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HDIAC TECHNICAL INQUIRY (TI) RESPONSE REPORT

Specific Information on Removal of Memory Effect From an Incinerator's Pollution Abatement System After Becoming Contaminated With Dioxins and Furans

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The Homeland Defense and Security Information Analysis Center (HDIAC) was asked to provide information on the removal of the memory effect from an incinerator’s pollution abatement system after it becomes contaminated with dioxins and furans. The overarching objective is to eliminate dioxin and furan emissions. However, realistic goals are centered on locating the most cost-effective way to maintain a subthreshold dioxin and furan emission. The inquirer’s primary interests are in finding technological approaches that are not only effective but also economically feasible. These are addressed in this report. HDIAC partnered with SciTech Services, Inc., to research this topic and generate a report on the various technological approaches for reducing the dioxin and furan emissions during the incineration process.

15. SUBJECT TERMS
polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), dibenzo-furans (DFs), pollution abatement system (PAS), demilitarization, memory effect

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TI Research

A chief service of the U.S. Department of Defense's Information Analysis Centers is free technical inquiry (TI) research limited to four research hours per inquiry. This TI response report summarizes the research findings of one such inquiry. Given the limited duration of the research effort, this report is not intended to be a deep, comprehensive analysis but rather a curated compilation of relevant information to give the reader/inquirer a "head start" or direction for continued research.

Abstract

The Homeland Defense and Security Information Analysis Center (HDIAC) was asked to provide information on the removal of the memory effect from an incinerator's pollution abatement system after it becomes contaminated with dioxins and furans. The overarching objective is to eliminate dioxin and furan emissions. However, realistic goals are centered on locating the most cost-effective way to maintain a subthreshold dioxin and furan emission. The inquirer's primary interests are in finding technological approaches that are not only effective but also economically feasible. These are addressed in this report. HDIAC partnered with SciTech Services, Inc., to research this topic and generate a report on the various technological approaches for reducing the dioxin and furan emissions during the incineration process.

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1.0 TI Request

1.1 Inquiry

How can you remove the “memory effect” from an incinerator’s pollution abatement system (PAS) after it becomes contaminated with dioxins and furans?

1.2 Description

The Homeland Defense and Security Information Analysis Center (HDIAC) staff was asked to provide information on the research to date for the memory effect found in PAS equipment after the incineration of materiel.

1.3 Focus

The focus of this technical inquiry (TI) is to provide specific information on removal of the memory effect from an incinerator’s PAS after it becomes contaminated with dioxins and furans [1].

1.4 Purpose

Based on a discussion between the inquirer and the HDIAC-assigned point of contact for this TI, the purpose was documented [1]:

> This particular agency is demilitarizing a specific “ammunition item” where there is an epoxy agent and molding compound, which, postincineration, is causing dioxin and furan particulates to pass through the filters of the PASs, and then they interact and precipitate postfilter, which makes the exhaust exceed the allowable emission limits if not [be] eliminated/mitigated.
>
> [The] big picture is to eliminate dioxin and furan emissions but, realistically, will most likely settle with finding the most cost-effective capabilities for maintaining a subthreshold dioxin and furan emission (whether that means constantly cleaning the PAS, replacing parts to the system, changing the filters used/preventative maintenance schedule, including additional “catches/controls” for dioxins/furans, etc.).

1.5 Background

Additionally, relevant background information was provided from the tasking agency as follows [1]:

> Incineration is a method of destroying hazardous wastes and is used for the demilitarization of obsolete conventional ammunition items. The combustion that occurs in an incinerator creates pollutants. Incinerators are regulated by state environmental agencies to control air emissions of specific pollutants to within allowable emissions levels. Control is accomplished by using a PAS, which removes or destroys the regulated pollutants.
>
> The PAS consists of ductwork that routes the incinerator combustion gases through a series of pollution abatement equipment that each treat or remove different pollutants. At the end of the duct work is a stack that emits the treated gases into the atmosphere. Air sampling of this gas stream is periodically conducted at the stack to measure the levels of pollutants and ensure they are below regulatory limits.
>
> Dioxins and furans are one of the regulated pollutants [and] are a very toxic byproduct of the combustion of hazardous wastes. Products of the combustion sometimes condense on the internal surface of the duct work or pollution abatement equipment and can generate additional dioxin and furan emissions in subsequent operation. The combination of the dioxins and furans from this contamination combined with that from the waste that is presently being combusted can sometimes increase emissions at the stack to above allowable levels.
>
> This lingering and continuing generation of dioxins and furans from contamination in the system is called the “memory effect.” It is particularly troublesome if the contamination somehow gets through the pollution control devices and deposits downstream of the control device and continues to generate dioxins and furans from that location. It is alleged that the memory effect is very persistent and difficult to remove from the PAS.

Additional information provided by the inquirer indicated that the ammunition item being processed in the incinerator consists of a large portion of epoxy that is comprised of two parts of Part A (i.e., resin) to one part of Part B (i.e., hardener) [1].

Part A comprises the following components [1]:

- Epoxy Novolac Resin (Dow Chemical Company DEN 438 or equivalent): 17.39% by weight
- 2,3-Epoxy Propanol (Glycidol): 3.07% by weight
- Gamma-Glycidoxypropyltrimethoxy Silane: 1.37% by weight
- Granular Silica: 53.2% by weight
- Powdered Silica: 24.96% by weight
- Foam Reducer (Dow Corning Antifoam A or equivalent): 0.01% by weight

Part B comprises the following components [1]:

- Maleic Anhydride: 4.8% by weight
- Chlorendic Anhydride: 6.41% by weight
- Methyl Tetrahydrophthalic Anhydride: 9.58% by weight
- Dipropylene Glycol: 0.41% by weight
- Uranyl Acetylacetonate: 0.3% by weight
- Gamma-Glycidoxypropyltrimethoxy Silane: 1.35% by weight
- Granular Silica: 52.37% by weight
- Powdered Silica: 24.77% by weight
- Foam Reducer (Dow Corning Antifoam A or equivalent): 0.01% by weight

Furthermore, in addition to the epoxy, the inquirer noted that there are a variety of other components that include electronics, rubber tubing, metal parts, energetic materials, and polyester thread [1].

