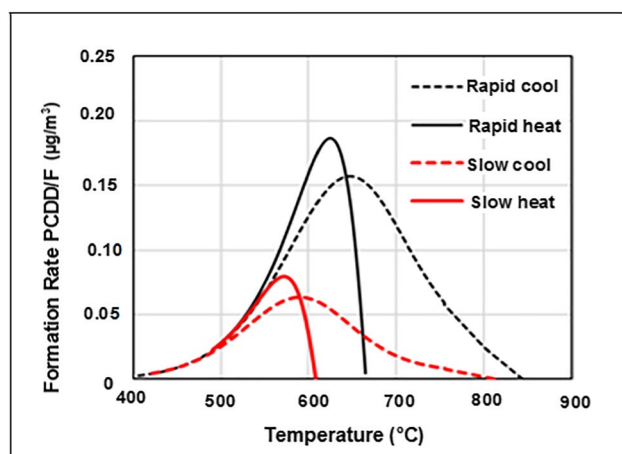
and secondly, the condensation reaction beginning with the rearrangement of the molecular structure of the precursor compound. In both pathways, chlorine compounds, metal catalysts, and carbonaceous particles are present at the surface of the particles (Altarawneh et al. 2009).

The predominant PCDD/F formation mechanism is the reaction of chlorination and de-chlorination; on the other hand, PCDDs are formed by condensation reactions of phenolic precursors (Babushok and Tsang 2003; Neuer-Etscheidt et al. 2006). Babushok and Tsang (2003) narrated that the pathways to PCDFs and PCDDs differ, with the formation of dioxins mainly being produced from chlorophenols condensation while furan compounds are formed mainly via the chlorinated naphthol's, oxy-PAHs, and PCBs. During the thermal destruction of PCBs on fly ash, PCDFs are formed but not the PCDDs (Khairy et al. 2016). At low temperatures, Kao et al. (2006) stated the formation rate exceeds the destruction rate and the PCDD/F concentration increases significantly. However, the accumulation of product continues to decompose over time, which results in a steady state in which the concentration of PCDD/Fs no longer increases (Tejima et al. 2007). Figure 2 shows the simulation of gas phase dioxin formation, at 800°C; the system reaches equilibrium after a total residence time of 2 s. Thus, these measurements are in constant condition over a set period and not instantaneous rates.

Figure 3 illustrates the experimental conditions of Sidhu at a cooling rate of 250°C per second often known as the “rapid cooling.” In this phase, at top temperatures, net instantaneous formation rates are greater than in data demonstrated in Fig. 3 with a maximum rate taking place at 650°C as compared to 600°C. At



**Fig. 2** Simulation of gas phase dioxin formation from trichlorophenol (Khairy et al. 2016)



**Fig. 3** The effect of non-isothermal conditions on gas phase PCDD formation (Khairy et al. 2016)

low temperatures of 250°C and 1 s, rapid cooling occurs but any formation of PCDD/Fs ends abruptly around 660°C.

Dioxin levels are much lower during homogeneous combustion processes between 500 and 800°C than in a subsequent low-temperature heterogeneous process between 200 and 400°C (Trinh et al. 2019). A precursor compound, such as chlorinated benzenes or chlorinated phenols, undergoes thermal breakdown and molecular rearrangement (Cao et al. 2018). Fly ash, for instance, forms dioxins after the precursor has been adsorbed to its surface and inorganic compounds catalyze these reactions (Chang et al. 2007). At low temperatures, most dioxins' formation occurs at temperatures between 250 and 450°C, so the process is confined to low temperatures (Chen et al. 2021).

The formation of PCDD/Fs is also influenced by several other factors, such as residence time, precursors, combustion temperature, and polycyclic aromatic hydrocarbons (PAHs) or

carbonaceous material, oxygen availability, and the presence of PCBs and chlorine in the feed (Ma et al. 2019). Safavi et al. (2021) found that PCDD/Fs are formed between 200 and 800°C with a maximum formation of PCDFs reaction rate between 350 and 400°C (Altarawneh et al. 2009). A study by Vermeulen and Caneghem (2014) suggested that the rate can be very slow between 200 and 250°C. Almost all organic compounds, including PCDD/Fs, are destroyed above 800°C under optimum combustion conditions such as adequate oxygen, mixing, and airflow (Vermeulen and Caneghem 2014). In contrast, at high temperatures, PCDD/Fs can be formed under conditions less optimum such as insufficient oxygen (Safavi et al. 2021). The formation of PCDD/Fs correlates with the presence of precursors, such as carbon monoxide (CO), un-combusted carbon, or combustion products, metal salts, and hydrogen chloride/chlorine (Vermeulen and Caneghem 2014).

### Chlorine in feed

PCDD/Fs are formed when fuel is enriched with chlorine (Altarawneh et al. 2009; Khairy et al. 2016; Angalakuditi et al. 2021). Chlorine has shown to affect PCDD emissions. For example, during coal combustion in the presence of chlorine, only PCDDs were produced and were also produced during the combustion of pine in the presence of hydrogen chloride (HCl) while no PCDDs were formed when pine was combusted alone (Altarawneh et al. 2009; Axegård 2019; Kirkok et al. 2020). In the absence of gaseous chlorine, the formation of PCDD/Fs involving chlorination through solid-state-chlorination may occur via a series of metal-catalyzed-reactions, though the mechanism is still not well understood (Altarawneh et al. 2009). Combustion of vegetable waste in the presence of polyvinyl chloride (PVC) and inorganic chlorine the formation of PCDD/Fs in fly ash was detected (Khairy et al. 2016). Even though most studies report on the precursor theory, studies of inorganic chlorine demonstrate that the methods by which PCDD/Fs are formed are unclear and complex (Altarawneh et al. 2009; Khairy et al. 2016). Studies showed that the presence of sulfur dioxide during the incineration process lowers the emission of PCDD/Fs (Chang et al. 2006; Wu et al. 2018). Though the presence of chlorine has an effect on the PCDD/F formation, other factors such as particulate matter, temperature, and filtration systems also have an impact on the formation and emission of PCDD/Fs during the incineration process (Altarawneh et al. 2009; Angalakuditi et al. 2021).

