MINIMIZATION OF COMBUSTION BY-PRODUCTS: TOXIC METAL EMISSIONS

by

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ABSTRACT

It has been well recognized that, although there are many potential solid waste treatment technologies, none is as universally applicable as incineration for the treatment of the many types of waste which are governed by the many different Federal laws and State regulations. However, incinerators may release trace amounts of unwanted combustion by-products (CBPs), particularly if the incinerators are not well designed or properly operated.

Control of the emissions of CBPs is one of the major technical and sociological issues surrounding the implementation of incineration as a waste treatment alternative. Much of this is due to the lack of detailed knowledge about CBPs. The Clean Air Act Amendment is emphasizing the control of toxic air pollutants from all combustion and process sources; some of these pollutants are CBPs. CBPs include: (1) unburned principal organic hazardous constituents (POHCs); (2) products of incomplete combustion (PICs); (3) metal emissions; (4) residuals/ashes; and (5) acid gases.

This Paper is a part of a series of writings on the subject of the CBP issue from EPA's Risk Reduction Engineering Laboratory in Cincinnati, Ohio and is one of the first metal emission papers in the series. It specifically

addresses the aspect of potential toxic metal emissions from combustion/ incineration processes. The main objective of the series is to ultimately compare combustion by-products from all major combustion activities including fossil fuel combustion and waste incineration. Hopefully, the series will serve as an initial step in the eventual minimization of the release of CBPs to the environment.

INTRODUCTION

It has been well documented that incineration is the best available technology for disposing of various waste streams, when compared to other treatment technologies (1). A recent study has shown that essentially only four technologies were active in treating Superfund waste through 1989 and three out of the four technologies were thermal processes. These three thermal technologies have more than 80% of the market share in remediating Superfund sites (2).

Compared with other treatment technologies, incineration has the following major advantages: (1) volume reduction (the reduction rate depends on the ash content of the waste incinerated); (2) detoxification (incineration can achieve nearly 100% destruction of any pathogenic, toxic or hazardous substance); (3) potential energy recovery (it has been a general practice for many industries to recover energy from waste incineration processes); (4) no long-term liability (once a waste is incinerated, the problem will not resurface again as it often does when landfills are used); and (5) effectiveness (it only takes seconds to destroy what landfills may take years to decompose). However, waste incineration can produce unwanted combustion by-products (CBPs) such as partially burned ash and toxic air pollutants such as particulate (heavy metals) and dioxins and furans (PCDD and PCDF), particularly if the incinerators are not well designed and operated. The general issue of CBPs has been one of the major technical and sociological issues surrounding the implementation of incineration as a waste treatment alternative. In addition, the public has developed the so-called "NIMBY" (not in my back yard) attitude which makes siting an incineration facility extremely difficult.

The authors have been writing a series of papers addressing the issues of CBPs. The series of already published papers cover:

(1) Regulatory aspects: Papers published in this area are:
- Regulatory Framework for Combustion By-Products from Incineration Sources (3)
- Environmental Law Relating to Medical Waste in the United States of America (4)

(2) Theoretical aspects: Papers published in this area are:
- Incineration of Solid Waste (5)
- Thermodynamic Fundamentals Used in Hazardous Waste Incineration (6)
- Incinerability Ranking Systems for RCRA Hazardous Constituents (7)

(3) Waste characteristics: Papers published in this area are:
- Minimization of Combustion By-Products: Characteristics of Hazardous Waste (8)

(4) Organic combustion by-products: Papers published in this area are:
- PIC Formation - Research Status and Control Implications (9)

(5) Metals: Papers published in this area are:

- A Model Analysis of Metal Partitioning in a Hazardous Waste Incineration System (10)
- Metals Behavior During Medical Waste Incineration (11)

EPA defines toxic metals as metallic elements with high atomic weight and density such as mercury, chromium, cadmium, arsenic, and lead. They are toxic to living organisms and can damage living things at low concentrations and tend to accumulate in the food chain (12).