Some of the elements contained in the ammunition item being demilitarized include [1]:

- Metals: aluminum, arsenic, beryllium, cadmium, chromium, copper, gold, lead, iron, and zinc
- Chlorine

2.0 TI Response

A comprehensive literature search entailed leveraging three critical sources of information as follows:

1. Unclassified/Unlimited and Unclassified/Limited information from the Defense Technical Information Center
2. Unclassified/Unlimited and Unclassified/Limited information from the technical library at the U.S. Army Combat Capabilities Development Command Chemical Biological Center
3. Unclassified/Unlimited information located in various internet search engines (e.g., Google, Yahoo, Bing, Swisscows, DuckDuckGo)

2.1 Technical Approach

The technical approach used to conduct this response to the TI entails a four-step approach.

Step 1. Identify the mechanisms that cause the formation of dioxins and furans. By having this understanding, one can better understand and determine approaches on how to reduce/remove the memory effect from an incinerator’s PAS after becoming contaminated with dioxins and furans.

Step 2. Identify relevant data associated with the disposal of epoxy (resin and hardener), components, and chemical elements listed with the ammunition item being processed in the incinerator.

Step 3. Identify technologies and/or technical approaches that have been considered/used to remove the memory effect from an incinerator’s PAS after becoming contaminated with dioxins and furans.

Step 4. Recommend the most cost-effective capabilities to maintain a subthreshold dioxin and furan emission for an incinerator.

2.2 Mechanisms That Cause the Formation of Dioxins and Furans

By understanding the mechanisms that cause the formation of dioxins and furans, one can better determine approaches on how to reduce/remove the memory effect from an incinerator’s PAS after becoming contaminated with dioxins and furans.

Incineration is a thermal treatment process that, “in recent years…has become one of the most widely used alternatives for waste management,” resulting from combustion of organic matter. However, this process does have limitations. According to a review by Mukherjeea et al.” [2].

> One of the major and serious threats toward the environment and society is the emission of flue gases. The gas contains bulk species, such as oxides of sulfur and nitrogen, fine dust, trace elements such as mercury and nickel, and super-toxics such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs), respectively. Dioxins are the generic terms for the…PCDDs and PCDFs that are generated unintentionally from waste incinerators [3–5].
>
> Dioxins…have generated a lot of controversy, mainly because they are among the most toxic environmental compounds on the earth and, particularly, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has the highest toxicity, which is assigned a [toxic equivalency factor] TEF value of 1 [6].

Research investigations have demonstrated that the formation of PCCDs and PCDFs in incinerators occurs mainly by two pathways or mechanisms [2]:

> Firstly, the homogeneous reactions [are] at temperatures between 773 and 1,073 K…the main mechanism behind the process is the rearrangement reaction of chlorinated precursors such as chlorophenols (CP), chlorobenzenes (CBs) in the gas phase, and the PCDD/PCDFs formed undergoing this process are either called homogeneous PCDD/PCDFs or high-temperature PCDD/PCDFs. [Secondly are] the heterogeneous reactions in the postcombustion zone at temperatures between 473–673 K, and the main process is the surface catalytic effect of fly ash or soot, which [results from the] de novo process [7, 8] where the PCDD/PCDFs formed known as heterogeneous PCDD/PCDFs or low-temperature PCDD/PCDFs, which may come from CPs, CBs [9, 10], or carbon in fly ash. The two pathways of dioxins formation are said to occur simultaneously and independently.

In 1996, Huang and Buekens [11] presented a chemical reaction scheme for de novo synthesis of PCCD and PCDF from carbon in fly ash. In simplistic terms, the de novo synthesis involves heterogeneous reactions between the gas phase and the fly ash catalyzed by some constituents of the fly ash such as copper and iron chlorides.

As mentioned earlier [2]:

> The precursors of PCDD/PCDFs can be CPs, CBs, polycyclic aromatic hydrocarbons [PAHs], or de novo reactions of fly ash. For CPs, both the homogeneous (high temperature) and heterogeneous (low temperature) reactions for the formation of PCDD/PCDFs are equally important [12]. For heterogeneous reactions, a 523–723-K range of temperature is the favorable range. Fly ash plays an important role for the conversion reaction of CPs to PCDD/PCDFs. The chlorination of dibenzo-furans (DFs) under the influence of [copper chloride] $CuCl_2$ (metal catalyst) at 473–673 K is one of the obvious reasons of PCDD/PCDFs formation. There are two mechanisms of chlorination: one is direct chlorination of DF and Cl_2, and the other one is the reaction of DF and $CuCl_2$. Researchers have found that residual carbon and soot in fly ash are also one of the main sources of PCDD/PCDFs formation [10]. The release of PCDD/PCDFs is directly proportional to the carbon consumption rate [13]. Beside CPs, PAHs, and residual carbon, there are some other important factors that affect the formation of PCDD/PCDFs that include combustion temperature, residence time, precursors in feed, PCDD in feed, chlorine in feed, oxygen availability, processing of feed, [and] supplemental fuel [14].

According to an article by Cunliffe and Williams [15]:

> It has been shown that there is a “memory effect” associated with PCDD/PCDF where desorption of previously adsorbed or newly formed PCDD/PCDF from fly ash in the incinerator system can take place over several days. The memory effect has been demonstrated in association with the plastics used in wet scrubber systems, where the PCDD/PCDFs were adsorbed into the plastics followed by subsequent desorption into the flue gas stream [16–18]. There have been other studies of the memory effect where the fly ash/soot deposited in the boiler or air pollution control system acts as an adsorption matrix for PCDD/PCDF.

> The fly ash acted as a reaction matrix for PCDD/PCDF formation and subsequent desorption into the flue gas stream [19, 20]. Consequently, the memory effect can have a significant impact on the implementation of PCDD/PCDF emissions control strategies since the effect of any control measure introduced to the waste incinerator plant may be masked by the emission of PCDD/PCDF into the flue gas stream from PCDD/PCDF contained and formed in previously deposited fly ash.

2.3 Relevant Data Associated With the Disposal of Epoxy (Resin and Hardener), Components, and Elements Listed With the Ammunition Item Being Processed in the Incinerator

Another important and integral aspect associated with the removal of dioxins and furans resulting from the incineration of ammunition items is to address the safe and effective disposal of the constituents/components comprising the ammunition items. In particular, the ammunition items consist of an epoxy (resin and hardener), a variety of other components (electronics, rubber tubing, metal parts, energetic materials, and polyester thread), metal chemical elements, and chlorine.