### Combustion temperatures

According to experiential evidence, PCDD/Fs are formed between 500 and 800°C while temperatures above 900°C destruct them (Hatanaka et al. 2002). However, 90% of PCBs are destroyed by pyrolysis at temperatures above 700°C with no detection of PCDFs (Hatanaka et al. 2002). Mi et al. (2010)

suggested that the combustion temperature depends on the amount of fuel or fuel supplement, the oxygen content, and the heating value of the fuel. Hatanaka et al. (2002) reported that the incineration of municipal waste is a common source of PCDD/Fs at temperatures between 500 and 800°C. Low combustion temperatures are characteristic of large mass burn units of PCDD/Fs. Several factors contribute to this, including the excessive amount of moisture, insufficient heating value of the gas, and insufficient air/feed mixing caused by an inadequate processing of feed system and the absence of additional fuel (Mi et al. 2010). Hatanaka et al. (2002) using external burners set the temperature independently at 700°C, 800°C, and 900°C in the primary and 1200°C in the secondary combustion chamber of the reactor. They discovered that with an increase in temperature in the secondary chamber, the PCDD/F concentration decreased. They concluded that to reduce the release of PCDD/Fs during waste incineration, it is effective to keep the temperature of the secondary combustion zone higher (Hatanaka et al. 2002; Wikström et al. 2004) albeit at a cost of damage to the chamber. Meanwhile, Passamani et al. (2017) in their recent study of PCDD/F emissions produced by burning treated wood and virgin wood made use of a simulation using a gasification boiler. The boiler was divided into three sections, namely, the wood loading chamber, the primary inlet, and the secondary inlet.

The operating temperature was sustained between 900 and 1000°C where pyrolysis and char oxidation took place. They concluded that more PCDD/F emissions were destructed at the temperature between 900 and 1000°C. Most incineration facilities operate at temperature between 850 and 1000°C as it was found to be high enough to be sufficient to ensure complete combustion but not so high enough to damage the equipment or generate excessive nitrogen oxides (Aurell and Marklund 2009). However, for complete destruction of PCDD/Fs in the secondary combustion chamber, higher temperatures are required for their complete destruction. Balance needs to be obtained between higher temperatures and residence times in the secondary combustion chambers to obtain complete destruction of PCDD/Fs (Hatanaka et al. 2002; Aurell and Marklund 2009).

### Residence time

Combustion temperature and residence time are inversely proportional to the destruction of PCDD/Fs (Hatanaka et al. 2002). PCDD/Fs are destroyed more rapidly at higher combustion temperatures and shorter residence time. Additionally, low-temperature sources need an extensive amount of residence time to destroy PCDD/Fs. Mi et al. (2010) found that in a chlorophenol combustion, the formation of PCDD/Fs decreased when temperature and residence time were

increased. According to Martínez-Guijarro et al. (2017), similar results were found in hazardous waste incinerators that operate with residence times of 1.5 to 2.0 s at temperatures above 850°C. An extended residence time combined with temperature reduced the probability of producing PCDD/Fs in flue gas (Hatanaka et al. 2002).

### Oxygen availability

According to Hatanaka et al. (2002) when burning solid fuels, the ratio of air to fuel, the mixing efficiency is largely responsible for the oxygen availability. Waste tars, for example, become particulates or large droplets when burning; therefore, it must be burned in pyrolysis or low oxygen conditions because it is a high-viscosity liquid (Mi et al. 2010). A low oxygen level or insufficient air and fuel mixing can lead to an inadequate combustion process which generates PCDD/Fs (Mi et al. 2010). The combustion of chlorophenol produces more PCDD/Fs when the air supply is inadequate (Mi et al. 2010). Most municipal waste incinerators use excessive amounts of air during incineration processes. However, Wu et al. (2018) concluded that a poorly designed fuel distribution system or a lack of fuel processing results in poor air/fuel mixing in large mass burn units and generates more PCDD/Fs.

### Feed processing

Wu et al. (2018) analyzed the liquids, solids, or gases that can be used as fuel for combustion sources. They concluded that fuels such as liquids and gases can easily be mixed with air in order to produce high combustion efficiency, while solids need some processing before they can burn effectively. Lee et al. (2003) concluded that the most common way to increase combustion of solid feeds was by drying, shredding, or separation. Similarly, preheating and atomization are necessary to prepare high-viscosity fuels for combustion (Wu et al. 2018). Oxygen availability and residence time are determined in part by feed processing (Ruokojärvi et al. 2004). According to Lundin (2007), air/fuel mixing and combustion are improved with fine homogeneous feed particles. Due to poor mixing, larger particles require a longer residence time and can lead to oxygen deficiencies and incomplete combustion (Ruokojärvi et al. 2004; Mi et al. 2010). Combustion efficiency is also reduced by high moisture content; therefore, the presence of PCDD/Fs in highly processed homogeneous feeds is unlikely to be due to incomplete combustion of waste (Lundin 2007). Table 1 demonstrates PCDD/F concentrations from different incineration plants.

## Brief summary of PCDD/F sources from other combustion processes

### E-waste recycling facilities as PCDD/F source

The e-waste recycling is one of the fastest-growing waste streams around the developing world (Chan and Wong 2013; Akortia et al. 2018; Chokwe et al. 2019). The presence of halogenated compounds in e-wastes results in the formation of persistent organic pollutants like PCBs, PCDD/Fs during recycling processes. These are unintentionally released during low tech e-waste recycling operations such as manual disassembling, shredding/comminution, roasting circuit boards, acid-stripping metals, and open burning (Zennegg et al. 2014; Cheruiyot et al. 2016; Roosen et al. 2020; Conesa et al. 2021). According to Dai et al. (2020), about 80% of the e-waste generated worldwide is disposed of informally, especially in developing countries of Asia and Africa. Globally, the top countries producing e-waste are Canada, France, the USA, and the UK (Andeobu et al. 2021). In Africa, the top three countries producing highest e-waste are South Africa, Nigeria, and Egypt (Chokwe et al. 2019) with Ghana receiving most of the e-waste from developed countries (Akortia et al. 2018). There are many different materials and additives found in these unwanted electronic products, some of which are toxic. Incorrect recycling can result in toxic substances, such as PCDD/

Fs being released into the environment (Zennegg et al. 2014). Crude methods of recycling like open burning and acid bath for recoveries of materials from e-waste have been identified as the source of PCDD/Fs in the terrestrial environment (Li et al. 2007; Awasthi et al. 2016). However, the method/or conditions of PCDD/F formation during e-waste recycling through reports suggested that their formation is favored by the de novo synthesis with their lower temperature processing during recycling operations (Hu et al. 2013; Ma et al. 2019; Roosen et al. 2020).