Metals present in the feed to combustion devices are typically emitted in combustion gases as particles rather than vapors. However, some of the more volatile elements (e.g., mercury and selenium) or their chemical compounds may be released to the atmosphere partially in the vapor state. The processes involved in the formation of particles are very complex and are only partially understood at present. Most of the current state of knowledge on metal behavior in combustion has come from research on coal combustion (1).

This Paper supplies general information about toxic metals. Specific subjects covered include: (1) metals regulated under various Federal laws; and (2) selected properties of regulated metals and their potential chlorinated species resulting from incineration.

METALS REGULATED UNDER VARIOUS FEDERAL LAWS

Metals Regulated Under the Resource Conservation and Recovery Act (RCRA)

It has been well documented that hazardous waste contains various metals such as arsenic, barium, beryllium, chromium, lead, mercury, nickel, zinc, etc. Incineration changes the form but not the content of metal fractions in waste streams. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as they were in the input feed (i.e., exiting in both the flyash and bottom ash streams).

Because of the public interest in early 1991, EPA promulgated the BIF (Boiler and Industrial Furnaces) Rules. The rules contain regulations (provisions) on the emissions of ten metals. The summary of metal information contained in the BIF rules is as follows (40CFR-260, 1991):

> The rules establish emission limits for 10 toxic metals listed in Appendix VIII of 40 CFR Part 261 based on projected inhalation health risks to a hypothetical maximum exposed individual (MEI). The standards for the carcinogenic metals (arsenic, beryllium, cadmium, and chromium) limit the increased lifetime cancer risk to the MEI to a maximum of 1 in 100,000. The risk from the four carcinogens must be summed to ensure that the combined risk is no greater than 1 in 100,000. The standards for the non-carcinogenic metals (antimony, barium, lead, mercury, silver, and thallium) are based on reference doses (RfDs) below which adverse health effects have not been observed.
>
> The standards are implemented through a three-tiered approach. Compliance with any tier is acceptable. The tiers are structured to allow high emission rates (and feed rates) as the owner or operator elects to conduct more site-specific testing and analyses (e.g., emissions testing, dispersion modeling). Thus, the feed rate limits

under each of the tiers are derived based on different levels of site-specific information related to facility design and surrounding terrain.

Under Tier I, the Agency has provided very conservative waste feed rate limits in "reference" tables as a function of effective stack height and terrain and land use in the vicinity of the stack and assumed reasonable, worst-case dispersion. The owner or operator demonstrates compliance by waste analyses, not emissions testing or dispersion modeling. Consequently, the Tier I feed rate limits are based on an assumed reasonable, worst-case dispersion scenario, and an assumption that all metals fed to the device are emitted in the stack gases [i.e., no partitioning to bottom ash or products, and no removal by an air pollution control system (APCS)].

Under Tier II, the owner or operator conducts emissions testing (but not dispersion modeling) to get credit for partitioning to bottom ash or to products, and for APCS removal efficiency. Thus, the Agency has developed conservative emission rate limits in reference tables, again as a function of effective stack height and terrain and land use in the vicinity of the stack. The Agency also assumed reasonable, worst-case dispersion under Tier II.

Under Tier III, the owner or operator would conduct emissions testing and site-specific dispersion modeling to demonstrate that the actual (measured) emissions do not exceed acceptable levels considering actual (predicted) dispersion.

The standards are implemented through limits on specified operating parameters, including hazardous waste feed rate and metals composition, feed rate of metals from all feed streams, combustion chamber temperature, and air pollution control parameters.

The rules limit particulate matter (PM) emissions to 0.08 grains/dry standard cubic foot (dscf) corrected to 7 percent oxygen (O_2) This is the same standard that currently applies to hazardous waste incinerators and is intended to supplement the risk-based metals controls. Compliance with the standard is demonstrated by emissions testing, and the standard is implemented by operating limits set in the permit.

All boilers and industrial furnaces must comply with the standard; however, cement and aggregate kilns need not monitor the ash content of all feed streams to demonstrate compliance with the standard given that particulate matter from these devices is generated primarily from raw materials. Instead, the rule provides that these devices must comply with the operating limits on the particulate matter control system to ensure continued operation at levels achieved during the compliance test (under "Interim Status") or trial burn (under the Part B permit application).