It is important to point out that no specific details were provided by the TI inquirer regarding the quantity of the epoxy material, number of components, and number of chemical elements associated with the ammunition items that are to be demilitarized. Consequently, it is not possible to predict the magnitude of their impact on the incineration process in terms of enhancing or exacerbating the removal of dioxins and furans and their likelihood of increasing or decreasing the possibility of an environmental hazard/risk.

Consequently, lacking such definitive information, the approach implemented was to extract appropriate data from the safety data sheets (SDSs) for the constituents comprising the epoxy and the chemical elements contained in the ammunition item. These appropriate data focused on three specific characteristics: (1) incompatible materials, (2) hazardous decomposition products resulting from a thermal process, and (3) disposal considerations.

For the components associated with the ammunition item, only general statements could be made regarding the effect of thermal destruction (via incineration) on the components.

2.3.1 Appropriate SDS Data for the Constituents Comprising Epoxy (Resin and Hardener)

The following lists SDS data for epoxy novolac resin; 2,3-epoxy propanol (glycidol); gamma-glycidoxypropyltrimethoxy silane; granular silica; powdered silica; foam reducer; maleic anhydride; chlorendic anhydride; methyl tetrahydrophthalic anhydride; dipropylene glycol; and uranyl acetylacetonate.

- SDS Data for Epoxy Novolac Resin [21, 22]:
    - Incompatible Materials: Acids, bases and amines [21].
    - Hazardous Decomposition Products Resulting From a Thermal Process: Byproducts expected in incomplete pyrolysis or combustion of epoxy resins are mainly phenolics, carbon monoxide (CO), and water (H_2O) [21].
    - Disposal Considerations: While most "D.E.N.™ liquid epoxy resins may be disposed of by controlled burning in an approved incinerator, always confirm that the method chosen is in compliance with all applicable government requirements regarding identification and disposal of wastes" [22].

- SDS Data for 2,3-Epoxy Propanol (Glycidol) [23]:
    - Incompatible Materials: Violent reaction with strong oxidizer and nitrates. Decomposes on contact (especially in the presence of heat) with strong acids, strong bases, H_2O, metal salts (e.g., aluminum chloride, ferric chloride, tin chloride), or metals (copper, zinc), causing fire and explosion hazard. Attacks some plastics, rubber, and coatings.
    - Hazardous Decomposition Products Resulting From a Thermal Process: When heated to decomposition, emits acrid smoke and fumes.
    - Disposal Considerations: This combustible material may be burned in a chemical incinerator equipped with an afterburner and scrubber.

- SDS Data for Gamma-Glycidoxypropyltrimethoxy Silane [24]:
    - Incompatible Materials: Bases, H_2O, strong oxidizing agents, strong acids, peroxides.
    - Hazardous Decomposition Products Resulting From a Thermal Process: CO, carbon dioxide (CO_2), silicon dioxide (SiO_2), and methanol.
    - Disposal Considerations: Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste.

- SDS Data for Granular Silica [25]:
    - Incompatible Materials: Strong acids, strong bases, hydrogen fluoride, oxidizing agents, ammonia (NH_3), oxygen difluoride, and chlorine trifluoride.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Not combustible.
    - Disposal Considerations: Waste material must be disposed of in accordance with national and local regulations.

- SDS Data for Powdered Silica [26]:
    - Incompatible Materials: Strong oxidizing agents.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Silicon oxides may arise from the substance.
    - Disposal Considerations: Offer surplus and nonrecyclable solutions to a licensed disposal company.

- SDS Data for Foam Reducer [27]:
    - Incompatible Materials: No data provided.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Thermal breakdown of this product during fire or very high-heat conditions may result in decomposition products such as carbon oxides and traces of incompletely burned carbon compounds, SiO_2, or formaldehyde.
    - Disposal Considerations: Not considered a hazardous waste.

- SDS Data for Maleic Anhydride [28]:
    - Incompatible Materials: No data provided.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Forms explosive mixtures with air on intense heating. Development of hazardous combustion gases or vapors possible.
    - Disposal Considerations: Waste material must be disposed of in accordance with national and local regulations.

- SDS Data for Chlorendic Anhydride [29]:
    - Incompatible Materials: Strong oxidizing agents, strong acids, and strong bases.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Carbon oxides and hydrogen chloride (HCl) gas may arise from the substance.
    - Disposal Considerations: Offer surplus and nonrecyclable solutions to a licensed disposal company.

- SDS Data for Methyl Tetrahydrophthalic Anhydride [30]:
  - Incompatible Materials: No data provided.
  - Hazardous Decomposition Products Resulting From a Thermal Process: Combustible.
  - Disposal Considerations: Removal at a licensed chemical destruction plant or controlled incineration with flue gas scrubbing.

- SDS Data for Dipropylene Glycol [31]:
  - Incompatible Materials: No data provided.
  - Hazardous Decomposition Products Resulting From a Thermal Process: CO and CO_2 may be liberated.
  - Disposal Considerations: Consult appropriate local waste disposal expert about waste disposal.

- SDS Data for Uranyl Acetylacetonate [32]:
  - Incompatible Materials: Strong oxidizing agents.
  - Hazardous Decomposition Products Resulting From a Thermal Process: No data provided.
  - Disposal Considerations: Observe all federal, state, and local regulations when disposing of this substance.

2.3.2 Relevant Data Associated With the Disposal of Components Listed With the Ammunition Item Being Processed in the Incinerator

Since specific information was not provided by the TI inquirer regarding the type, quantity, and condition of the electronics to be included in the disposal of the ammunition items, it is not possible to provide detailed information on how the electronics should be disposed of. It is reasonable to assume that these electronics may contain certain toxic substances such as lead, mercury, and/or cadmium. If so, these electronics would need to be disposed of in accordance with the relevant environmental regulations. In general, If the electronics do not contain such toxic substances, electronics declared as waste are usually discarded, donated, or recycled.

Regarding the rubber tubing items, it is reasonable to assume that the tubing is made of natural and/or synthetic rubber. The different types of rubber tubing are quite numerous and diverse. By not having specific information on the type, quantity, and condition of the rubber tubing to be included in the disposal of the ammunition items, it is not possible to provide detailed information on how the rubber tubing should be disposed of.

Disposal of metal parts associated with the ammunition items is presented with the same questions as mentioned previously. By not having specific information on the type, quantity, and condition of the metal parts to be included in the disposal of the ammunition items, it is not possible to provide detailed information on how the metal parts should be disposed of.