### Iron sintering plants as PCDD/F emission source

The main sources of PCDD/Fs among metallurgical facilities are sintering plants, electric arc furnace (EAF), aluminum smelters, secondary copper smelters, and dust treatment facilities for EAFs (Cheruiyot et al. 2016). According to Cheruiyot et al. (2016), PCDD/F emissions from metallurgical facilities accounted for 31.8% of total PCDD/F emissions in Japan, 35.7% in Taiwan (Taiwan 2008), 43.8% in China, 17.6% in the EU (Quaß et al. 2004), 20.5% in Australia (Bawden et al. 2004), 38.4% in Brazil, and 64.8% in South Africa (DEA 2011). Cheruiyot et al. (2016) reported that certain components in the raw material play a role in PCDD/F formation, such as chlorine, organic compounds, and metal catalysts like copper. Even though it is generally believed

**Table 1** PCDD/Fs concentrations (pg/Nm<sup>3</sup>) from incineration plants

City / Country	Sampling site	PCDD/Fs	Sampling period	References
Taiwan	Stack emissions	0.08–3.01	2004	Hu et al. 2004
Italy, Lombardy Region	Stack emissions	13.0–88.0	-	Caserini and Monguzzi 2002
China	Stack emissions	0.042–2.461	2002	Ni et al. 2009
China	Stack emissions	0.64–61.15	2009	Deng et al. 2011
Eastern China	Stack emissions	11.32	2015	Chen et al. 2015
China	Stack emissions	0.73–24.6	2017	Wang et al. 2017
Vietnam	Stack emissions	26.2–28.4	2019	Pham et al. 2019
Taiwan	Stack emissions	1.05–0.08	2018	Minh et al. 2019
Vietnam	Ambient air	4.89–11.4	2019	Mai et al. 2019
China	Stack emissions	4.3	2020	Gabryszewska and Gworek 2020
Lithuania	Ambient air	0.015–0.52	2020	Klima et al. 2020
China	Ambient air	0.01–0.89.	2012	Li et al. 2013
Northern China	Stack emissions	0.11–2.53	2016	Zhu et al. 2018
Central Taiwan	Ambient air	0.015–0.261	2006–2007	Hsu et al. 2008
Shenzhen	Stack emissions	0.115 and 0.096	2006	Chen et al. 2007
Huanjing	Ambient air	0.034–2.152	2016	Du et al. 2017
Southwest China	Ambient air	0.30–7.50	2020	Bo et al. 2022
China	Stack emissions	0.016–0.29	2019	Qiu et al. 2020
China	Stack emissions	5.1–390	2011	Liu et al. 2013
Taiwan	Ambient air	38.0–43.4	2006–2016	Ngo et al. 2018

that PCDD/Fs are primarily formed in the sinter bed, a study of dust particles from wind boxes revealed considerable quantities of unburned carbon and chlorine making it a potential area for PCDD/F formation (Dai et al. 2020). Temperature, sinter time, oxygen concentration and combustion efficiency, bed thickness, and permeability are some of operating conditions that contribute to the formation of PCDD/Fs. Sun et al. (2016) reported the de novo synthesis as the dominant mode of PCDD/F formation in the iron sintering process due to the dry zone layer. This layer has temperatures ranging from 100 to 1000°C with carbonaceous material from coke or, in recycling, soot from the electrostatic precipitator (ESP) which contribute to the formation of PCDD/Fs (Dai et al. 2020).

### Secondary metal smelting plants as PCDD/F emission source

Secondary metal smelters differ largely in the types of emissions they emit based on the raw materials processed. According to Hu et al. (2013), pure copper scrap has the highest emission factors of 102 pg I-TEQ. Nm<sup>-3</sup>, compared to scrap and blister copper with 24.8 pg I-TEQ. Nm<sup>-3</sup>. These processes generate secondary pollution, most notably PCDD/Fs due to high presence of chloride ions based on the usage of sodium and potassium chloride salts as fluxes in the raw materials such as plastics, paints, and solvents (Cheruiyot et al. 2016). Consequently, primary smelters generate fewer PCDD/Fs than secondary smelters due to high content of chlorine in the feed of secondary smelters (Cheruiyot et al. 2016). Secondary copper smelting processes include feeding fusion, oxygenation, and de-oxidation. About 54 to 88% of the PCDD/F emissions occur during the feeding-fusion stage (Hu et al. 2013). In China, secondary metal smelting plants contributed 10.6% to overall inventories, followed by Japan at 3.6% and Taiwan at 3.5% (Sun et al. 2016). The wide range of emission factors among these metal smelters is likely due to a variety of different factors, including the composition of feed materials, auxiliary fuel, and the furnace type used (Hu et al. 2013). Cardellicchio (2020) reported that a secondary copper smelter generally emits more PCDD/Fs than a secondary aluminum smelter because copper chloride promotes more condensation reactions suggesting that copper is a stronger catalyst. Secondary copper smelters have been reported to emit PCDD/Fs 3 to 13 times higher than secondary aluminum smelters (Cheruiyot et al. 2016). Copper was observed to promote the de novo synthesis of PCDD/Fs on the surface of flue particles due to its catalytic nature (Cheruiyot et al. 2016).

### Crematories as PCDD/F emission source

The crematorium processes have been identified as a source of PCDD/Fs (Mari and Domingo 2010). A crematorium generally contributes low levels of PCDD/F inventories between 0.63 and 1.4% as a result, and crematories are becoming a popular choice for disposing of deceased bodies worldwide (Dai et al. 2020). Since 1987, the cremation ratio in the USA has significantly increased, rising from 15.2% in 1987 to 25.0% in 2020 (Dai et al. 2020). As of 2014, the cremation rate in Taiwan increased from 66.9% in 2000 to 95.7% in 2020. Because of governmental policies encouraging cremation, countries like Japan have a cremation rate of 99% (Dai et al. 2020). When crematorium facilities are poorly maintained, PCDD/F emissions may also have a large impact on the environment due to their proximity to residential areas and their low-lying stacks (Dai et al. 2020). Xue et al. (2016) collected PCDD/F emissions in flue gas from 13 crematories in China. They reported PCDD/F emissions (as toxic equivalent concentrations, TEQ) ranging from 0.027 to 15.8 ng m<sup>-3</sup>, with the average result of 3.2 ng m<sup>-3</sup>. EPA (2016) audit report on crematories industry sector recommend that for the reduction of POPs, the temperature in the secondary chamber must be pre-heated to at least 850°C prior to the coffin insertion, and then maintained above 1000°C for the entire cremation process. The presence of silver-mercury amalgams in the body causes mercury to be emitted into the environment and the formation of PCDD/Fs (Green et al. 2012).

### Remediation processes for the reduction of PCDD/F formation during MSW incineration processes

PCDD/Fs enter the environment mainly from the flue gas and the fly ash (residue originating from heating and combustion of waste) produced during the incineration and combustion processes (Petrlik and Ryder 2005; Kulkarni et al. 2008; Altarawneh et al. 2009). This section discusses the reported remediation and prevention of these pollutants to threaten the environment.