Metals Regulated Under the 1990 Clean Air Act (CAA) Amendments

The 1990 Amendments completely overhaul the regulatory approach used for air toxics, originally regulated under the 1970 Clean Air Act. Under this new regulatory strategy, 189 substances were listed as hazardous air pollutants

(HAPs) by the Act and these will be regulated by EPA. Substances can be added to or deleted from the list after rulemaking. The HAPs contain many metal compounds.

All metals are regulated under the "PM-10" approach. "PM-10" means the particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers as measured by an applicable reference method (12). Under the 1990 CAA Amendments: (1) EPA is directed to promulgate control technique guidelines for reasonably available control measures and best available control measures for PM-10 emissions from both major stationary sources and area sources; and (2) States must implement all reasonably available control measures and designate periodic milestones until attainment is achieved.

PM-10 plan revisions are to provide for automatic implementation of contingency measures if the area fails to attain the PM-10 NAAQS (National Ambient Air Quality Standards) by the mandated deadline. States are to adopt these contingency measures as regulations prior to the deadline for attainment to ensure that these back-up measures can go into effect without delay if the target date is missed.

Metals Regulated under the Clean Water Act (CWA)

In general, sludge waste includes both municipal sludge and industrial sludge. Incineration of sludge is regulated under Section 405(d) of the CWA. EPA's Office of Water is currently developing standards for municipal sludge incineration. The standards for industrial sludge incineration have not been developed yet.

Metals Regulated under the Superfund Act (CERCLA)

In general, thermal equipment used at CERCLA sites will not require formal RCRA incineration permits; however, in most cases, consent orders will be negotiated which will generally require that the RCRA incineration performance standards be achieved. The consent order route can reportedly save up to a year of permitting time for a clean-up project. The RCRA performance standards are 99.99 percent destruction and removal efficiency for specific Appendix VIII principal organic hazardous constituents (POHCs), particulate emissions no greater than 0.08 grains per dscf corrected to 7 percent oxygen, and either 99 percent HCl removal or a maximum stack emission of four pounds of HCl per hour. Metals contained in CERCLA waste are regulated under the RCRA particulate standards (2).

SELECTED PROPERTIES OF REGULATED METALS AND THEIR CHLORINATED COMPOUNDS

Because metals are increasingly receiving more attention due to their potential impact on the environment, being aware of the properties of regulated metals is important in that these properties often influence the degree of metal partitioning that takes place during combustion. Because many chlorinated metal compounds have lower volatility temperatures than that of their corresponding metal elements, the chlorinated metal compounds are easier to vaporize and to escape from air pollution control devices. Common chlorinated metal compounds are provided in the metal property information provided below (most information was excerpted from Merck)(13).

Antimony (Sb)

- Melting point: 630°C
- Boiling point: 1635°C
- Common chlorinated compounds:
  - Antimony chloride oxide (SbOCl): Monoclinic crystals or crystalline powder;
  - Antimony pentachloride ($SbCl_5$): Colorless to yellow, oily liquid. Fumes in air; and
  - Antimony trichloride ($SbCl_3$): Fumes in air.
- Health effect: Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes or dust. Antimony can react with nascent hydrogen to form stibine (H_3Sb) which is extremely toxic. Stibine can cause vomiting, headache, stomach pain and even death.

Arsenic (As)

- Melting point: 818° at 36 atm. (at atmospheric pressure, it sublimes)
- Boiling point: 615°C (sublimation temperature)
- Common chlorinated compounds:
  - Arsenic trichloride ($AsCl_3$): Oily liquid, intensely poisonous, fumes in air.
- Health effect: Most forms of arsenic are toxic. This substance and certain other arsenic compounds have been listed as carcinogens by EPA.