Energetic materials to be included in the disposal of the ammunition items would need to be disposed of in a proper manner. These energetic materials are probably considered waste explosives. Since no specific information was provided by the TI inquirer regarding the type, quantity, and condition of the energetic materials, it is not possible to provide detailed information on how the energetic materials should be disposed of. However, the following statements can be made about the disposal of such energetic materials.

In June of 2022, the Environmental Protection Agency (EPA) acknowledged in a memorandum that open burn/open detonation (OB/OD) would be needed to treat waste explosives that do not yet have other safe modes of treatment [33]. Where OB/OD is needed, the EPA provides guidance regarding recommended permit conditions for OB/OD units to reduce impacts to human health and the environment. This memorandum further notes that, under the existing EPA Resource Conservation and Recovery Act requirements, “Where safe alternatives are available, facilities must use those alternatives in lieu of OB/OD” to treat their waste explosives.

Disposal of polyester thread associated with the ammunition items is presented with the same questions as mentioned previously. By not having specific information on the type, quantity, and condition of the polyester thread to be included in the disposal of the ammunition items, it is not possible to provide detailed information on how the polyester thread should be disposed of. Nevertheless, some general statements can be made regarding the disposition of the polyester thread. It is assumed that the polyester thread being cited is a thread used in the textile industry. If that assumption is correct, the polyester thread has a high likelihood of being recycled if it is not contaminated with toxic substances.

2.3.3 Appropriate SDS Data for the Chemical Metal Elements and Chlorine Contained in the Ammunition Items

The following lists SDS data for metal elements aluminum, arsenic, beryllium, cadmium, chromium, copper, gold, lead, iron, and zinc and for chlorine.

- SDS Data for Aluminum [34]:
    - Incompatible Materials: May react with strong acids, bases, and oxidizing agents to produce hydrogen gas, which is highly flammable. Contact with chlorinated solvents may release toxic and corrosive HCl gas. Hot aluminum may react with chlorinated solvents to produce phosgene, which is a highly irritating and toxic gas.
    - Hazardous Decomposition Products Resulting From a Thermal Process: When heated to decomposition, may yield metallic oxides, such as aluminum oxide. Decomposition of coating oils present on some products will release CO, CO_2, and other hydrocarbon species. Emits acrid smoke and fumes.
    - Disposal Considerations: Dispose of waste material according to local, state, federal, and provincial environmental regulations.

- SDS Data for Arsenic [35]:
    - Incompatible Materials: When in contact with acid or acid fumes, emits highly toxic fumes. Can react vigorously on contact with oxidizing materials.
    - Hazardous Decomposition Products Resulting From a Thermal Process: When heated to decomposition, may emit toxic fumes.
    - Disposal Considerations: Review all federal, state, and local regulations that may apply before proceeding.

- SDS Data for Beryllium [36]:
    - Incompatible Materials: Acids, bases, halocarbons, oxidizing materials, halogens, metals, and combustible materials.
    - Hazardous Decomposition Products Resulting From a Thermal Process: When heated to decomposition, emits oxides of beryllium.
    - Disposal Considerations: Dispose of in accordance with all applicable regulations. Consider recovering and recycling as an alternative to disposal.

- SDS Data for Cadmium [37]:
    - Incompatible Materials: Strong oxidizing agents, strong acids, and sulfur oxides.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Emits toxic fumes.
    - Disposal Considerations: Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

- SDS Data for Chromium [38]:
    - Incompatible Materials: Bases, oxidizing materials, halogens, peroxides, and metals.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Thermal decomposition can lead to release of oxides of chromium.
    - Disposal Considerations: Dispose of in accordance with all applicable regulations.

- SDS Data for Copper [39]:
    - Incompatible Materials: Violent reaction with acetylene, ammonium nitrate, bromates, chlorates, and iodates. Copper foil burns spontaneously in gaseous chlorine. Avoid contact with chlorine and oxygen difluoride, ethylene oxide, fluoride, hydrogen peroxide, hydrazine mononitrate, and hydrazoic acid. Incompatible with hydrogen sulfide, lead azide, and potassium peroxide.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Does not decompose.
    - Disposal Considerations: Recover for recycling. Follow applicable regulations. Dispose of in compliance with local regulations.

- SDS Data for Gold [40]:
    - Incompatible Materials: No data provided.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Nature of decomposition products unknown.
    - Disposal Considerations: Waste material must be disposed of in accordance with national and local regulations.

- SDS Data for Lead [41]:
    - Incompatible Materials: Acids and bases.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Thermal decomposition generates fume.
    - Disposal Considerations: Dispose of in a safe manner in accordance with national and local regulations. Reuse or recycle following decontamination.

- SDS Data for Iron [42]:
    - Incompatible Materials: Strong acids.
    - Hazardous Decomposition Products Resulting From a Thermal Process: Thermal decomposition generates hazardous vapors of iron oxides.

  - Disposal Considerations: Waste material must be disposed of in accordance with national and local regulations.

- SDS Data for Zinc [43, 44]:
  - Incompatible Materials: Strong oxidizing agents, acids, and bases [43].
  - Hazardous Decomposition Products Resulting From a Thermal Process: Thermal decomposition generates zinc/zinc oxides [43].
  - Disposal Considerations: If material cannot be returned to process or salvage, dispose of in accordance with applicable regulations [44].

- SDS Data for Chlorine [45, 46]:
  - Incompatible Materials: Reacts with most materials, especially flammable materials and other reducing agents. At temperatures below 250 °F, certain common metals (e.g., iron, copper, steel, lead, nickel) resist reaction with dry chlorine but others (e.g., aluminum, arsenic, gold, mercury, tin, titanium) react. Moist chlorine is highly corrosive except to glass, stoneware, porcelain, and certain alloys and only at low pressure. Titanium ignites spontaneously on contact with dry chlorine. Carbon steel ignites in chlorine at temperatures near 483 °F [45].
  - Hazardous Decomposition Products Resulting From a Thermal Process: Hazardous thermal decomposition products may include halogenated compounds [46].
  - Disposal Considerations: Product, solutions, and any byproducts should, at all times, comply with the requirements of environmental protection and waste disposal legislation and any regional, local authority [46].