### Treatment of fly ash

Incineration of solid waste generates a thick solid residue or cake, containing POPs such as dioxin-like compounds and metals, referred as fly ash (Abad et al. 2003; Finocchietto et al. 2006; Wey et al. 2006; Kulkarni et al. 2008). The reported concentrations of PCDD/Fs detected in these fly ash vary from 100 to 5000 ng/kg and as such, in many

countries around the globe, the fly ash from incineration process is classified as hazard waste by their environmental protection legislation (Kulkarni et al. 2008). Thus, further treatment of fly ash is required before disposal to the landfill sites. A recent review on fly ash (i.e., Zhang et al. 2021) compared element recoveries from municipal waste incineration fly ash using thermal separation, chemical extraction, bioleaching, and electrochemical technologies. Due to its ability to decompose organic pollutants at such a high temperature and to effectively immobilize leachable heavy metals in melted slags, melting technology has attracted more and more attention for the treatment of MSW fly ashes over the past decade.

It has become increasingly popular for hazardous waste treatment to use plasma melting technology among several melting methods for fly ash treatment. The advantage of a thermal plasma system over a fuel melting furnace is that it has a higher temperature and a higher energy density, which facilitates faster heat transfer at the reactor boundaries and, therefore, shorter treatment times (Pan et al. 2013). Lin et al. (2008) used an older technology of a dual bag filter system to reduce the concentration of PCDD/Fs in the stack flue gases of a fly ash treatment plant. In comparison with the original single bag filter system with activated carbon injection (ACI) of 40 kg h<sup>-1</sup>, they found that the dual bag filter system significantly reduced PCDD/F concentrations in stack flue gases (Lin et al. 2008). Qiu et al. (2019) used the microwave-assisted hydrothermal process for the degradation of PCDD/Fs in MSWI fly ash. They found that removal efficiency of PCDDs was higher than that of PCDFs. With the combined impact of microwave and Na<sub>2</sub>HPO<sub>4</sub>, the degradation of PCDD/Fs was sharply accelerated under the microwave hydrothermal conditions of 220°C and 2 h (Qiu et al. 2019).

Mechanochemical degradation (MCD) is one of the non-thermal methods for fly ash treatment that has received considerable attention due to its simplicity, efficiency, and environmental friendliness (Zhiliang et al. 2019). By combining mechanical energy with solid reactants, such as additives and POPs, ball milling induces chemical reactions. In the study of Zhiliang et al. (2019), they discovered that PCDF results were less recognizable because 2,4,6,8- and 1,2,3,8p-TCDF are anti-correlated. Guo et al. (2017) stated that the stable solidification of a geopolymers method is popular among many scholars because it does not only encase heavy metals, PCDD/Fs, and other toxic substances in the geopolymer grid, but reduce the toxicity of MSWI fly ash while generating geopolymers that have better mechanical properties and corrosion resistance. Tang et al. (2020) classified the geopolymers' thermal treatment into melting and vitrification based on the processing temperatures. Despite its ability to greatly reduce toxic substances in MSWI fly ash, thermal treatment remains limited in most countries due to its high heat consumption and processing costs (Tang et al. 2020).

## Treatment of flue gas

Both incineration and combustion processes release enormous amount of flue gases which are the most sources of PCDD/F emissions in the environment (Chen et al. 2008; Atkinson et al. 2015; Zhou et al. 2015; Cui et al. 2017). As reported, the formation of PCDD/Fs in the flue gases of the incineration system occurs via either the homogeneous or heterogeneous pathways (Khachatryan et al. 2003; Karademir and Korucu 2013; Cao et al. 2018). The concentrations of PCDD/Fs and dl-PCBs in flue gases vary between 1 and 500 ng I-TEQ.Nm<sup>-3</sup>; thus, further treatment to reduce the emission concentration to the acceptable limit of 0.1 ng I-TEQ.Nm<sup>-3</sup> before entering the environment is required (Kulkarni et al. 2008; Atkinson et al. 2015; Zhou et al. 2015). The following remediation methods were discussed for the reduction of PCDD/F emissions to the environment.

### Activated carbon injections

Activated carbon injections (ACI), referred to as adsorbent injections, adsorb PCDD/Fs from gas streams but can simultaneously allow PCDD/Fs to be generated via de novo synthesis between 250 and 400°C if the temperatures are not controlled (Atkinson et al. 2015). High surface area, microporous structure, and high degree of surface reactivity make the activated carbon versatile adsorbents particularly effective in the adsorption of organic pollutants (Chi et al. 2006; Zhou et al. 2015). The adsorption mechanisms are driven by van der Waal's forces together with smaller pore sizes of the activated carbon (Bell et al. 2011; Atkinson et al. 2015; Cui et al. 2017). Figure 4 presents an activated carbon injection for remediation of PCDD/Fs from flue gases during incineration.

Altarawneh et al. (2009) in their study found that activated carbon is a useful technique for adsorption of PCDD/Fs particularly when amounts in part per million (ppm) concentrations must be removed from flue gas. In solvent recovery processes, adsorbent is used only when traditional extraction or absorption is too expensive or not effective enough to meet the requirements. Activated carbon is widely used for pollution control as an adsorbent in the environment (Altarawneh et al. 2009). Mukherjee et al. (2016) discovered that activated carbon injections are most effective when they are used in conjunction with injection rate, injection method, carbon properties, flue gas temperature, and particulate matter control method. Abad et al. (2003) made use of activated carbon and achieved a removal efficiency approximately 92 to 96%; Li et al. (2021) achieved 96.1% (97.2% I-TEQ); Hajizadeh et al. (2011) achieved an average of 85%; Hung et al. (2011) achieved PCDD/F removal efficiencies of >90%, with some exceeding 99%; Atkinson et al. (2015) achieved a mass removal efficiencies exceeding 98% and 96% for all tested surface functionalized carbons; Zhou



et al. (2014) 96%; and Qiang et al. (2018) achieved 99.6% removal efficiency.