Barium (Ba)

- Melting point: 710°C
- Boiling point: 1600°C

- Common chlorinated compounds:
  - Barium chlorate [$Ba(ClO_3)_2$]: Monohydrate, monoclinic prismatic crystals, and poisonous;
  - Barium chloride ($BaCl_2$): Dihydrate, crystals or granules or powder; bitter salty taste and poisonous; and
  - Barium perchlorate [$Ba(ClO_4)_2$]: Trihydrate, crystals and poisonous.
- Health effect: All water or acid soluble barium compounds are poisonous.

Beryllium (Be)

- Melting point: 1287°C
- Boiling point: 2500°C
- Common chlorinated compounds:
  - Beryllium chloride ($BeCl_2$): White to faintly yellow, very deliquescent; and
  - Beryllium perchlorate [$Be(ClO_4)_2$]: Trihydrate, very hygroscopic crystals.
- Health effect: Death may result from exposure to the element and its compounds.

Cadmium (Cd)

- Melting point: 321°C
- Boiling point: 765°C
- Common chlorinated compounds:
  - Cadmium chloride ($CdCl_2$): Hygroscopic, rhombohedral crystal.
- Health effect: This substance and certain cadmium compounds have been listed as carcinogens by EPA.

Chromium (Cr)

- Melting point: 1900°C
- Boiling point: 2642°C
- Common chlorinated compounds:
  - Chromous chloride ($CrCl_2$): Lustrous needles or fused, fibrous mass; and
  - Chromyl chloride ($CrCl_2O_2$): Deep red liquid; appears black under reflected light. Fumes in moist air. Burns and blisters skin.
- Health effect: This substance and certain cadmium compounds have been listed as carcinogens by EPA.

Lead (Pb)

- Melting point: 327°C
- Boiling point: 1740°C
- Common chlorinated compounds:
  - Lead chlorate [$Pb(ClO_3)_2$]: Colorless, deliquescent crystals, poisonous.
  - Lead chloride ($PbCl_2$): White, crystal powder, poisonous.
- Health effect: Acute: most common in children with history of pica; anorexia, vomiting etc. Chronic: Children show weight loss, weakness, etc. Lead poisoning in adults is usually occupational due mainly to inhalation of lead dust or fumes.

Mercury (Hg)

- Melting point: - 38.87°C
- Boiling point: 356.72°C

- Common chlorinated compounds:
  - Mercuric chloride ($HgCl_2$): Crystals or white granules or powder, highly toxic;
  - Mercury amide chloride ($HgNH_2Cl$): Odorless powder, poison, may produce allergic dermatitis;
  - Mercurous chlorate [$Hg_2(ClO_3)_2$]: White crystals; decomposes at about 250°C to form oxygen, mercuric oxide and mercuric chloride; and
  - Mercurous chloride (Hg_2Cl_2): white, odorless, tasteless, heavy powder; slowly decomposes by sunlight into mercuric chloride and metallic mercury.
- Health effect: <u>Acute</u>: violent corrosive effects on skin and mucous membranes, vomiting, abdominal pain, etc. <u>Chronic</u>: inflammation of mouth and gums, excessive salivation, loosening of teeth; kidney damage, etc.

<u>Silver (Ag)</u>

- Boiling point: 960.5°C
- Boiling point: 2000°C
- Common chlorinated compounds:
  - Silver chlorate ($AgClO_3$): White, tetragonal crystals;
  - Silver chloride ($AgCl$): White powder; darkens on exposure to light; and
  - Silver perchlorate ($AgClO_4$): Deliquescent crystals, irritating to skin, mucous membranes.

- Health effect: Does not cause serious toxic manifestations, but prolonged absorption of silver compounds can lead to grayish blue discoloration of skin. Many silver salts are irritating to skin and mucous membranes.

Thallium (Tl)

- Melting Point: 303°C
- Boiling point: 1457°C
- Common chlorinated compounds:
  - Thallium chloride (TlCl): White crystal powder; poisonous.
- Health effect: Acute: vomiting, diarrhea, tingling, pain in extremities, etc. Chronic: weakness and pain in extremities, loss of hair.

CONCLUSION

This Paper has provided some general technical information regarding the toxic metals often found in incinerator stack emissions. It described the metals that are regulated under various Federal laws. It also has provided selected properties of the ten metals that are regulated under RCRA.

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