2.4 Technologies Investigated to Reduce Dioxin and Furan Emissions During the Incineration Process

A number of technologies/methods have been investigated and implemented to remove/reduce dioxin and furan emissions during the incineration and combustion processes. "Since PCDD/PCCDFs enter the environment mainly from the flue gas and the fly ash produced during the incineration and combustion processes," the focus has been on two primary areas: (1) treatment of fly ash and (2) treatment of flue gas [47].

Some technologies/methods for the treatment of flue gas that have demonstrated promising results in the removal/reduction of dioxin and furan emissions from an incinerator are:

- Activated Carbon Injection (ACI)
- Selective Catalytic Reduction (SCR) or Selective Catalytic Oxidation (SCO)
- Electron Beam System
- Use of Thiourea
- Good Combustion Practice Treatment

A brief discussion of the treatment of fly ash and flue gas and some technologies/methods and their effectiveness in removing/reducing dioxin and furan emissions from the incinerator is presented next.

2.4.1 Treatment of Fly Ash

Themba et al. [47] conducted a review and found that incineration of solid waste generates a thick solid residue or cake, containing persistent organic pollutants such as dioxin-like compounds and metals, referred to as fly ash. Their review discusses several articles [47]:

> In many countries around the globe, the fly ash from the incineration process is classified as hazard waste by their environmental protection legislation [48]. Thus, further treatment of fly ash is required before being disposed of at the landfill sites. A recent review on fly ash (i.e., Zhang et al. [49]) 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 [municipal solid waste] MSW fly ashes over the past decade.
>
> Despite its ability to greatly reduce toxic substances in [municipal solid waste incineration] MSWI fly ash, thermal treatment remains limited in implementation by most countries due to its high heat consumption and processing costs [50].
>
> Lin et al. [51] used an older technology of a dual-bag filter system to reduce the concentration of PCDD/PCDFs in the stack flue gases of a fly ash treatment plant.

> Mechanochemical degradation (MCD) is one of the nonthermal methods for fly ash treatment that has received considerable attention due to its simplicity, efficiency, and environmental friendliness [52].

2.4.2 Treatment of Flue Gas

The review by Themba et al. [47] also discusses treatment of flue gas. "Both incineration and combustion processes release enormous amounts of flue gases, which are the most sources of PCDD/PCDF emissions in the environment. The following sections discuss remediation methods for the reduction of PCDD/PCDF emissions to the environment."

2.4.2.1 ACI

ACI is mentioned in the Themba et al. review, which states [47]:

> ACI, referred to as adsorbent injections, adsorb PCDD/PCDFs from gas streams but can simultaneously allow PCDD/PCDFs to be generated via de novo synthesis between 250 and 400 °C if the temperatures are not controlled [53]. 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 [54, 55]. Figure [1] presents an ACI for remediation of PCCD/PCDFs from flue gases during incineration.
>
> Altarawneh et al. [56], in their study, found that activated carbon is a useful technique for adsorption of PCDD/PCDFs 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 [56]. Mukherjeea et al. [2] 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. [Various studies that have used activated carbon] achieved PCDD/PCDF removal efficiencies [ranging from 85 to 99.6%].

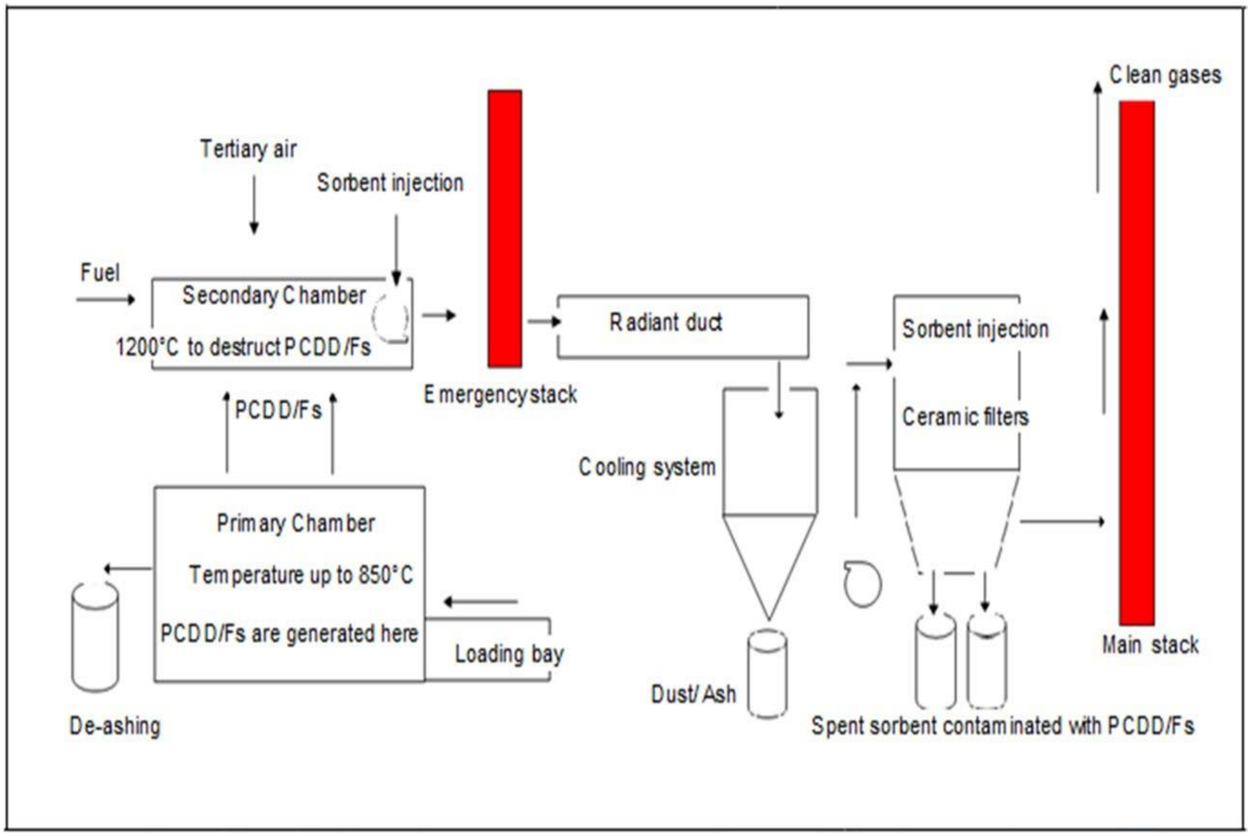

Figure 1. An ACI for Remediation of PCCD/PCDFs From Flue Gases During Incineration [47].