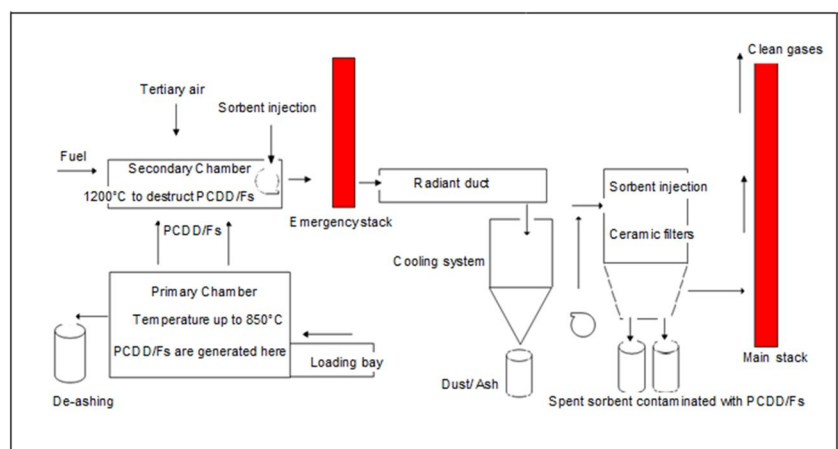
According to Hsu et al. (2015), carbon injection has primarily been applied to mass burn MWCs with electrostatic precipitation (ESP) systems in the USA and Europe. However, Hsu et al. (2015) confirmed that by injecting powdered carbon into the flue gas, it can increase the concentration of solid-phase carbon. By increasing the carbon injection rate, the average and variability of emissions are reduced. High carbon injection rates are generally sufficient to capture PCDD/F emissions (Hsu et al. 2015). However, the presence of mercury (Hg) reduces the adsorption of PCDD/Fs as high levels of Hg compete with PCDD/F adsorption on the active site of the carbon leading to high load of carbon for the process (Hsu et al. 2015). This can be calculated based on variations in flue gas concentrations. Due to the high variability in Hg inlet concentrations, it is necessary to inject high amounts of excess carbon to capture PCDD/F emissions (Hsu et al. 2015).

Qiang et al. (2018) and Mukherjee et al. (2016) are all in agreement that injection of activated carbon upstream of a particulate matter collection device is the least expensive method used to reduce PCDD/Fs, due to carbon injection system capital cost that includes low injection rates, sorbent recycling, low sorbent disposal rate, and the overall net plant capacity. Everaert et al. (2003) agree with Mukherjee et al. (2016) that the efficiency of adsorbent removal is affected by the adsorbent injection quality, the adsorbent flue gas mixing system, and the operation of the filter as well as the mass flow rate of the adsorbent. Hsu et al. (2015) found that, ideally, injectable adsorbents should be applied through a fabric filter with 2 kPa and due to the additional contact time between the adsorbent and the flue gas in the gas stream and in the filter cake on the bags. A high pressure of, i.e., 5 kPa will reduce the contact time between flue gases and the adsorbent and that may increase the PCDD/F emissions.

Everaert et al. (2003) and Hsu et al. (2015) all recommended that for better results, to remove PCDD/Fs from the flowing gas, activated carbon must be injected before the bag filter and carried by the flue gas to the filter bags. Each time a bag is cleaned off, the spent sorbent is removed along with other particulates (Hsu et al. 2015). Everaert et al. (2003) continued and report it is necessary to keep the exit temperature on the stack at 200°C during cleaning and pulsing in order to avoid burning the filter bags. As a result of the loss of adsorption capacities and the increased formation of PCDD/Fs at higher temperatures, this must be considered the absolute maximum temperature for this technology/process. However, applying the same process as described, Altarawneh et al. (2009) reported, due to safety concerns associated with ignitable materials such as activated carbon, a temperature range of 130 to 170°C is recommended for PCDD/F emission reduction using the same process. Cui et al. (2017) reported a high adsorption efficiency of activated carbon using dibenzofuran initial concentration of 95.6 mg/m<sup>-3</sup>.

A study by Atkinson et al. (2015) reported on adsorption and destruction of PCDD/Fs using surface-functionalized activated carbon. In their study, it was observed that all functionalized activated carbon (i.e., oxygen, bromine, sulfur, and nitrogen-functionalized activated carbon) adsorbs PCDD/Fs efficiently, with I-TEQ removal efficiencies exceeding 99% and mass removal exceeding 98%. It was further observed through mass balance estimation that the sulfur-surface-functionalized activated carbon was particularly effective in destroying PCDD/Fs up to 27% (Atkinson et al. 2015). Zhou et al. (2015) compared activated carbon and multiwall carbon nanotubes (MWCNTs) for the removal of PCDD/Fs with an initial concentration of 8.3 ng I-TEQ. Nm<sup>-3</sup>. It was observed from their experiments that MWCNTs reached the removal rate of 86.8% while the activated carbon reached removal of 70 and 54.2% for the tested activated carbon (Zhou et al. 2015).

**Fig. 4** Activated carbon injection for the remediation of PCDD/Fs in flue gases

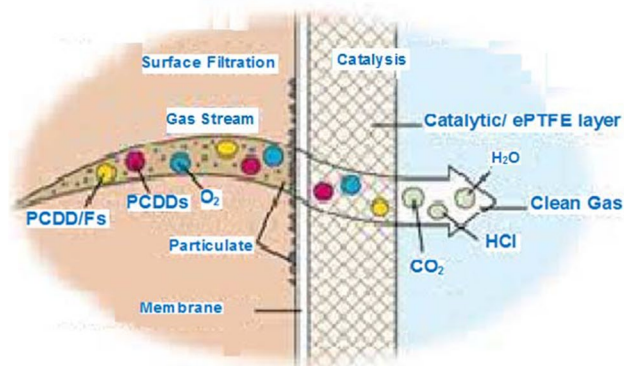


## Selective catalytic reduction (SCR) system

Selective catalytic reduction is a major air pollution controlled device (APCDs) for PCDD/F removal as these compounds are known to adsorb on particulate matter. According to Finocchio et al. (2006), adsorption and absorption methods are only capable of transferring PCDD/Fs from the vapor phase to solid or liquid phases, while SCR destroy them by producing carbon dioxide and HCl. PCDD/Fs and related compounds can be catalytically destroyed from incineration processes at low temperatures, providing a promising alternative for end-of-pipe treatment. Based on the operating temperature and catalyst used, removal efficiency of PCDD/Fs is between 21 and 97% with SCR systems (Chang et al. 2007). According to Chang et al. (2006), the catalytic filtration technique is a two-step process to adsorb and destroy PCDD/Fs in flue gases. Firstly, the PCDD/Fs diffuse to the catalyst surface and secondly, the PCDD/Fs will react to form trace amounts of CO<sub>2</sub>, H<sub>2</sub>O, and HCl (Bontea et al. 2002). The use of metal catalysts (i.e., copper/carbon (Cu/C), iron/carbon (Fe/C), vanadium oxide-tungsten oxide on titanium oxide (V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>)) is used for this purpose (Chang et al. 2008; Hung et al. 2014; Mukherjee et al. 2016). Limited studies utilized fabric filters (expanded polytetrafluoroethylene (ePTFE)) for the adsorption and destruction of PCDD/Fs from flue gases (Xu et al. 2019). Figure 5 presents the catalytic filtration as remediation of PCDD/Fs in flue gases during incineration process.