According to Hsu et al. [57], carbon injection has primarily been applied to mass burn [municipal waste combustors] MWCs with electrostatic precipitation (ESP) systems in the USA and Europe. However, [they] confirmed that injecting powdered carbon into the flue gas 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/PCDF emissions. However, the presence of mercury (Hg) reduces the adsorption of PCDD/PCDFs as high levels of Hg compete with PCDD/PCDF adsorption on the active site of the carbon leading to high load of carbon for the process.

Injection of activated carbon upstream of a particulate matter collection device is the least expensive method used to reduce PCDD/PCDFs, 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. [58] and Hsu et al. [57] all recommended that for better results, to remove PCDD/PCDFs 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 [57]. Everaert et al. [58] 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/PCDFs 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. [56] 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/PCDF emission reduction using the same process.
>
> A study by Atkinson et al. [53] reported on adsorption and destruction of PCDD/ PCDFs 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/PCDFs efficiently, with the [international toxic equivalent] 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/PCDFs up to 27%.

2.4.2.2 SCR/SCO

SCR is described in the Themba et al. review as [47]:

> [SCR] is a major air-pollution-controlled devices (APCD) for PCDD/PCDF removal as these compounds are known to adsorb on particulate matter. According to Finocchio et al. [59], adsorption and absorption methods are only capable of transferring PCDD/PCDFs from the vapor phase to solid or liquid phases, while SCR destroys them by producing carbon dioxide and HCl. PCCD/PCDFs 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/PCDFs is between 21 and 97% with SCR systems [60]. According to Chang et al. [61], the catalytic filtration technique is a two-step process to adsorb and destroy PCDD/PCDFs in flue gases. Firstly, the PCDD/PCDFs diffuse to the catalyst surface, and secondly, the PCDD/PCDFs will react to form trace amounts of CO_2, H_2O, and HCl [62]. The use of metal catalysts (i.e., copper/carbon [Cu/C], iron/carbon [Fe/C], vanadium oxide-tungsten oxide on titanium oxide [V_2O_5–WO_3/TiO_2]) is used for this purpose.
>
> A separate study conducted by Axegård [63] demonstrated that a catalytic filter was able to reduce PCDD/PCDFs below the desired limit of 0.1 ng Nm^{-3}. According to [the study], filter membranes collect flue gas particles while catalytic filters oxidize gaseous components. More than 99.9% of PCDD/PCDFs 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. Hung et al. [64] and Xu et al. [65] reported that catalytic filtration is still an effective method for removal of PCDD/PCDFs.
>
> Different authors achieved different efficiency rates for PCDD/PCDF destruction [59]. For example, Weber et al. [66] reported a high destruction efficiency of >98% catalyzed by TiO_2-based V_2O_5–WO_3 at 200 °C. Xu et al. [65] reported 98 to 99.75% efficiency at 200 °C, while Cunliffe and Williams [15] reported a degradation efficiency of 65 to 86.0% with an increasing temperature of up to 300 °C, and finally, Xu et al. [65] obtained a high efficiency of more than 99.9% from a MSW incinerator at the temperatures of 200 to 230 °C.

As previously discussed, the SCR technology using metal catalysts can effectively promote the decomposition of PCCD/PCDFs without hampering the normal operating conditions of the incinerator. Figure 2 presents a graphic layout of how this can be accomplished with the aid of the metal catalyst V_2O_5–WO_3/TiO_2 [67].

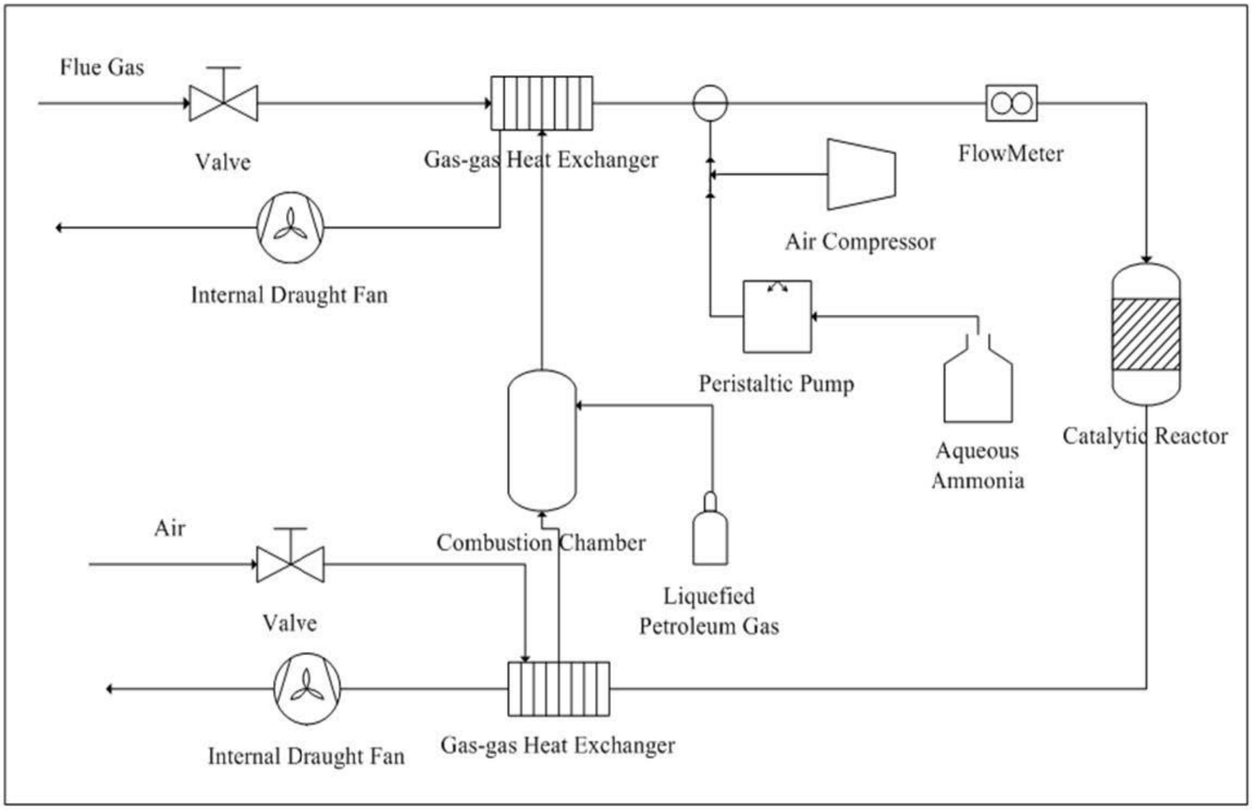

Figure 2. Inhibition of PCDD/PCDFs by the Aid of V_2O_5–WO_3/TiO_2 Catalysts During the Incineration Process [67].

The previously mentioned review by Mukherjee et al. states [2]:

> The whole treatment requires a set of operating conditions to be obeyed to achieve the desired result on reduction of [PCDD/PCDFs]. Firstly, the flue gas should be reheated after it leaves the main combustion chamber from 398–403 K to 493–503 K in a (gas-gas) heat exchanger, then the reheated flue gas enters the catalytic reactor where the decomposition takes place at 573 K, which is the preferable temperature for the decomposition over V_2O_5-WO_3/TiO_2 catalysts. The main mechanism behind the inhibition of [PCDD/PCDFs] is that [they] possess oxidation reactions over the catalyst V_2O_5–WO_3/TiO_2 and generate inorganic and nontoxic substances like H_2O, CO_2, and HCl in the catalytic reactor at 573 K, and, with the aid of internal-draught fan (ID-fan), purified gas should be discharged [68]. Higher temperature facilitates the catalytic oxidation with a discharge efficiency of dioxins to 97.24%, whereas low

> temperature causes deactivation of catalysts, which promotes PCDD/PCDF formation. This process is found to be equally important for [nitrogen oxides] NO_x decomposition at 573 K with 90.3% efficiency [68, 69].

2.4.2.3 Electron Beam System

Themba et al. discuss the electron beam system in their review, describing it as [47]:

> An electron beam system is a [relatively] new technology that uses a radiation process for the destruction of dioxin. It breaks down the toxic chlorine compounds into nontoxic organic acids such as formic acid, acetic acid, and chloroacetic acid with fairly low energy consumption [70]. Figure [3] presents the application of the electron beam system as a remediation strategy for PCDD/PCDFs.

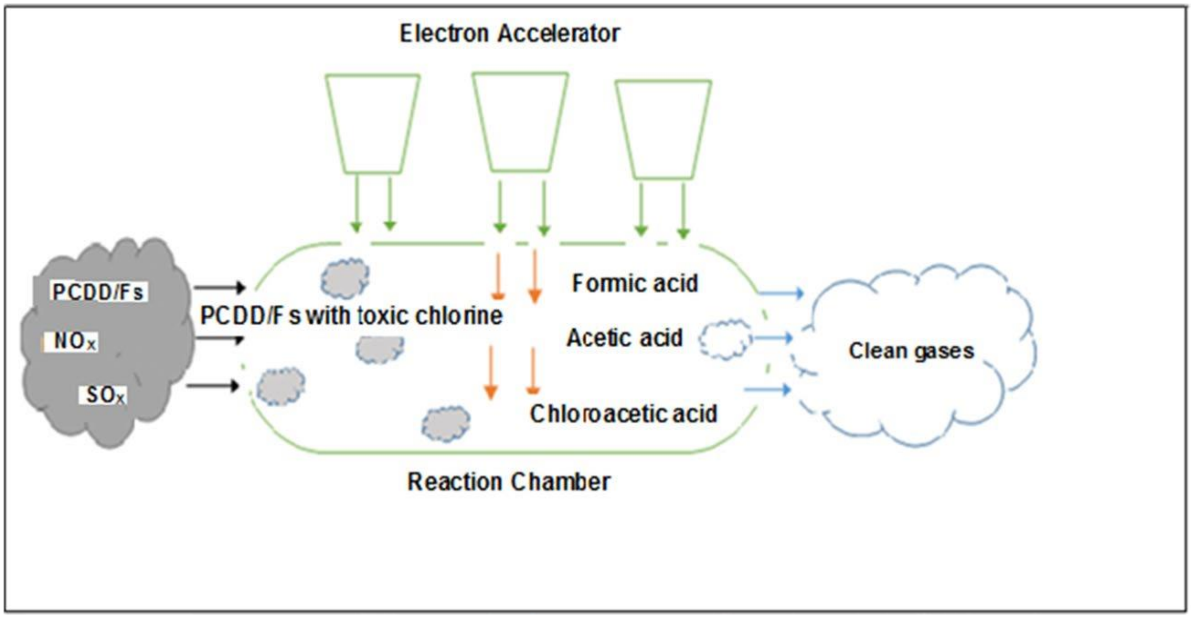

Figure 3. Electron Beam System as Remediation for PCCD/PCDFs During Incineration [47].

> Liu et al. [70] stated that an electron beam [technology provides] the following advantages:
>
> - The direct decomposition of dioxins means there is no risk of secondary pollution, like those produced with a filter-based recovery process.

- Temperature control should be maintained around 200 °C.
- Installing an electron beam system to the existing incinerators is a simple process.

> The findings of different studies regarding the application of electron beam technology to destroy PCDD/PCDFs suggest that this technology is the least popular method.

2.4.2.4 Use of Thiourea

Mukherjeea et al. describe the use of thiourea as [2]:

> Nitrogen-containing compounds such as ethanolamine, mono-ethanolamine (MEA), urea, NH_3, triethanolamine, [and] di-methylamine are confirmed inhibitors [71]. Thiourea is a suitable dioxin inhibitor with high [sulfur] S and [nitrogen] N content [72]. Numerous operating parameters affect the inhibition process of dioxins by thiourea. Firstly, the combustion temperature should be maintained at 1123–1129 K, coupled with injection pressure of the nozzle at 0.50 MP and maintaining the flow rate of aqueous thiourea at 350 L/hr. The [sulfur dioxide] ((SO_2 + NH_3)/HCl) molar ratio in the flue gas is adjusted to 1.0, increasing the concentration of SO_2 and NH_3. Thiourea undergo complex reactions with the metal catalysts, forming strongly bonded organometallic nitride comp lexes, thus resulting in the irreversible deactivation of catalytic site as well as block the chlorination to hinder the formation of dioxins [73]. It has been indicated that nitrogen-containing compounds can inhibit the formation of dioxins to more than 95%, and further examination revealed that thiourea reduces dioxins by 91.0% weight and the concentration of dioxins to 0.08 ng I-TEQ/m3.