Xu et al. (2019) monitored the performance of a catalytic filter at the IVRO incinerator for over 42 months to comply with PCDD/F emission standard in Belgium. Catalytic filters were adopted by the IVRO municipal waste incinerator to be used in conjunction with existing fabric filters. Xu et al. (2019) found that, in flue gas streams, PCDD/Fs can exist in gaseous form or in solid particulate form. Fabric filters are usually efficient at removing solid/particulate phase PCDD/Fs from municipal waste incinerators. Flue gas cleaning equipment like fabric filters can clean the flue gas of trapped PCDD/Fs. Adsorption on carbon-based additives, catalytic destruction, or a combination of these methods are recommended to be used to remove gas phase PCDD/Fs (Xu et al. 2019).

In the vapor phase, PCDD/F removal efficiency at the incineration facility with higher operating temperature of 290°C is lower than that of lower operating temperature (220°C) (Ma et al. 2022). There may be three possible causes of that: Firstly, PCDD/Fs are formed within SCR via de novo synthesis when the operating temperature exceeds 250°C. The second possible cause is the high PM concentration measured before and after the SCR may provide enough carbon source, chlorine, and catalysts (copper and iron) to form PCDD/F. PCDD/F concentration in flue gases may rise due to these two causes, further reducing SCR's efficiency in removing PCDD/F. The third possible cause is the SCR



**Fig. 5** Catalytic filtration membrane removes particulate while the catalytic destroys gaseous PCDD/F emissions (Xu et al. 2019)

system with a higher space velocity and a lower surface area of the catalyst. With this, the removal efficiency of PCDD/F with SCR decreases with increasing space velocity. The higher PCDD/F removal efficiency observed was attributed to its lower space velocity (Lin et al. 2020).

A separate study conducted by Axegård (2019) demonstrated that a catalytic filter was able to reduce PCDD/Fs below the desired limit of 0.1 ng. Nm<sup>-3</sup>. According to Axegård (2019), filter membranes collect flue gas particles while catalytic filters oxidize gaseous components. More than 99.9% of PCDD/Fs is destroyed by the filter depending on the volatility and oxidative behavior of semi-volatile compounds like PAHs, polychlorinated naphthalene (PCN), or oxy-PAHs in the flue gas (Axegård 2019). Hung et al. (2014) and Xu et al. (2019) reported that catalytic filtration is still an effective method for removal of PCDD/Fs. Hung et al. (2014) found that with catalytic filtration, it is possible to separate solid materials from fly ash and at the same time separate PCDD/Fs present in filtered gas through a unique type of fabric filter used in filtration bags. Axegård (2019) confirmed that in this process, cleaned gas enters a filtration layer with components which act as catalysts to break down PCDD/Fs with 98.8% efficiency.

Fritsky et al. (2011) conducted a similar study to Xu et al. (2019) and confirmed that PCDD/Fs exist as gases or as adsorbed contaminants on aerosols and solids. Fritsky et al. (2011) concur that catalytic filtration has been the most prevalent control technology to date. Yeh et al. (2004) demonstrated that PCDD/Fs can be destroyed effectively by catalytic filtration through oxidation to achieve 0.001 ng TEQ.Nm<sup>-3</sup>. In their study, Yeh et al. (2004) demonstrated that using catalytic filtration, PCDD/F levels are reduced from 0.1 ng TEQ.Nm<sup>-3</sup> to less than 1% using an efficiency of 99%. Different authors achieved different efficiency rates for PCDD/F destruction (Finocchio et al. 2006). For example, Weber

et al. (2018) reported a high destruction efficiency of >98% catalyzed by TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> at 200°C. Xu et al. (2019) reported 98 to 99.75% efficiency at 200°C, while Cunliffe and Williams (2009) reported a degradation efficiency of 65 to 86.0% with an increasing temperature of up to 300°C, and finally, Xu et al. (2019) obtained a high efficiency of more than 99.9% from a MSW incinerator at the temperatures of 200 to 230°C.

### Entrained flow reactor

The entrained-phase injection is the simplest technique of pulverized adsorbents in the flue gas. In the entrained-phase adsorption, the pulverized sorbent dissipates uniformly into the waste gas stream. The solid-separation unit, which is usually a fabric filter unit, then transports the PCDD/F emissions and removes it concurrently (Everaert et al. 2003). PCDD/Fs exist both in the gas phase and particulate phase in the incineration flue gases, and the gas PCDD/F changes as the flue gas flows through the incineration system (Yan et al. 2006). In entrained flow adsorption, the adsorption takes place in the entrained-phase transport at high gas velocities, and the fine-particle cake exhibits a high degree of dispersion in low-velocity cake filtration. To determine the effectiveness of adsorption, these steps are followed: (1) The mass transfers from the gas phase to the external surface of the adsorbent particles; (2) the mass transfers through pore diffusion within the particles and the adsorption at the phase boundary is usually very fast. Two adsorption processes occur simultaneously: the first is that powdered activation carbon (PAC) is homogeneously dissipated into the flue gas and concurrently transported with the gas; the second is entrained flow passes through the filter membrane (Yan et al. 2006a).

Lu et al. (2015) detailed a process in which adsorbent is continuously supplied and injected, a fabric filter for the removal of the used adsorbent, an adsorbent circulation system, and a spent adsorbent storage system. To destroy the adsorbed PCDD/Fs thermally, the used adsorbent is re-cycled by typically injecting it back into the combustion zone of the furnace (Liu et al. 2012). Through the adsorbent recirculation system, the adsorbent is utilized to its fullest extent possible. Moreover, the entrained flow reactor's adsorbent is kept at a high concentration without the need to use fresh adsorbent (Everaert et al. 2003). Because of the required distribution of adsorbent in the flue gas duct and the need for cleaning intervals of the filter bags, a minimum concentration of adsorbent particulates in the reactor is important. For the purpose of particulate removal only, a conventional fabric filter usually results in slightly low pressure across a fabric filter (Everaert et al. 2003).