Figure 4 provides a flow diagram of the waste incinerator that uses thiourea.

2.4.2.5 Good Combustion Practice Treatment

The Themba et al. review describes good combustion practice treatment as [47]:

> The combustion temperature plays a significant role in the formation of PCDD/PCDFs as they are formed due to incomplete combustion.

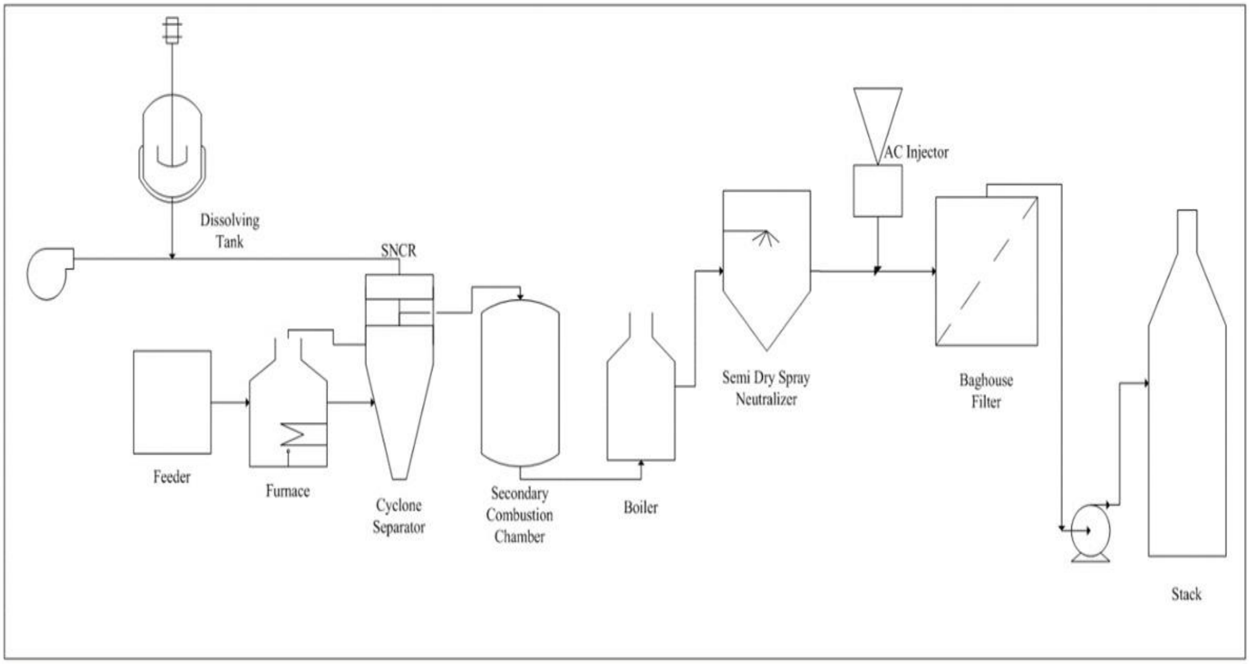

Figure 4. Flow Diagram of the Waste Incinerator That Uses Thiourea [72].

Combustion efficiencies include combustion temperature, residence time, supplemental fuel, fuel processing, and oxygen availability [2, 48, 74, 75]. In order to destroy PCDDs or prevent their formation, the combustion efficiency must be high [76]. PCDDs/PCDFs are formed under specific conditions that are determined by the composition of the fuel and combustion conditions. Mukherjeea et al. [2], in their recent study of combustion practice, [specified] a set of optimal operating conditions…that mitigated the production of PCDD/PCDFs. Two stages of the combustion process were recommended, namely a design that facilitates the complete combustion to [first] reduce the formation of PCDD/PCDFs [and] secondly to ensure maximum reduction of PCDD/PCDFs; the end-of-pipe treatment was used. [They] went on to declare that the first guideline was to monitor the CPs periodically as they are the source of HCl and chlorine.

Mukherjeea et al. [2] suggested that PCDD/PCDFs are formed due to incomplete combustion when combustion temperature drops below 800 °C. To achieve complete combustion, [they] recommended that the temperature should range between 850 and 1,000°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 recommended, while for 1,000°C, a residence time of 1 s is recommended. For complete combustion and complete destruction, a 3 to 6% ([volume per volume] v/v) excess of oxygen is recommended. To prevent PCDD/PCDFs from forming in the flue gas, the postcombustion temperature needs to be kept at 200 °C.

2.5 Recommendations Regarding the Most Cost-Effective Capabilities for Maintaining a Subthreshold Dioxin and Furan Emission for an Incinerator

Detailed information was not provided by the TI requestor regarding the type of incinerator that will be used for destruction of the ammunition items. Consequently, it is difficult to provide relevant suggestions/recommendations on what are the most cost-effective solutions for maintaining a subthreshold dioxin and furan emission for the associated incinerator system. However, based on the information presented in this TI response and not having detailed information on the incinerator system of interest, the following general suggestions/recommendations are submitted for consideration:

- If not currently being used with the incinerator system, MCD should be considered. It is one of the nonthermal methods for fly ash treatment that has received considerable attention due to its simplicity, efficiency, and environmental friendliness.
- If not currently being used, ACI should be considered as a method of choice for the adsorption of PCDD/PCDFs in flue gases.
- If not currently incorporated into the incinerator system, the use of ceramic filters that can sustain higher temperatures should be considered for use during the incineration process.
- If not currently being used, the SCR catalyst used for NO_x reduction has been found to be effective for PCDD/PCDF reduction and should be considered. The metal catalyst comprised of V_2O_5–WO_3/TiO_2 has been reported to achieve PCDD/PCDF removal and destruction efficiencies of >98% at temperature ranges of 200 to 250 °C.
- If not currently incorporated into the incinerator system, the use of thiourea to reduce dioxin emissions may be a viable option, as it has been found to reduce the concentration level of dioxins with more than 95% efficiency.

- Due to the high cost of activated carbon, the use of cheaper activated carbon impregnated with SCR catalysts or surface functionalized compounds derived from biomass could be considered if activated carbon is not currently used in the incinerator system.
- End-of-pipe treatment options have shown good potential for reduction of dioxin and furan emissions. Hybridization of good combustion practice and end-of-life pipe treatment has been suggested, which will not only improve the process efficiency from the operational aspect but also from the economical aspect.

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