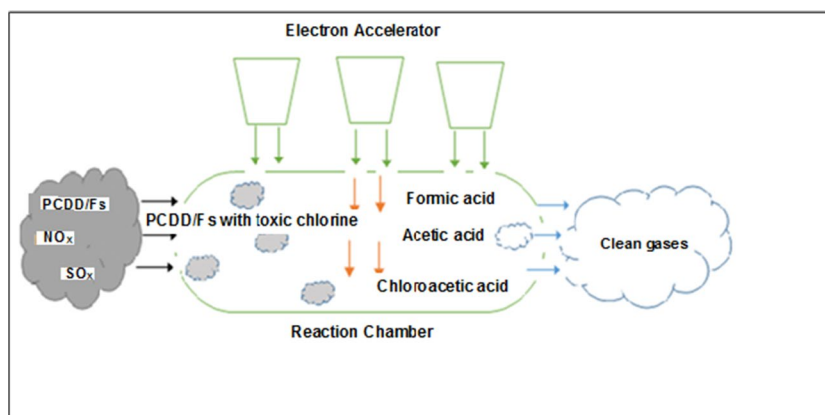
### Application of electron beam system

An electron beam system is a new technology that uses a radiation process for the destruction of dioxin. It breaks down the toxic chlorine compounds into non-toxic organic acids such as formic acid, acetic acid, and chloroacetic acid with fairly low energy consumption (Liu et al. 2012). Figure 6 presents the application of the electron beam system as a remediation strategy for PCDD/Fs.

Many studies have been conducted on the use of electron beam technology on toxic substance processing (Hirota et al. 2003; Ruokojärvi et al. 2004). Liu et al. (2012) stated that an electron beam has been announced as a new process to destroy PCDD/Fs in the flue gas. The method has the following advantages: (i) the direct decomposition of dioxins means there is no risk of secondary pollution, like those produced with a filter-based recovery process; (ii) temperature control should be maintained around 200°C; and (iii) installing an electron beam system to the existing incinerators is a simple process (Liu et al. 2012). Hirota et al. (2003) explained that, in general, the electron beam system consists of power supplies, beam accelerators that accelerate electrons, scanning systems that deliver the required dose, cooling systems for the accelerator and assemblies, vacuum systems for maintaining vacuum, shields to protect workers, conveyor systems to transport waste, and sensors and controls. In addition to concrete vaults, cavities and integral shields can be used to shield the area being treated. There are no significant physical changes to waste as a result of electron beams, except perhaps that their temperature may increase a few degrees (Hirota et al. 2003).

Hirota et al. (2003) utilized electron beam technology to reduce PCDD/Fs in a flue gas of 1000 m<sup>3</sup>N/h from the municipal solid waste incinerator at a temperature of 200°C. They found that with a dose of 14 kGy, an electron accelerator was able to decompose PCDD/Fs by more than 90%. By exposing flue gases to OH radicals, decomposition of PCDD/Fs by oxidation such as ring cleavages, dissociation of bonds, and a de-chlorination process takes place (Hirota et al. 2003). Ruokojärvi et al. (2004) also used both a bag filter system and an electron beam filter system, and the cost analysis estimated that the electron system cut the annualized cost by approximately 50% for the treatment of PCDD/Fs in the flue gas as compared to the bag filter system. Additionally, they found that electron beam technology reduces PCDD/Fs in an industrial waste flue gas in an economically and technologically useful way. The electron beam destructs PCDD/F emissions through reactions with OH radicals produced by the irradiation of flue gases, followed by oxidation such as the ring cleavage of the aromatic ring, the dissociation of ether bond, and de-chlorination (Hirota et al. 2003). Using this technology, Hirota et al. (2003)

**Fig. 6** Electron beam system as remediation for PCDD/Fs during incineration



achieved a reduction efficiency of more than 90% at a dose of 14 kGy while Koichi (2019) achieved an overall removal efficacy of 42% for PAHs. The findings from this review suggest that electron beam technology is the least popular method for PCDD/F destruction.

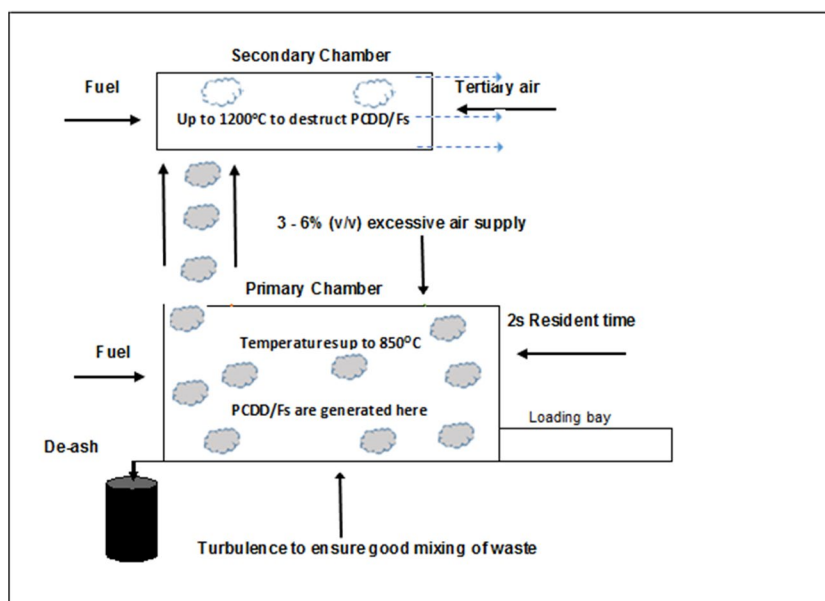
### Good combustion practice treatment

The combustion temperature plays a significant role in the formation of PCDD/Fs as they are formed due to incomplete combustion. Combustion efficiencies include combustion temperature, residence time, supplemental fuel, fuel processing, and oxygen availability (Fig. 7) (Kulkarni et al. 2008; Qu et al. 2009; Mukherjee et al. 2016; Cui et al. 2017). In order to destroy PCDDs or prevent their formation, the combustion efficiency must be high (Streibel et al. 2007). PCDD/Fs are formed under specific conditions that are determined by the composition of the fuel and combustion conditions. Mukherjee

et al. (2016) in their recent study of combustion practice, a set of optimal operating conditions were specified that mitigated the production of PCDD/Fs. Two stages of the combustion process were recommended, namely a design that facilitates the complete combustion to reduce the formation of PCDD/Fs; secondly to ensure maximum reduction of PCDD/Fs, the end-of-pipe treatment was used. Mukherjee et al. (2016) went on to declare that the first guideline was to monitor the chlorophenols periodically as they are the source of hydrogen chloride (HCl) and chlorine.

Secondly, Mukherjee et al. (2016) suggested that PCDD/Fs are formed due to incomplete combustion when combustion temperature drops below 800°C. To achieve complete combustion, Mukherjee et al. (2016) recommended that the temperature should range between 850 and 1000°C if the combustion chamber is to destroy the carbonaceous particles. For a combustion zone with a temperature of 800°C, a residence time of 2 s is

**Fig. 7** Good combustion practice during incineration process



recommended, while for 1000°C, a residence time of 1 s is recommended. For complete combustion and complete destruction, a 3 to 6% (v/v) excess of oxygen is recommended. To prevent PCDD/Fs from forming in the flue gas, the post combustion temperature needs to be kept at 200°C (Mukherjee et al. 2016).

Several other researchers, including Ruokojärvi et al. (2004) and Mukherjee et al. (2016), are in agreement with Mukherjee et al. (2016) for they reported combustion-related variables that are considered to affect the destruction when calculating furnace emissions, namely, combustion temperatures, as well as residence times. Combustion temperature, excessive air, and distribution are important, as well as mixing. Ruokojärvi et al. (2004) reported that the organic components of waste and the waste products associated with thermal decomposition must be destroyed fully by heat for a sufficient period of time. In Wang et al. (2007) study, gaseous compounds in active flame zones were measured in milliseconds for destruction time. They recommended that combustion temperatures and residence times of 980°C and 1 to 2 s, respectively, are generally sufficient to destroy thermally gaseous phase compounds. However, Mukherjee et al. (2016) contradicted that and reported that even at temperatures above 980°C, only 2 s of residence time is insufficient, resulting in heterogeneous reactions which form PCDD/Fs. Li et al. (2019) proposed that the combustion excess air should be at least 10% to prevent the formation of fuel-rich pockets and to prevent quenching of combustion reactions. It is also crucial to distribute combustion air evenly so that each zone can burn fuel. PCDD/Fs are formed when there is poor mixing of organic materials. Organic gaseous and solid phases cannot be fully oxidized due to insufficient local stoichiometry. A good mix can be achieved using furnace configurations and air jets over the fire (Li et al. 2019).

### Major research gaps for PCDD/Fs associated with incineration processes

Waste incineration and combustion processes are the major route of PCDD/Fs in the atmosphere; therefore, more attention is required for enhanced understanding of the precursor and de novo mechanisms of PCDD/F formation. The use of activated carbon injection has shown to reduce the levels of PCDD/Fs in the atmosphere; however, there is a need to use sorbent that will adsorb and destruct the PCDD/Fs. This can be achieved by using cheaper activated carbon (i.e., from biomass) impregnated with functionalized compounds such as sulfur, and metallic catalysts as they have provided promising results on removal and destruction of PCDD/Fs. It is also not possible to sample each and every step during the incineration process. Operating temperatures in each stage of

incineration makes it impossible to follow the comprehensive formation of dioxins/furans.

Another research gap identified in our review was that as waste material may contain products with different halogens (i.e., fluorine, chloride, and bromine), studies on the presence of mixed halide dioxins and furans are of utmost importance to monitor their presence in the atmosphere. Thus, this mixed halides furans and dioxins should be studied to evaluate their potential threat to the environment and human health. To achieve this goal, research should include, among other things,

- I. Developing analytical methods to measure these mixed-halides-dioxins and furans in different matrices at trace levels.
- II. The levels or co-existence of individual dioxins/furans with mixed halide dioxins/furans during incineration.
- III. Toxicity of mixed halides dioxin/furans due to long-term exposure at trace levels.

### Conclusions

PCDD/Fs are persistent, bio-accumulative, and toxic compounds that enter the atmosphere through thermal processes such as incineration and combustion processes. Human exposure to such compounds can lead to damage of the immune system leading to increased susceptibility and disruptions of several hormones. The emission and remediation of these compounds during incineration process have been discussed in this review. It has been observed that both the homogeneous and heterogeneous pathways are sources by which these pollutants are emitted to the environment. Thus, further attention is needed for understanding of the precursor and de novo mechanisms on PCDD/F formation.

Activated carbon injection was reported as method of choice for the adsorption of PCDD/Fs in flue gases around the globe. Though higher adsorption efficiency was reported, the disadvantage of this remediation techniques was in the disposal of the adsorbed PCDD/Fs into the landfill site which needed a pre-treatment. Thus, the use of adsorption and destruction techniques for the reduction of PCDD/Fs in the atmosphere was developed. Among the techniques, the use of ceramic filters that can sustain higher temperatures was used during the incineration process. Recently, the use of selective catalytic reduction catalyst used for NO<sub>x</sub> reduction was also found to be effective for PCDD/Fs reduction. The catalyst comprises of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> with reported PCDD/F removal and destruction efficiencies of >98% at temperature range of 200 to 250°C.

Other studies reported the use of surface-functionalized activated carbon (Atkinson et al. 2015) and the removal and

destruction of PCDD/Fs reached 99 and 27%, respectively, with increasing sulfur content impregnated activated carbon. Recent destruction technology includes the use of electron beam radiation that converts PCDD/Fs to non-toxic compounds such as formic acid, acetic acid, and chloroacetic acid with low energy. Due to high cost of activated carbon, the use of cheaper activated carbon impregnated with selective catalytic reduction catalysts or surface functionalized compounds derived from biomass can be incorporated during incineration of waste especially in developing countries. Further studies are needed to understand the reduction of precursor(s) and/or factors affecting the de novo synthesis during the incineration processes to minimize the emission of PCDD/Fs to the surrounding environment.

Although the problem of PCDD/Fs was reported more than 20 years ago and since then intensive research on specification of the conditions for dioxin generation and methods for reduction of these compounds has been carried out, it seems that today we can declare that we have managed to learn the process well enough to be able to prevent dioxin formation efficiently and to reduce emissions to the level which no longer poses a hazard to man's health and to the environment. It can also be reported that the latest incineration facilities are now equipped with modern systems that can make flue gas treatment easier to achieve the concentration below 0.001 ng I-TEQ/Nm<sup>3</sup>.

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**Availability of data and material** The data that support the findings of this study are openly available in Science Direct at <https://scienicedirect.com> and ResearchGate at <https://www.researchgate.net> and are discussed in the manuscript.

**Author contribution** Nomathemba Themba: conceptualization, methodology, writing — initial draft, writing — editing and review; Linda L. Sibali: project administration, supervision, writing — review and editing; Tlou B. Chokwe: conceptualization, methodology, supervision, writing — review and editing.

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## Declarations

**Ethics approval and consent to participate** Not applicable

**Consent for publication** The manuscript does not contain any individual person's data in any form (for example individual details, images, or videos).

**Competing interests** The authors declare no competing interests.

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